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Metals and Corrosion

A Handbook for the Conservation Professional

Lyndsie Selwyn

Canadian Heritage
Patrimoine canadien

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A HANDBOOK FOR THE CONSERVATION PROFESSIONAL

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PRINTED IN CANADA

Available from:

Canadian Conservation Institute
1030 Innes Road
Ottawa ON K1A 0M5
Canada

Library and Archives Canada Cataloguing in Publication

Selwyn, Lyndsie

Metals and corrosion : a handbook for the conservation professional

Issued also in French under title: Métaux et corrosion.
Includes bibliographical references.
ISBN 0-662-37984-5
Cat. no. NM95-59/11-2004E

1. Metals – Corrosion fatigue – Handbooks, manuals, etc.
2. Metals – Handbooks manuals, etc.
3. Museum conservation methods.
I. Canadian Conservation Institute.
II. Title.

TA462.S44 2004 669 C2004-980261-5

Cover Photograph: Copper vase after polishing (rear image) and after application of different patination recipes.

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ACKNOWLEDGEMENTS

CCI is a unique workplace that combines the talents of conservators, conservation scientists, and other professionals with expertise in a wide variety of fields. This book would not have been possible without the help of many of these individuals. I would like to extend my sincere thanks to the following people (both CCI staff and other professionals) for contributing information and photographs, proofreading various drafts, and helping with the production of this publication: Richard Alcuin, Bessie Argyropoulos, Andre Audette, André Bergeron, Malcolm Bilz, Carl Bigras, Nancy Binnie, Malcolm Black, Christine Bradley, the late Helen Burgess, Leslie Carlyle, David Carter, Tom Chase, Marie-Claude Corbeil, Charlie Costain, Doris Couture-Rigert, Vicki Davis, Christian Degrigny, Mary Devine, Carole Dignard, Steve Duffield, Heather Dumka, Michael Eisen, Lisa Ellis, the late Gordon Fairbairn, Lucie Forgues, Tara Grant, David Grattan, Chuck Gruchy, Jack Harman, Mike Harrington, James Hay, Paul Heinrichs, Kate Helwig, Natalie Huet, Sumi Grover, Elzbieta Kaminska, Malgorzata Kaminska, Raymond Lafontaine, Suzanne Lewis, Judy Logan, Maureen MacDonald, Sue Maltby, Janet Mason, Ross McKinnon, the late Michael McNeil, Wanda McWilliams, Elizabeth Moffatt, Lorne Murdock, Alison Murray, Nora Nagy, Kathy Nanowin, Charlotte Newton, Alice Paterakis, Jeremy Powell, Tracy Power, George Prytulak, France Rémillard, Anne Rinuy, Geneviève Sansoucy, Carl Schlichting, Bob Senior, Chris Sergeant, Jane Sirois, Susan Stock, Tom Stone, Tom Strang, Jean Tétreault, Season Tse, Harry Turner, Henry Unglik, Jan Vuori, Ian Wainwright, Phil White, Scott Williams, Donna Woods, Nicola Woods, Gregory Young, Lisa Young, and Bernie Ziomkiewicz. I would especially like to thank Bob Barclay for his help in converting my workshop notes into the framework of this publication. Finally, I am indebted to the publication team for their tireless efforts: Barbara Patterson (English editing), Françoise Guyot of Services T&A Inc. (translation of English text to French), Linda Leclerc (French editing), and Sophie Georgiev (design and layout).

TABLE OF CONTENTS

PREFACE

This book arose from the CCI workshop *What's New in Old Metals*?, which deals with common metals and alloys in museums. While preparing the didactic materials for this workshop, I was struck by the difficulty of finding easy-to-use reference material to recommend to the participants. Instead, I resorted to compiling a collection of notes for them that summarized information on the various metals covered in the workshop. These notes were well received, and I became convinced that a more detailed reference would be useful.

I hope I have created a publication that conservators or conservation scientists can turn to before considering treatment for metals: a reference to refresh their memory or get them started reading the literature; a place to look up alloys, plating combinations, or particular corrosion problems encountered with metals in museums. I have included a lot of information that I have looked up when asked questions about metals and corrosion problems, whether it be metals indoors, outdoors, or in archaeological settings. In fact, much of the information in this book is a summary of what I have learned as I answered questions from across the country.

The book concentrates on the chemical and physical characteristics of metals and their corrosion products. It does not review conservation treatments for metals, nor does it discuss details of the metallurgy. The intended audience is heritage professionals who survey, care for, and treat metals, or who come across metals during the course of their work. A general comprehension of chemistry at the first-year-university level is assumed.

This publication is not intended to be an exhaustive survey of metals, but rather a summary of some of their most important properties. I welcome any suggestions that readers might have for improvements and additions, as well as other comments or identification of errors.

Lyndsie Selwyn

ABOUT THE AUTHOR

Lyndsie Selwyn graduated in 1985 from the University of California at San Diego with a Ph.D. in Physical Chemistry, followed by post-doctoral research at the National Research Council of Canada in Ottawa. In 1987 she joined CCI where she is presently a senior conservation scientist. Her research focuses on the corrosion and conservation problems associated with metals.

ACRONYMS AND ABBREVIATIONS

Å	Angstrom (10^{-10} metres)
Ag	Silver
AISI	American Iron and Steel Institute
Al	Aluminum
ASTM	American Society for Testing and Materials
at%	Atomic percent
Au	Gold
a_x	Atomic percentage of element x
a_y	Atomic percentage of element y
bcc	Body-centred cubic
°C	Degree Celsius
$°C^{-1}$	Per degree Celsius
C	Carbon
Cd	Cadmium
Cl^-	Chloride ion
cm	Centimetre (10^{-2} metres)
CO	Carbon monoxide
CO_2	Carbon dioxide
COS	Carbonyl sulphide
CPNS	Chrome-plated nickel silver
Cr	Chromium (chrome)
ct	Carat
Cu	Copper
e^-	Electron
E_c	Corrosion potential
E_{cell}	Cell potential
EDTA	Ethylenediaminetetraacetic acid
E_h	Equilibrium potential
$E_{h,anode}$	Equilibrium potential for anodic half-reaction
$E_{h,cathode}$	Equilibrium potential for cathodic half-reaction
E_h^0	Standard equilibrium potential
EPBM	Electroplated Britannia metal
EP copper	Electroplated copper
EP lead	Electroplated lead
EPNS	Electroplated nickel silver
ETP	Electrolytic tough pitch
fcc	Face-centred cubic
Fe	Iron
FTIR	Fourier transform infrared spectroscopy
(g)	Gas
g	Gram
g cm^{-3}	Gram per cubic centimetre
g mol^{-1}	Gram per mole
GC/MS	Gas chromatography/mass spectrometry
Ge	Germanium
G.F.	Gold filled
H^+	Hydrogen ion
H_2	Hydrogen gas
HCl	Hydrochloric acid
HNO_3	Nitric acid
H_2O	Water
H_2S	Hydrogen sulphide
H_2SO_4	Sulphuric acid
HSLA	High-strength low-alloy
ICP/AES	Inductively coupled plasma/atomic emission spectroscopy
Ir	Iridium
K_{sp}	Solubility product
kt	Karat
(l)	Liquid
M	Metal
M	Mole per litre
M^+	Metal ion
mg	Milligram (10^{-3} gram)
mg m^{-3}	Milligram per cubic metre
MIC	Microbially induced corrosion
mm	Millimetre (10^{-3} metre)
MO	Metal oxide
NAA	Neutron activation analysis
NH_4^+	Ammonium ion
NHE	Normal hydrogen electrode
Ni	Nickel
nm	Nanometre (10^{-9} metre)
NO_x	Nitrogen oxides
O_2	Oxygen gas
OH^-	Hydroxyl ion
Os	Osmium
Pb	Lead
Pd	Palladium
p_{H_2}	Partial pressure of hydrogen gas
p_{O_2}	Partial pressure of oxygen gas
ppm	Parts per million
ppt	Parts per thousand
Pt	Platinum
RH	Relative humidity
Rh	Rhodium
Ru	Ruthenium
(s)	Solid
SAE	Society of Automotive Engineers
SCE	Saturated calomel electrode
SHE	Standard hydrogen electrode
Sn	Tin
SSE	Saturated mercury/mercurous sulphate electrode
UNS	Unified numbering system
UV	Ultraviolet
VCI	Volatile corrosion inhibitor
VPI	Vapour phase inhibitor
W	Tungsten
wt%	Weight percent
w_x	Weight percentage of element x
w_y	Weight percentage of element y
x	Atomic weight of element x
XRD	X-ray diffraction
XRF	X-ray fluorescence
y	Atomic weight of element y
Zn	Zinc
α	Coefficient of linear expansion
ΔL	Change in length
ΔT	Change in temperature
μg	Microgram (10^{-6} gram)
$\mu g\ m^{-3}$	Microgram per cubic metre
μm	Micrometre (10^{-6} metre)
$\mu m\ yr^{-1}$	Micrometre per year

1 METALS

INTRODUCTION

Metals have had a tremendous impact on both the industrial and artistic legacies of human societies. The extent and range to which they and their compounds have been used and applied throughout history is remarkable, and testifies to their diverse properties. Metals have been used as tools, weapons, and construction materials. They have been finely crafted to produce artistic sculptures and ornate decorative elements, and added to non-metallic objects to enhance their appearance and beauty. Lustrous metals have been prized in jewelry, ornaments, medals, and religious objects, serving to signify beauty, wealth, prestige, or endearment. Metals have also been employed both decoratively and functionally in furniture and decorative art objects and their components. Many of the pigments that compose the artistic palette are chemical compounds containing a metal combined with other elements. Metals have played key roles in modern architecture, transportation, and communications, including the recent computer and Internet revolutions. All modern-day electrical and electronic devices have been made at least partly of metal. The magnetic properties of metals have been widely employed, as have their abilities to conduct heat and reflect light. With such a broad range of applications, it is not surprising that metals are present in some form or another in almost all museum collections.

A metal is, by definition, any of a class of chemical elements with certain characteristic properties:
- is a good conductor of heat and electricity
- is often lustrous
- is a ductile solid (meaning it can be bent, formed, hammered, drawn, or rolled when either hot or cold without breaking)
- can be cast by being poured into moulds when liquified
- forms positive ions in solution when it corrodes

In fact, most of the chemical elements in the periodic table of the elements are metals.

The term "metal" is also used to describe any material with metallic properties. As such, alloys (which are mixtures containing one or more of the metal chemical elements) are described as metals.

The following nine metals are covered in this book: aluminum (Al), copper (Cu), gold (Au), iron (Fe), lead (Pb), nickel (Ni), silver (Ag), tin (Sn), and zinc (Zn).

METAL FROM ORES

Ores are naturally occurring minerals from which metals can be extracted. Of the nine metals listed above, only three (gold, silver, and copper) can be found relatively pure and unbound to other elements, i.e. in their "native" state. The other six do not exist naturally in their pure elemental state; instead they are found combined with other elements as chemical compounds (ores). They can be combined with oxygen from the atmosphere as oxide minerals or with sulphur from the earth as sulphide minerals. To obtain these non-native metals in their pure elemental state, they must be extracted from their chemical compounds. Table 1.1 lists some of the common minerals from which the nine metals discussed in this publication can be extracted.

TABLE 1.1. METAL ORES

Metal	Mineral	Chemical formula
aluminum	gibbsite	$Al(OH)_3$
copper	chalcocite	Cu_2S
gold	(native)	Au
iron	hematite	Fe_2O_3
lead	galena	PbS
nickel	pentlandite	$(Ni,Fe)_9S_8$
silver	argentite	Ag_2S
tin	cassiterite	SnO_2
zinc	smithsonite	$ZnCO_3$

Converting a metal oxide (MO) to a metal (M) requires the addition of energy. One common method for carrying out this conversion is smelting, a process in which a metal oxide is heated in the presence of excess carbon (C) until the metal separates (usually by melting). This reaction can be described as follows:

$$MO(s) + C(s) \rightarrow M(l) + CO(g)$$

where (s) is a solid, (l) is a liquid, and (g) is a gas. The temperature required for this type of reaction to proceed depends on which metal is involved.

Once separated from its ore, the metal is unstable (because it is in a high energy state) and wants to return to a more stable, lower energy state (e.g. the natural state as found in the ore). This can be accomplished in a process known as corrosion, the best known example of which is the rusting of steel where the metal (iron) is converted to a non-metallic iron oxide (rust).

Reference material: Barraclough (1991); Street and Alexander (1995).

HISTORY OF METALS

Table 1.2 (adapted from Killick 2001) provides the approximate date of first widespread use for each of the metals covered in this publication.

TABLE 1.2. FIRST WIDESPREAD USE OF METALS

Metal	Approximate date of first widespread use
copper	~ 7000 B.C. (Near East) for native copper ~ 5000 B.C. (Near East) for smelted copper
lead	6000–5000 B.C. (Near East/Balkans)
gold	5000–4000 B.C. (Balkans)
tin	4000–3000 B.C. (Near East)
silver	4000–3000 B.C. (Balkans/Near East)
nickel	2000–1000 B.C. (Near East) for copper/nickel alloys
iron	1000–0 B.C. (Near East)
zinc	100–200 A.D. (Rome) for copper/zinc alloys 900–1000 A.D. (India) for zinc metal
aluminum	1800–1900 A.D. (Europe/United States)

It is not the intention of this publication to review the entire history of metals and the important technologies associated with their use, as the reference material at the end of this section includes some excellent resources on this subject. These books cover the early use of native copper and the development of copper smelting that led to the Bronze Age (~3000–1200 B.C.), as well as the improved technology that led to the Iron Age (~1200 B.C.) and the Industrial Revolution (~1750–1850 A.D.).

North American Aboriginal societies made use of metal long before permanent European settlements were established in what is now Canada. There is evidence of Inuit exploitation of iron meteorites for metal, using material found in the vicinity of Cape York, northwest Greenland. Aboriginal people from around Lake Superior and in the Northwest Territories also took advantage of native copper, which they treated as malleable stone and used to make tools and ornaments. However, it was not until after the arrival of the Europeans that metals were extracted from ores.

European metal first appeared in Canada as early as 1000 A.D. with the Norse settlement at L'Anse aux Meadows in Newfoundland. In the 16th century, European explorers such as Jacques Cartier and Martin Frobisher looked for Canadian ores suitable for extracting metals. Between the 17th and early 19th centuries, European metal (particularly silver) was used for trading with the Aboriginal people. With the completion of the Canadian Pacific Railroad in 1885, the exploration and development of mining and smelting in Canada grew significantly.

Reference material: Day and Tylecote (1991); Franklin et al. (1981); Hamilton (1995); Hancock et al. (1991); Jenness (1934); Killick (2001); Lambert (1997); Mouat (2000); Raymond (1984); Singer (1954); Street and Alexander (1995); Tylecote (1976, 1987).

PURE METALS

All metals contain atoms packed together in regular arrays. In pure metals, all the atoms are of the same kind. Each individual atom consists of:

- a small nucleus of protons and neutrons (number of protons and neutrons in the nucleus is unique to each element in the periodic table), and
- a large volume (mostly empty) in which the electrons are found (it is the nature of these clouds of electrons that surround metal nuclei that gives metals the ability to conduct electricity and heat)

Metals form crystals, which are regular, repeated patterns of atoms in a three-dimensional arrangement called a lattice. Within this lattice, the unit cell makes up the smallest group of atoms that are repeated to produce the lattice. A simple schematic diagram of a unit cell for gold, which has a lattice known as face-centred cubic (fcc), can be seen in Figure 1.1(a). Solid metal is not usually a single crystal but generally consists of many crystals clustered together into a polycrystalline (many crystal) structure. This pattern is often visible when metal is broken, and can also be seen on zinc-plated surfaces (see Figure 13.2 on p. 151). The crystals of a metal are called grains, and the junctions between them are referred to as grain boundaries. To see the grains, which are often quite small, it is usually necessary to etch the surface of a polished metal with an acid and view the surface with a microscope.

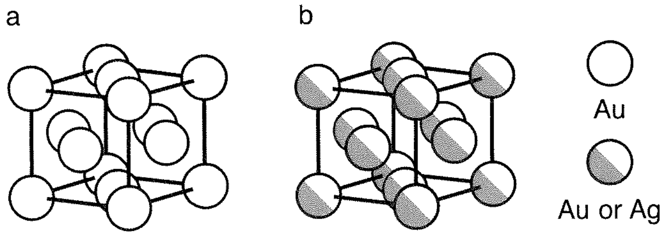

Figure 1.1. Unit cell for a face-centred cubic structure. (a) The position of atoms in the unit cell of pure gold. (b) Gold and silver atoms randomly occupy positions in the unit cell of gold–silver alloys. Adapted from Selwyn (2000).

ALLOYS

Alloys are formed by combining a metal with one or more other elements. For instance:

- two metals can be combined, e.g. brass (copper mixed with zinc), bronze (copper mixed with tin), and soft solder (tin mixed with lead)
- a metal can be combined with a non-metal, e.g. steel is a combination of iron (metal) and carbon (non-metal)
- a metal can be combined with mercury to form an amalgam, e.g. gold amalgam is a mixture of gold and mercury

The microstructure of an alloy (i.e. its structure on a microscopic level) depends on the solubility of the individual components in each other, as well as the heat treatment used to melt and cool the mixture. The microstructure can be made up of grains all having the same composition (i.e. single phase) or of grains having different compositions (i.e. multiple phases). Some of these phases may have ordered structures (i.e. ordered phases known as intermetallics). The various possibilities are discussed below.

SINGLE-PHASE ALLOYS

If two metals are soluble in one another, their mixtures (after melting and cooling slowly) have a single, uniform phase in the solid, i.e. the atoms of the two metals are completely miscible in one another and form a continuous single-phase solid solution over the entire composition range. This results when the atoms of the two metals are similar in size, so that atoms of one metal can easily occupy places in the lattice normally held by atoms of the other. For any given alloy composition, each grain has the same composition and structure. Figure 1.1(b) illustrates this arrangement for gold and silver, which are soluble in one another. The phase diagram in Figure 1.2 also demonstrates that mixtures of gold and silver are single phase. In a phase diagram, the horizontal axis shows the composition of the alloy and the vertical axis represents the temperature. Any point within the diagram represents the composition and phase of the alloy at that temperature. Above the horizontal line, mixtures of gold and silver are liquid; below it, they are solid.

MULTIPLE-PHASE ALLOYS

Multiple-phase alloys are formed when the metals are not soluble in each other, or only partially soluble. Following melting and cooling, the metals separate (on a microscopic level) into two or more solid phases. The phase diagram in Figure 1.3 illustrates an example of this based on mixtures of copper and silver. When the mixture has solidified after melting, it consists of a two solid phases, one silver-rich and the other copper-rich (except at high silver or high copper concentrations, where only one phase exists). The region where the two phases co-exist is labelled α_1 (for the copper-rich phase) and α_2 (for the silver-rich phase). In the transition between liquid and solid, the liquid and solid phases co-exist in some regions; in Figure 1.3 these regions are labelled as liquid and the symbol for the appropriate solid phase. Figure 1.4 contains an example of a cross section through a silver–copper alloy (~25 wt% silver, ~75 wt% copper) showing two phases.

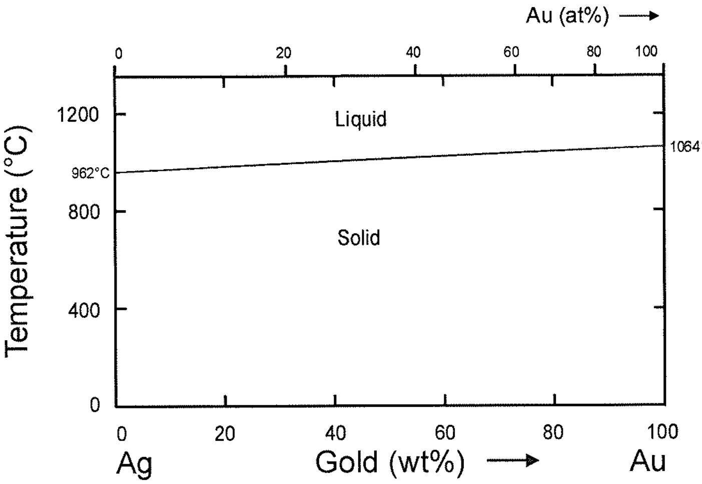

Figure 1.2. Equilibrium phase diagram for silver and gold. The bottom scale is weight percent and the top scale is atomic percent. Solids exist below the line, melt at the temperature specified by the line, and form liquids above the line. Mixtures of silver and gold form solids with a single phase because these two metals are soluble in one another. Adapted from ASM International (1992).

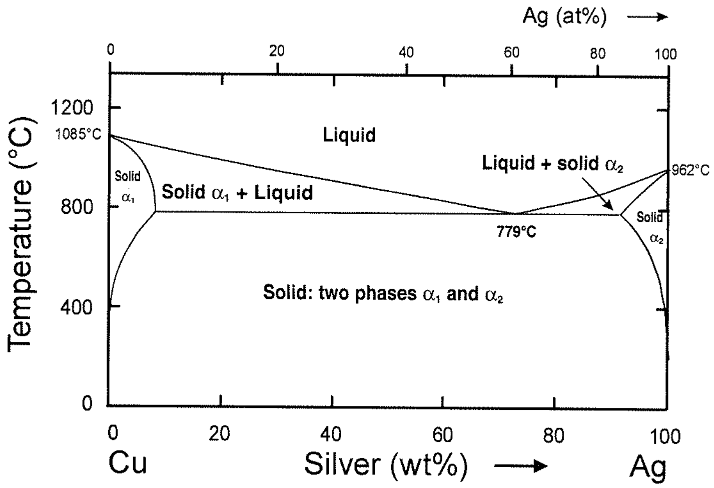

Figure 1.3. Equilibrium phase diagram for copper and silver. The bottom scale is weight percent and the top scale is atomic percent. Copper and silver are not appreciably soluble in one another. As molten copper and silver mixtures cool, they solidify into mixtures of two solid phases, labelled in the diagram as α_1 (rich in copper) and α_2 (rich in silver). Adapted from ASM International (1992).

ORDERED PHASES (INTERMETALLICS)

In some mixtures of two elements, the atoms may form intermetallic compounds. These compounds have an ordered structure, and may exist at a single composition or over a wide compositional range. Under certain conditions, mixtures of gold and copper can form these ordered phases. At high temperatures, gold and copper are soluble in one another and normally form solids with a single phase when cooled fairly rapidly after melting. However, at low temperatures, certain mixtures of gold and copper atoms can form new solid phases with ordered structures, especially if they have been warmed to these low temperatures. The gold–copper phase diagram in Figure 1.5 shows areas of ordered structures. Instead of being randomly distributed, the gold and copper atoms reorganize themselves into ordered structures, such as AuCu, $AuCu_3$, and Au_3Cu. Schematic diagrams of the unit cells for these ordered structures are shown in Figure 1.6.

Tin forms intermetallic compounds with many different metals, contributing to its importance in soldering, e.g. the tin in molten lead–tin solder reacts with many commonly soldered metals to form intermetallic compounds. Several tin–metal intermetallic compounds with approximate compositions are listed in Table 1.3.

TABLE 1.3. TIN–METAL INTERMETALLIC COMPOUNDS

Metal	Intermetallic compounds formed with tin (Sn)
gold	Au_5Sn, AuSn, $AuSn_2$, $AuSn_4$
silver	Ag_3Sn
copper	Cu_6Sn_5, Cu_3Sn, $Cu_{31}Sn_8$
nickel	Ni_3Sn_4, Ni_3Sn_2, Ni_3Sn
iron	FeSn, $FeSn_2$

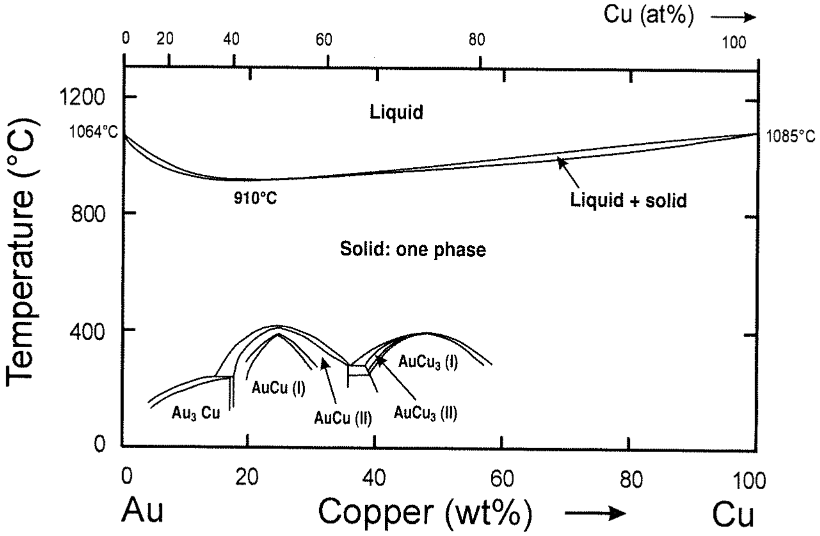

Figure 1.5. Equilibrium phase diagram for gold and copper. The bottom scale is weight percent and the top scale is atomic percent. The temperature range over which these alloys melt is given by the upper (liquid) and lower (solid) lines. At higher temperatures (i.e. just below the melting point), mixtures of gold and copper form single-phase solids. At lower temperatures, certain gold and silver mixtures form solids with ordered structures (intermetallic compounds) — Au_3Cu, AuCu(I), AuCu(II), $AuCu_3$(I), and $AuCu_3$(II). Adapted from ASM International (1992).

Figure 1.4. A cross section through a silver–copper alloy (~25 wt% silver and ~75 wt% copper) showing two phases; the white areas are rich in silver and the yellow ones are rich in copper. Photograph by Charlie Costain, CCI. Courtesy Laboratoire des Musées d'art et d'histoire de Genève. (A colour version of Figure 1.4 is available on p. 81.)

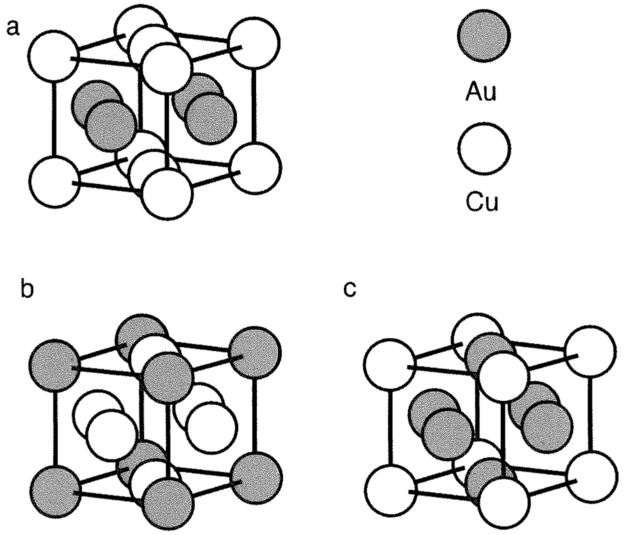

Figure 1.6. Three examples of ordered unit cells with face-centred cubic structure in gold–copper alloys: (a) ordered AuCu, (b) ordered AuCu$_3$, and (c) ordered Au$_3$Cu. Adapted from Wells (1984).

The formation of these intermetallic compounds at the soldering interface is important because they produce a metallurgical bond which makes the solder join strong. Intermetallic compounds also play a role in forming a strong metallurgical bond between zinc and iron in galvanized steel.

Reference material: ASM International (1990a, 1990b, 1992); Scott (1991); Selwyn (2000); Street and Alexander (1995); Wells (1984).

DUCTILITY, MALLEABILITY, WORK-HARDENING, AND ANNEALING

Pure metals are characterized by the ability of their atoms to slide over one another, thus allowing the metal to deform under pressure rather than breaking or cracking. This property is known as ductility when metals can be drawn into wires, and malleability when they can be shaped by hammering. Gold is the most malleable of all metals and can be hammered into extremely thin sheets. As a metal is worked cold (i.e. when a stress is applied through hammering, rolling, or other means), the crystal structure is elongated in the direction of working. Working builds up internal stresses and causes the metal to become harder (i.e. work-hardened). Work-hardened metals can be made soft again by reheating the metal to a temperature that is high enough to relieve internal stresses, allow the crystals to return to a more uniform shape, and restore ductility and malleability; this process is known as annealing. Examination of the grain structure of historic metals can reveal important technological information about how that metal was worked to produce the artifact (provided, of course, that such information has not been destroyed by heat treatments).

Alloys are typically less malleable than pure metals because they consist of a mixture of two or more elements. This can result in a distortion of the crystalline lattice, especially if the metal atoms are of significantly different sizes. Because of this distortion, it becomes more difficult to shift and slide the atoms over one another by hammering or other means, and in practice this results in a harder, less malleable material.

Reference material: Barclay (1992); Carter (1979); Scott (1991); Street and Alexander (1995).

PLATING

ELECTROPLATING AND HOT-DIPPING

Electroplating is a process in which a solid conducting surface can be coated with a layer of metal by means of electrolysis. (More information on electrolysis is provided in Appendix 2 on p. 17.) Electroplating was patented in 1840 by Elkington and Co. of Birmingham, England. The process requires an external source of electric current and a suitable electrolyte (a solution containing a metal salt of the metal to be plated). A current is passed through the solution and the reduction reactions taking place on the cathode surface reduce the metal ions in solution to metal.

A layer applied by electroplating (e.g. tin electroplated onto iron) is not usually as well bonded to the base metal as a layer applied by hot-dipping (e.g. dipping iron into molten tin). This is due to the fact that hot-dipping allows for the formation of intermetallic compounds and a strong metallurgical bond between the layers, and electroplating alone does not. However, if electroplated objects are heated enough to melt the surface and then quenched, the intermetallic compounds can form and the bond will be strengthened.

ELECTROFORMING (ELECTROTYPING)

Electroforming was introduced at the same time as electroplating, and is a specific type of electroplating used to make reproductions of metal objects. The early term for this process, often used to describe the electroplating of plaster, was "galvanoplasty" and the process was called the "galvano process."

This process involves coating a non-metallic mould of the object to be reproduced with a conducting agent (e.g. graphite) and then plating it with a relatively thick layer of metal, usually copper. After plating, the original mould is removed, leaving an exact replica of the original object. Although it can be difficult to distinguish the replica from the original, electroform reproductions usually have a granular texture on the back or inside of the piece.

ELECTROLESS PLATING

Electroless plating is a process that uses chemicals rather than an applied electric current to produce the plating layer. Two solutions are prepared, one containing a metal salt and the other a reducing agent. When these solutions are mixed together, the metal ions in solution are reduced to metal and precipitate from solution. An electroless silvering process was introduced in the 1830s to deposit metallic silver onto glass. By the 1850s this had led to the production of silver-backed mirrors. Electroless nickel solutions for coating metals with nickel became commercially available in the mid 1940s. By the mid 1960s, electroless nickel solutions were capable of plating nickel onto plastics at room temperature.

ELECTROCHEMICAL REPLACEMENT PLATING

When a solid metal is placed in a solution containing ions of another more noble metal, the ions may be reduced and plate onto the solid as it corrodes. This interaction has been used intentionally to plate one metal onto another in a process referred to as "electrochemical replacement plating." For example, if copper metal is placed in a solution of silver nitrate, a thin layer of silver will plate onto the copper surface. Platinum and gold have been plated on copper surfaces using this process. As in electroless plating, the process does not involve the use of an applied electric current. It has also been called electrochemical plating, immersion plating, and replacement plating.

ELECTROPOLISHING

This process, also called electrolytic polishing, can be used to produce a smooth shiny finish on plated metals and on stainless steels. The metal to be polished is made the anode in an electrochemical cell, and forced to corrode. Microscopic deformations such as ridges and peaks are preferentially dissolved, resulting in a smoother finish.

Reference material: Bewer and Scott (1995); Child (1993); Krulik (1994); Larsen (1984); Lewis (1988); Raub (1993); Roberts (1999); Score and Cohen (1995); Scott (2002).

METAL IDENTIFICATION

Research, conservation assessment and treatment, and the need for informative exhibit labels often make it necessary to identify metals in museum collections. The following are various common and useful identification methods.

COLOUR OF METAL

When pure and uncorroded, gold is yellow, copper is salmon pink, and the other metals discussed in this publication are white. Alloys of these metals can have a range of colours (e.g. as alloying elements are added to copper, its colour changes from salmon pink to various shades of yellow or white). Some alloys are mixtures of several different elements, and their final colour depends on the relative amounts of the components. However, the metal of highest concentration does not necessarily impart its own colour. For example, copper–nickel alloys with as little as 12 wt% nickel are white (between 1982 and 2000, the Canadian 5-cent coin was made from an alloy containing 75 wt% copper and 25 wt% nickel — but it was white and known as the "nickel") . The application of plating over a base metal further confuses the issue of metal identification on the basis of colour.

Figure 1.7 shows the reflectivities of seven of the metals discussed in this publication. Copper and gold have a red or yellow colour because they do not have a high reflectivity at the blue end of the spectrum. The other metals are white with a slight yellowish or blueish sheen, depending on the reflectivity. Nickel and silver have a warm yellowish sheen because they have a slightly reduced reflectivity at the violet end of the spectrum. Zinc has a colder blue sheen because it has reduced reflectivity toward the red end of the spectrum.

Reference material: Nassau (1983); Weaver and Frederikse (1998).

CRYSTALLINITY

The crystallinity of metals can sometimes be seen on the surface, and may give a clue to the type of metal. Take, for example, galvanized iron made by dipping iron into molten zinc (hot-dipping). As the zinc cools, it forms a distinct crystalline pattern (see Figure 13.2 on p. 151) that can be felt with the fingers. Some tinplate (made by hot-dipping iron into molten tin) can also show this feature, but the pattern is usually finer. The crystalline nature of metals can also be seen in the ends of broken pieces, although identification is not necessarily possible.

Reference material: Canadian Conservation Institute (2002b).

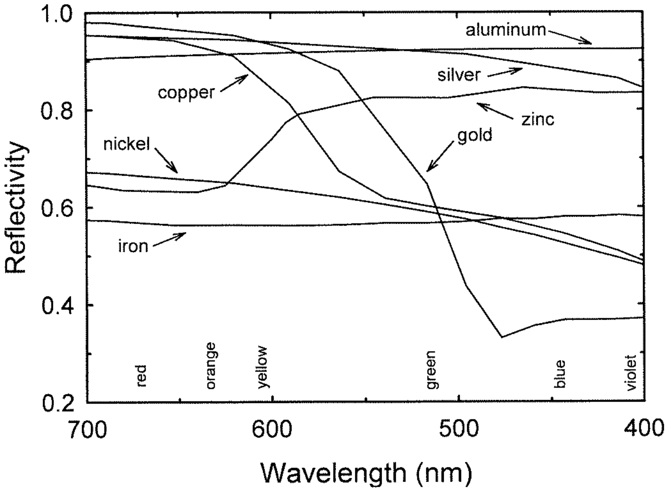

Figure 1.7. The reflectivity (normal incidence reflection) of seven of the nine metals discussed in this publication (lead and tin are missing). Adapted from Weaver and Frederikse (1998).

DOCUMENTARY EVIDENCE

When attempting to identify the metals that are present in an artifact, the first resources to check are books, trade catalogues, period magazines, or advertisements. Manufacturers often described their techniques and materials in detail. There may also be marks, stamps, and/or numbers on precious metals. For the last few centuries, it has been a standard practice in many countries for silver and gold objects to be hallmarked for purity and date of manufacture (see "Chapter 11. Silver" for more information on hallmarking). Objects made of other metals may also show trademarks, catalogue marks, and a range of other stamps.

Reference material: Canadian Conservation Institute (2002a); Child (1988).

UNIFIED NUMBERING SYSTEM (UNS)

For recently manufactured objects, reference may be made to national or international numbering systems that define metal alloys (and their composition) in current use. The designated number for an alloy is useful for documenting original material in a new object or added material in a repair.

In North America, the current alloy designation system is the Unified Numbering System (UNS) which is managed jointly by the American Society for Testing and Materials (ASTM) and the Society of Automotive Engineers (SAE). This system identifies commercial metals and alloys that are in regular production and use. Each UNS designation consists of a single-letter prefix followed by five digits (e.g. Axxxxx for aluminum, Pxxxxx for precious metals, Sxxxxx for stainless steels).

The UNS numbers for many alloys have been included in this publication (usually in tables).

Reference material: ASTM (2001a); SAE and ASTM (2001).

CONSTRUCTION TECHNIQUES

To construct a metal object, the metal must first be manipulated into the initial shape using one of two basic approaches: casting or working. A cast metal object is one that has been created by melting the metal and then pouring it into a mould. For example, a cast bronze statue is one that has been formed by the solidification of molten bronze in a mould. Iron that is to be cast must have enough carbon in it to allow it to be melted and poured. A worked ("wrought") metal object is one that has been created by hammering, rolling, extrusion, forging, or drawing the metal while still solid. Because metals are more ductile at higher temperatures, they are often heated (but not melted) while being worked. Iron can be hammered into useful shapes while red hot.

A wide range of techniques can be used for shaping and finishing metal. Determining what construction techniques were used to make a metal object may help to narrow down the metal(s) present (this is particularly useful for identifying iron). For example, raised mould lines indicate that the metal object was formed by casting, while tool marks on the surface indicate what kind of machining the object has undergone.

There are four basic stages in constructing an object:
- forming is the step where ingots of metal are given their initial shape
- shaping is the process of establishing the final dimensions of a piece
- assembling refers to putting together pre-made parts
- finishing is the process used for decorative purposes or for further protection

Table 1.4 contains some examples of forming, shaping, assembling, and finishing, although these lists are by no means complete.

TABLE 1.4. CONSTRUCTION TECHNIQUES FOR METAL OBJECTS

Construction step	Examples
forming	casting, forging, rolling
shaping	milling, turning, spinning, grinding, stamping, cutting, drilling
assembling	welding, soldering, brazing, rivetting, bolting, crimping, gluing
finishing	plating, burnishing, polishing, etching, sand-blasting, painting, lacquering, engraving, chasing, embossing, enamelling, patinating

Reference material: Hodges (1964); Maryon (1971); Scott (1991); Street and Alexander (1995); Young and Fennell (1980).

COLOUR OF CORROSION PRODUCTS

The colour and physical appearance of corrosion products on various metals can also be used to make a reasonable guess as to the type of metal present in an object. The colour may depend on the oxidation state of the metal in the corrosion product. For example, copper compounds with copper in the +1 oxidation state (written as Cu(I) or Cu^+) can be red, black, or colourless, whereas those in the +2 oxidation state (Cu(II) or Cu^{2+}) are usually beautiful greens or blues. Table 1.5 provides a brief summary of the typical colours of corrosion products (more information on the specific colour and composition of corrosion products is given in the subsequent chapters on individual metals).

An overview of the appearance of stable and unstable surfaces is provided below.

Stable surfaces: Stable corrosion layers on metal artifacts are generally adherent and the thickness does not increase (or increases only minimally) with time. They are usually thicker and more uneven on archaeological alloys than on non-archaeological ones. On copper and copper alloy artifacts, stable surfaces are characterized by a wide variety of natural and artificial (intentional) patinas, the colour of which can vary from red, brown, black, and blue to shades of green. On corroded iron, stable surfaces tend to be compact, adherent, and vary in colour between blue-black and red-brown. On lead and leaded pewter, stable surfaces are generally dark gray, although the colour may also vary from black to brown.

Active corrosion: The term "active corrosion" is generally used in conservation literature to refer to fresh or new corrosion on an object. Signs of active corrosion include spalling, cracking, or loose flakes of material surrounding an object. This kind of physical damage may be due to recent corrosion that has formed on the metal surface and expanded against the overlying material (corrosion products, paint, varnish, etc.), or to absorption of water by surface contaminants (e.g. salts) that has led to an increase in volume. Efflorescence and deliquescence are also indicators that corrosion-stimulating salts may be present on the surface. Efflorescence is powdery material on the surface caused by salts losing their water of crystallization, and deliquescence is water on the surface caused by salts absorbing water. Active corrosion may have a characteristic appearance on different metals and alloys:

- Copper and copper alloys — "Bronze disease" is a well recognized form of active corrosion that is characterized by the rapid development of a light-green powder erupting in spots over the surface (see Figure 6.6 on p. 66).

TABLE 1.5. TYPICAL COLOURS OF CORROSION PRODUCTS

Metal	Typical colours of corrosion products	Comments
aluminum	colourless or white	• can be difficult to identify by X-ray diffraction
copper	Cu(I): red, black, colourless Cu(II): green, blue	• wide variety of beautiful shades • active corrosion is light green • copper iron sulphides can be gold coloured
gold	—	• corrosion products usually associated with other alloying elements (e.g. copper, silver)
iron	Fe(II,III): black Fe(III): red, yellow, orange	• rapid rusting forms an orange rust • iron sulphides can be gold coloured
lead	white, red, yellow	• active corrosion is white
nickel	green	• rare because nickel is corrosion-resistant
silver	black, white	• white silver compounds may darken when exposed to light • thin tarnish can have interference colours
tin	black, white	• tin sulphides can be gold coloured
zinc	colourless or white	• metallic zinc dust is dark blue-gray

- Iron — Active corrosion usually results from contamination by chloride ions, with fresh corrosion occurring between the metal core of an artifact and its outer corrosion layer. Fragments surrounding an object (Figure 1.8) or bright orange spots on the object (see Figure 8.13 on p. 107) are both clear indications of active iron corrosion. The corrosion product in these bright reddish-orange spots is often iron hydroxide oxide, β-FeO(OH) — the mineral akaganéite. Chloride ion contamination on iron may also produce another symptom of active corrosion referred to as "weeping" or "sweating," a form of deliquescence. Weeping initially takes the form of yellow, brown, or orange droplets when the relative humidity (RH) is high, and results in desiccated blisters after RH has decreased.
- Lead and leaded pewter — Active corrosion is characterized by the formation of loosely adherent white powder. Figure 1.9 illustrates this problem on lead tokens. The powder may form evenly over the entire surface or it may be localized in small spots. Powder surrounding an undisturbed object is a clear indication of this active corrosion. This white powder is lead carbonate hydroxide (better known as white lead, $Pb_3(CO_3)_2(OH)_2$), and is most commonly induced by the vapours of volatile organic acids.

Reference material: Canadian Conservation Institute (1995, 1997); Cronyn and Robinson (1990); Pearson (1987).

DENSITY

The density of an object can provide clues to the type of metal present. Density is a measure of the compactness of a substance expressed as its mass per unit volume (e.g. grams per cubic centimetre, g cm^{-3}). The density of an object made of a single metal or alloy (i.e. not a composite object made of more than one material) can easily be determined if it can be safely immersed in a liquid. Before submerging an object in any liquid, it is important to check that there is no paint, lacquer, varnish, or other surface treatment that might be damaged. If the liquid chosen is alcohol, the metal surface will dry quickly after removal (anhydrous ethanol does not contain any water, and should be used if possible).

Begin by weighing the object in air to determine its mass in air. Next submerge the object in the chosen liquid and weigh it again (a balance with a hook attachment on the underside is useful for this procedure) to determine its mass in liquid. The density of the object can then be calculated using the following equation:

$$\text{density of object} = \frac{(\text{mass in air}) \times (\text{density of liquid})}{(\text{mass in air}) - (\text{mass in liquid})}$$

(Note: At 20°C, the density of anhydrous ethanol is 0.789 g cm^{-3}, and the density of water is 0.998 g cm^{-3}.)

Once the density of the metal in the object has been calculated, it can be compared to literature values for pure metals or alloys to determine the closest match. The densities of the nine metals (in pure form) discussed in this publication are listed in Table 1.6.

Figure 1.8. The corrosion products surrounding the top nail provide evidence that this nail is unstable and is suffering from active corrosion. The two lower nails are stable.

Figure 1.9. The lead tokens covered with white corrosion and surrounded by white particles are suffering from active corrosion; the other tokens are not.

TABLE 1.6. DENSITIES OF METALS

Metal	Density at 20°C (g cm^{-3})
aluminum	2.70
copper	8.96
gold	19.3
iron	7.87
lead	11.35
nickel	8.90
silver	10.5
tin	7.31
zinc	7.13

For densities of various alloys, consult the reference material cited below.

Reference material: ASTM (2001b); Smithells (1976); Thompson (1971).

MAGNETIC PROPERTIES

Metals can range from strongly magnetic to weakly magnetic to non-magnetic. Iron and most of its alloys (carbon steels, cast irons, certain stainless steels) are strongly magnetic, although certain non-magnetic stainless steels may become weakly magnetic when cold-worked. Nickel and cobalt are also strongly magnetic although their alloys may or may not be, depending on the composition of the alloy and the temperature. For example, the nickel–copper alloy Monel (66 wt% nickel, 34 wt% copper) loses its magnetic properties when heated to 100°C. Non-ferrous metals and their alloys (except for cobalt and nickel) are not magnetic. Some corrosion products (e.g. magnetite) are also magnetic. A permanent magnet can be used to determine if a metal is magnetic, or if there is any metallic material remaining in a freshly excavated archaeological object, a piece of rusty sheet iron, or underneath a plating layer. If the metal in sheet iron has rusted completely, then it will be completely "mineralized" and will not be as strongly magnetic as uncorroded sheet iron.

CHEMICAL SPOT TESTS

Spot tests can be used in conjunction with other simple methods, such as magnetism and density measurements, to help determine what metals are present in an object. Chemical spot tests have been developed to identify metal ions in solution. Pure metals are usually easily distinguished with these spot tests, but alloys cannot be characterized unambiguously because concentrations of metals in an alloy can be well below the margin of error of the testing method. As spot testing may leave a mark on the surface of an object, it may not be appropriate for museum objects. Also, there is the possibility that different metal ions might cause the same colour change on the test paper, which interferes with the test. For definitive results, modern analytical techniques should be used.

Laver (1978), Townsend (1988), and Odegaard et al. (2000) deal specifically with the application of chemical spot testing to museum objects, and they are excellent resources for information on how to carry out these procedures. These publications provide details on how to identify the metals present in an object using various chemicals; they often recommend the use of electrolysis to introduce metal ions into solution where they can then be detected. Appendix 1 (on p. 16) and Appendix 2 (on p. 17) provide more information about spot test papers and electrolysis.

Reference material: Feigl and Anger (1972); Laver (1978); Odegaard et al. (2000); Townsend (1988); Wilson (1974).

ANALYTICAL METHODS

Modern analytical techniques remove the guesswork and provide far more information than the chemical spot tests discussed above. Radiography, for example, can provide information about the shape of an archaeological metal object covered with an obscuring crust of corrosion products and soil residues. It can also indicate the extent and location of metal and corrosion, as well as the presence of plating, welds, and cracks. A radiograph of an object is an image of that object produced on specially sensitized film by radiation (usually X-rays or gamma rays).

Many analytical techniques require that a sample be taken from the object. Before proceeding, it is important to consult all people involved (e.g. conservator, curator, owner) about the need for sampling, and to obtain permission from the owner of the object. An experienced analyst can best determine if a sample is required and what its size should be. Sampling requires great care to avoid damaging or disfiguring an object, and should preferably be done by a scientist specializing in this area or by a conservator. If the sample is large and the location will require infilling, a conservator should be consulted.

Analysis of metal: In an object made of metal, metallography and elemental analysis are usually combined to identify the microstructure and the elements present.

Metallography is the study of polished sections of samples taken from metal objects. It is conducted with a light microscope that allows the viewer to study the microstructure of the alloy. Metallographic samples are usually mounted in resin, polished, and etched to enhance the microstructure. In addition to the metal, the samples may also contain corrosion products, paint layers, or plating. By viewing the microstructures, metallurgists can determine the nature of the alloy, its thermal history and corrosion, and possibly even the manufacturing process. The example in Figure 1.10 illustrates a cross section of wrought iron, a type of relatively pure iron containing inclusions of glass-like slag.

Elemental analysis of a metal sample can be carried out using X-ray fluorescence (XRF) or X-ray microanalysis. However, X-ray microanalysis and XRF both detect elements from the surface of the sample. Therefore, if the sample is from the surface of an object rather than the interior, the result may not represent the true composition of the underlying metal, especially if plating is present or selective corrosion has depleted certain elements from the surface. Figure 1.11 contains an example of the elemental analysis of a piece of wrought iron.

Trace elements in metals can be identified by removing small samples from an uncorroded section and examining them with techniques such as neutron activation analysis (NAA) and inductively coupled plasma/atomic emission spectroscopy (ICP/AES). In NAA, the sample is irradiated in a nuclear reactor and the elements are detected by their characteristic gamma rays emitted after irradiation. In ICP/AES, a small sample is fully dissolved in a solution (e.g. by acid dissolution) which is then atomized in a high-temperature plasma. The identity of many of the elements in the solution can be determined by the light emitted by the elements after they have been atomized in the plasma.

Analysis of surface material: The chemical composition of surface material such as coatings and organic (e.g. metal soaps) and inorganic (e.g. metal salts) corrosion products can be identified using analytical techniques such as X-ray microanalysis in combination with X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), or gas chromatography/mass spectrometry (GC/MS).

XRD is used to identify the crystalline components present in a solid (e.g. metal, inorganic, organic) material. If the solid has crystallized in a well-ordered manner, XRD is very effective. However, if the crystallization is not well ordered (such a solid is described as amorphous), it may not be possible to discern it with XRD. Corrosion products such as aluminum oxides, iron oxides, and copper sulphides are often amorphous and difficult to identify using this technique.

FTIR is especially useful for identifying organic materials on the surface of a metal object (e.g. paints, waxes, metal soaps), but some inorganic materials

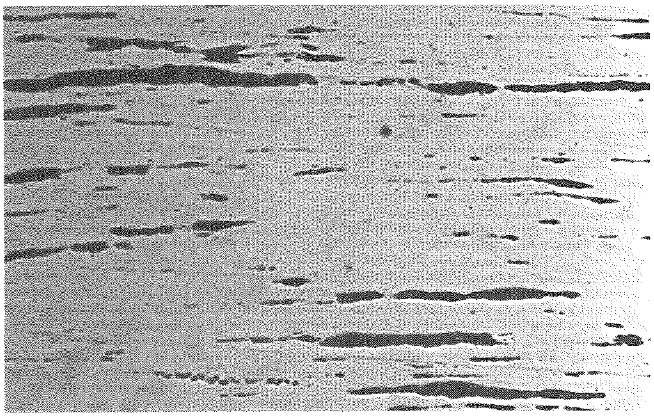

Figure 1.10. Cross section of wrought iron. Microstructure of wrought iron showing slag inclusions (dark areas) in a matrix of iron (ferrite, light areas). The slag is elongated in the direction of metal flow. Magnification x *50. Photograph by H. Unglik, Parks Canada.*

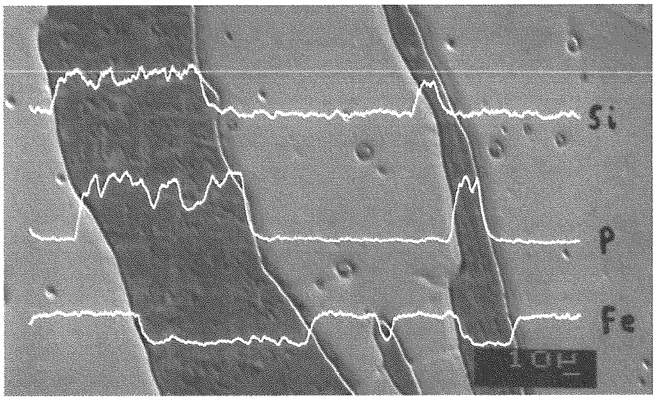

Figure 1.11. Scanning electron micrograph of a wrought iron nail from L'anse aux Meadows, NL. Elemental analysis shows that the light areas have high levels of iron (Fe) and the dark areas (i.e. slag) are rich in silicon (Si) and phosphorus (P). Magnification x *400. Photograph by H. Unglik, Parks Canada. Adapted from Unglik and Stewart (1999).*

can also be distinguished. If the material is a mixture of several compounds, it may be difficult to establish the exact chemical composition of each compound although the family or group of organic material (e.g. alcohol, acid) may be recognized. GC/MS can be used to separate and identify the compounds in a sample, often after FTIR has been used to obtain a general idea of what families of compounds are present.

Reference material: Canadian Conservation Institute (2002b); Scott (1991); Wainwright (1990); Wayman (1989).

APPENDIX 1: SPOT TEST PAPERS

The chemicals needed to carry out spot tests fall into two categories:

- chemical indicators (e.g. cacotheline nitrate) that change colour when exposed to a specific metal ion in solution, hence their usefulness in identifying that metal
- other chemical reagents (e.g. water, sodium chloride, hydrochloric acid) that may be needed to complete the test, often as an electrolyte into which the metal will corrode

Spot test paper can be made by soaking filter paper in a solution of a suitable chemical indicator and then allowing it to dry. Alternatively, ready-made spot test papers are available for many metal ions; these already have the chemical indicator incorporated into the paper. Some commercially available spot test papers (made in Germany by either Macherey-Nagel or E. Merck) relevant to the metals discussed in this publication are listed in Table 1.7.

Each brand has advantages and disadvantages. The spot test papers made by Macherey-Nagel are large enough to be cut up into many smaller pieces (thus providing for many tests) whereas the test papers by E. Merck are only large enough for a single test. On the other hand, E. Merck supplies the other chemical reagents needed in addition to the test papers but Macherey-Nagel does not.

There are no commercial spot test papers for gold or tin. However, Odegaard et al. (2000) describe some relatively simple spot tests for both: gold requires electrolysis, sodium chloride, tin(II) chloride, and hydrochloric acid; and tin requires electrolysis, sodium chloride, and cacotheline nitrate.

Reference material: Feigl and Anger (1972); Laver (1978); Odegaard et al. (2000); Townsend (1988).

SUPPLIERS FOR SPOT TEST PAPERS

Macherey-Nagel
www.mn-net.com
distributed in Canada by
Aldert Chemicals Ltd.
4889 Dundas St. West, Suite 5
Islington ON M9A 1B2
tel.: (416) 236-4222 or
1-800-268-6656

E. Merck
www.merck.com
distributed in Canada by
VWR International
2360 Argentia Road
Mississauga ON L5N 5Z7
tel.: (905) 813-7377 or
1-800-932-5000

TABLE 1.7. EXAMPLES OF COMMERCIALLY AVAILABLE SPOT TEST PAPERS FOR VARIOUS METALS

Metal	Commercial spot test paper	Other chemical reagents required	Electrolysis required	Cost (2004 price in CAN$)
aluminum	Aldert 90721 aluminum test paper	hydrochloric acid sodium acetate ammonium hydroxide acetic acid	yes	$55 for 100 pieces (each piece is 2 x 7 cm)
copper	Aldert 90601 cuprotesmo	distilled water	no	$70 for 40 pieces (each piece is 2.5 x 4 cm)
iron	Aldert 90725 dipyridyl	sodium chloride	yes	$55 for 200 pieces (each piece is 2 x 7 cm)
lead	Aldert 90602 plumbtesmo	distilled water	no	$70 for 40 pieces (each piece is 2.5 x 4 cm)
nickel	Aldert 90730 nickel test paper	sodium chloride	yes	$55 for 200 pieces (each piece is 2 x 7 cm)
silver	Aldert 90732 silver test paper	sodium chloride ammonium chloride hydrochloric acid	yes	$55 for 200 pieces (each piece is 2 x 7 cm)
zinc	Merckoquant 10038 zinc test	reagent provided (sodium hydroxide)	no	$106 for 100 pieces (each piece is 6 x 6 mm

APPENDIX 2: ELECTROLYSIS

Electrolysis is, by definition, the production of chemical changes by the passage of current through an electrochemical cell. A battery or power supply can be used as a source of current. Bubbles of gas may form at either electrode because of the electrolysis of water. Oxygen bubbles may form at the anode as water is oxidized ($2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$); and hydrogen bubbles may form at the cathode as water is reduced ($2H_2O + 2e^- \rightarrow 2OH^- + H_2(g)$).

ELECTROLYSIS TO FORCE CORROSION

To successfully identify the metal components in an object, it is often useful or necessary to apply electrolysis, as shown in Figure 1.12. An electrochemical cell is established by attaching the metal in the object to the positive terminal (red ⊕) of the battery (making the metal the anode), and attaching metal tweezers to the negative terminal (black ⊖) (making the tweezers the cathode). The circuit is completed by picking up moistened chemical spot test paper (the solution used to moisten the test paper depends on the specific test) in the tweezers and touching one end of the wet paper to the metal surface. (Note: It is important to ensure that the tweezers do not touch the metal surface directly.) When a metal is attached to a battery in this way, the metal corrodes and metal ions are forced into solution where they can be detected by the spot test papers, usually by a colour change.

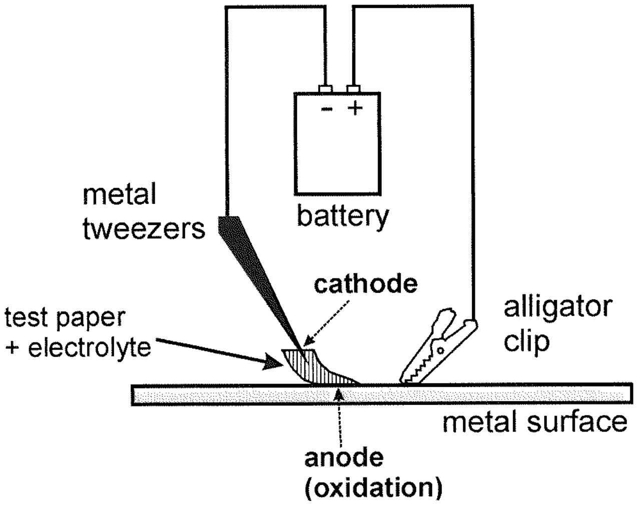

Figure 1.12. Schematic diagram showing the use of electrolysis in chemical spot testing. The test metal is made the anode and is forced to corrode, allowing metal ions to go into solution where they can be detected. Adapted from Laver (1978).

ELECTROLYSIS TO REDUCE CORROSION PRODUCTS

Electrolysis can also be used to reduce corrosion products. For example, by applying electrolysis to corroded iron, the red iron hydroxide oxide, FeO(OH), can be reduced to black magnetite, Fe_3O_4. The iron in FeO(OH) is initially present in the +3 oxidation state (i.e. Fe^{3+}), but during electrolysis some of the Fe^{3+} ions are reduced to the +2 oxidation state (i.e. Fe^{2+}), forming magnetite which contains a mixture of Fe^{2+} and Fe^{3+} ions.

To carry out electrolysis, the corroded metal is attached to the negative terminal of the battery or power supply, making it the cathode in an electrochemical cell. Another metal, such as stainless steel, is attached to the positive terminal to form the anode. When applied locally on a small scale, this procedure is referred to as spot electrolysis (see Figure 1.13 for an illustration of this technique).

Reference material: Laver (1978); Roberts (1999).

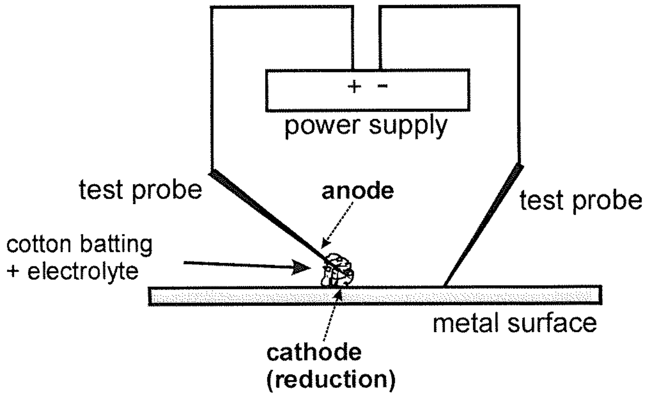

Figure 1.13. Schematic diagram showing the use of electrolysis for local corrosion reduction (spot electrolysis). The corroded metal is made the cathode and reduction reactions take place on the corroded metal surface.

2 CORROSION

INTRODUCTION

Corrosion on metal objects may be valued for its colour, beauty, or stability. But it may also be disfavoured if it masks the object's intended surface, and can even be dangerous if it weakens the object's physical structure. One of the first steps in caring for metal objects is therefore to determine whether corrosion is desirable or dangerous. If corrosion is found to be a problem, implementing strategies to prevent it from happening or successfully treating the problems it causes requires an understanding of how it occurs.

Most metals (except for precious metals such as gold) exist naturally as ores which can only be converted to pure metals through the addition of energy. In other words, most pure metals are essentially "an ore plus stored-up energy" — which makes them inherently unstable. The drive to release this stored-up energy and return to a more stable state is the force behind corrosion.

Corrosion of metals is almost always electrochemical in nature. It occurs when two or more electrochemical reactions take place on a metal surface, and results in some of the metal changing from the metallic state to a non-metallic state (e.g. a metal oxide). These products of corrosion may be dissolved or solid species.

CORROSION AND PATINA

When a metal reacts with its environment (i.e. corrodes), the compounds that form on the surface as a result of this process are known as corrosion products. When these products adhere to the surface of the metal, the resulting appearance is often called patina. Patina can develop naturally or can be artificially created. A natural patina is one that has developed slowly over many years of exposure, e.g. the ongoing corrosion of outdoor bronze statues or buried copper alloys results in a natural patina. Natural patinas contain a wide variety of corrosion products as well as dust, soot, etc. In contrast, an artificial patina is one that has been created intentionally by exposing the metal to specific chemicals to produce desired colours. Artificial patinas contain only a limited number of corrosion products.

Reference material: Brown et al. (1977); Hughes and Rowe (1982); Scott (2002); Young (2000).

CORROSION AND CORROSION TERMINOLOGY

A brief overview of some of the key corrosion terminology is given below (a more extensive list of terms can be found in the "Glossary" on p. 195). For more detailed explanations of terminology, consult the reference material cited at the end of this section.

Corrosion is an electrochemical process in which electrons are transferred from one metal or species to another during simultaneous reactions called **oxidation–reduction reactions** or **redox reactions** that occur in a solution or **electrolyte**. **Oxidation reactions** are chemical reactions in which the constituents lose electrons; if the constituent is a metal or metal ion and it is oxidized, the oxidation state is increased. **Reduction reactions** are chemical reactions in which the constituents gain electrons; if the constituent is a metal or metal ion and it is reduced, the oxidation state is reduced. During a redox reaction, both oxidation and reduction reactions occur simultaneously and in equivalent amounts.

An **electrode** is an electrical conductor in contact with an **electrolyte** or conducting medium; it serves as a site through which an electric current can enter or leave. An **electrochemical cell** is a combination of two electrodes in electrical contact and immersed in an electrolyte. Reduction reactions occur at the electrode called the **cathode**; oxidation reactions occur at the other electrode, the **anode**.

The **electrode potential** is the electric potential of an electrode immersed in an electrolyte. When two different electrodes are immersed in the same electrolyte, a difference in electric potential exists between them because of the difference in their relative electrode potentials. This difference in potential, measured in volts, is called the **electromotive force**.

A **reference electrode** is an electrode with a stable and reproducible potential. Reference electrodes are used in the measurement of other electrode potentials. The standard hydrogen electrode (SHE) is a reference electrode which has its electrode potential set, by definition, to zero. It can be used to produce a scale of electrode potentials, known as the **electrochemical series**, which lists **standard equilibrium potentials** for immersed electrodes in standard conditions with equilibrium conditions maintained throughout the measurement. **Equilibrium potentials** for an immersed electrode in non-standard conditions can be calculated using the standard equilibrium potential and the Nernst equation.

A **corrosion potential** is the electrode potential of a corroding metal surface immersed in an electrolyte. Because the metal is corroding, it is not at equilibrium.

Reference material: ASM International (1987); ASTM (2001a); Beale et al. (1988).

CORROSION REQUIREMENTS

Most metals will corrode when exposed to air and water, in an electrochemical process that involves the transfer of electrons between simultaneous oxidation and reduction reactions. This corrosion process can be characterized as a reaction taking place in an electrochemical cell consisting of an anode and a cathode in electrical contact (i.e. path for electrons) and immersed in an electrolyte (i.e. path for ions). Figure 2.1 presents a schematic diagram of this reaction. The anode (site of the anodic half-reaction) and cathode (site of the cathodic half-reaction) may be dissimilar areas on the same metal or separate areas on different metals. The two half-reactions, an oxidation half-reaction (a reaction that generates electrons) and a reduction half-reaction (a reaction that consumes these electrons), combine to give the net chemical reaction describing the corrosion process.

An electrochemical cell can operate only when the electrons and ions can flow between the anode and cathode. An electrolyte (e.g. water) provides a path for ions to flow, and an electrical conductor (e.g. metals) provides a path for electrons to flow. Therefore, the best way to minimize metal corrosion is to keep the metal dry. By removing water, the electrolyte is removed from electrochemical cells and the corrosion reactions cannot proceed.

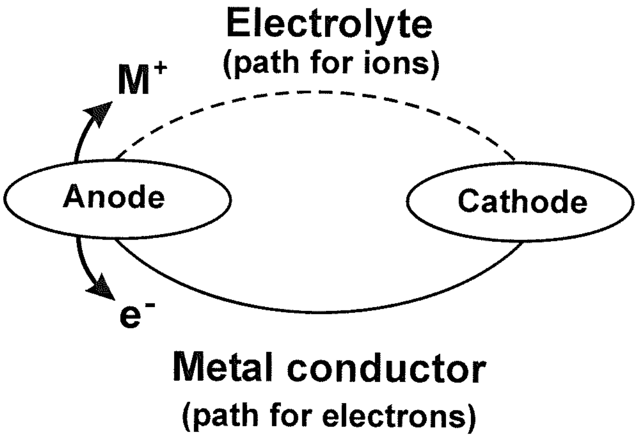

Figure 2.1. Schematic diagram of the corrosion process, which requires an anode, a cathode, a path for ions, and a path for electrons. M^+ = metal ions; e^- = electrons. Adapted from Payer (1992).

There are four requirements for a metal to corrode (i.e. for current to flow in an electrochemical cell):
(1) an anode where oxidation processes take place
(2) a cathode where counterbalancing reduction processes take place
(3) an electrical connection that allows electrons to flow from the anode to the cathode
(4) an ionic connection that allows ions to flow between the anode and cathode (i.e. an electrolyte)

ANODE

"The Anode is where the Action is." This sentence is useful because, by definition, the anode is the electrode at which oxidation half-reactions occur (and metal corrosion is an oxidation half-reaction, so the anode is where the action of corrosion occurs). These oxidation half-reactions take place at the surface of the metal (even if the metal is covered with corrosion products).

The term "oxidation" is sometimes used when corrosion of a metal results in the formation of a metal oxide. When a metal is oxidized, the oxidation state is converted from zero (e.g. iron metal, Fe^0) to a more positive value (e.g. iron(II) ions, Fe^{2+}) and the reaction is accompanied by the release of electrons. Two examples of oxidation half-reactions are presented below.

$$Fe(s) \rightarrow Fe^{2+} + 2e^-$$
$$Pb(s) \rightarrow Pb^{2+} + 2e^-$$

The positive metal ions enter the solution and either diffuse away from the surface (if they are soluble) or precipitate (if they are not soluble). The negative electrons flow through the metal.

CATHODE

The electrode at which reduction half-reactions occur is called, by convention, the cathode. The location of these reactions can be the surface of the corroding metal, the surface of corrosion products that are electrical conductors (e.g. magnetite), or another metal in electrical contact with the anode. Reduction half-reactions consume the electrons produced at the anode and usually involve species dissolved in the electrolyte (e.g. metal ions, oxygen gas) or the electrolyte itself (e.g. hydrogen ions, H^+).

Several examples of reduction half-reactions are presented below.

$$2H^+ + 2e^- \rightarrow H_2(g)$$
$$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g)$$
$$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$$
$$O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-$$
$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$
$$Cu^{2+} + 2e^- \rightarrow Cu(s)$$

The reduction of H^+ ions or O_2 gas at the cathode increases the local pH, making the region more alkaline.

ELECTRICAL CONDUCTOR

Because the corrosion process is electrochemical, it requires an electrical connection to allow electrons to flow from the anode where they are produced to the cathode where they are consumed. The conductor can be a metal, a conducting corrosion product (e.g. magnetite), or another conducting material (e.g. graphite). By convention, the direction of current (I) flow is the same as the direction of the flow of the positive charge, i.e. opposite to the flow of negatively charged electrons.

ELECTROLYTE

The corrosion process also requires an ionic connection (an electrolyte) between the anode and cathode to allow the flow of ionic species. In most corrosion processes this ionic connection is provided by water (e.g. condensation from humid air, rain, seawater). Whenever RH is above about 65%, there is enough adsorbed water on most clean metal surfaces to approach the behaviour of bulk water and support electrochemical reactions. Damp soil or a damp deposit may also hold water against the surface of metal.

The ionic conductivity of an electrolyte depends on many factors, including the absorption of atmospheric gases (e.g. sulphur dioxide), the dissolution of material already present on the surface (e.g. corrosion products), and the deposition of airborne material (e.g. dust, salts, etc.). As a general rule, the higher the conductivity of the electrolyte, the faster the rate of corrosion. Distilled water is a poor electrolyte, tap water is better, and seawater is excellent. In other words, metals usually corrode much faster in seawater than in freshwater, and faster in water contaminated with pollutants or salts than in uncontaminated water. This is discussed further in the section "Corrosion rates" on p. 32.

CONVENTIONS AND CONFUSION

Conventions for designating anodes and cathodes as positive or negative vary, and can create confusion. In a discharging battery, the anode is the negative terminal (labelled with a minus sign (⊖)) and the cathode is the positive terminal (labelled with a plus sign (⊕)). However, in terms of the chemical processes happening in the electrolyte surrounding an electrode, the anode is said to be positive (because the oxidation reaction at its surface produces positive metal ions (e.g. Fe^{2+}) which then attract negatively charged ions called anions (e.g. Cl^-, OH^-) to maintain charge balance) and the cathode is said to be negative (because reduction reactions on its surface produce negative ions (e.g. OH^-) which then attract positively charged ions called cations (e.g. H^+, Fe^{2+}) to maintain charge balance).

Reference material: Payer (1992); Phipps and Rice (1979).

CORROSION OF A SINGLE METAL

Most metals corrode when exposed to water and oxygen because the four requirements for corrosion (mentioned above) are in place. When a single piece of metal corrodes in water, the process is electrochemical. The water serves as the electrolyte and provides a pathway for ions. The metal itself acts as the conductor for electrons. The presence of heterogeneities in the metal allow anodic and cathodic areas to develop in separate locations on the same metal surface. As the metal corrodes, the surface becomes covered with a network of local corrosion cells (local electrochemical cells) that change constantly, so over time the corrosion may become fairly uniform over the entire surface.

Several microscopic conditions contribute to the development of local anodic and cathodic sites on a metal surface. The surface of a single piece of metal is never even and uniform; there are always local microscopic irregularities. These may be impurities in the metal, especially in older metals that are not as refined. They may be present in alloys with two or more phases if one phase is more anodic than the others, or they may be distortions and stresses that were created in some areas more than others as the metal was worked. Iron nails, for example, rust more quickly at their heads and points than on their cylindrical surfaces because of stress formed in the metal during fabrication.

One common example of the corrosion of a single metal is the rusting of a piece of iron left outside

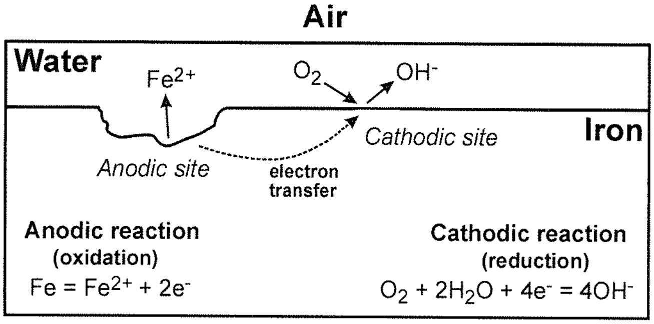

Figure 2.2. Illustration of the corrosion processes on a single piece of iron covered by a thin film of water. The indicated cathodic half-reaction generally applies when pH is greater than 4. However, when the pH is 4 or less, the cathodic half-reaction tends to be hydrogen ion reduction ($2H^+ + 2e^- \rightarrow H_2$). Adapted from Tullmin and Roberge (2000).

in the rain. The iron needs only to be covered with water containing dissolved oxygen gas from the air for corrosion to take place. This is illustrated in Figure 2.2, and can be described by the following net reaction:

$$Fe(s) + {}^1/{}_2O_2(g) + H_2O \rightarrow Fe^{2+} + 2OH^-$$

This electrochemical reaction for corroding iron can be separated into anodic (oxidation) and cathodic (reduction) half-reactions.

The anodic half-reaction describing the oxidation of iron is given by:

$$Fe(s) \rightarrow Fe^{2+} + 2e^-$$

The anodic areas are the sites where the "action" is — where the iron is oxidized and forms iron ions that, at least initially, dissolve in the electrolyte.

The cathodic half-reaction describing the reduction of oxygen gas dissolved in the water is given by:

$${}^1/{}_2O_2(g) + H_2O + 2e^- \rightarrow 2OH^-$$

The cathodic areas are the sites where the reduction half-reactions occur to counterbalance the iron oxidation half-reaction occurring at anodic areas.

When a metal corrodes, ions are formed and electrons are released at the anodic sites. For the corrosion to continue, the electrons produced by the metal oxidation half-reaction at the anode must be simultaneously consumed by a balancing reduction half-reaction at the cathode. The metal ions that form either remain in solution (particularly if the solution adjacent to the corroding area is acidic) and diffuse away from the surface, or react with the surrounding species and precipitate. For example, in the case of iron corrosion, the Fe^{2+} ions react with hydroxyl ions (OH^-) and precipitate as $Fe(OH)_2$. For metals corroding in relatively neutral water, the most common reduction half-reaction that supports (counterbalances) metal corrosion is the reduction of oxygen gas dissolved in the water. This can be seen in the example above. However, for metals corroding in acidic solutions ($pH < 4$), the supporting cathodic half-reaction tends to be hydrogen ion reduction ($2H^+ + 2e^- \rightarrow H_2(g)$).

Reference material: Tullmin and Roberge (2000).

ELECTROCHEMICAL SERIES

The potentials of various isolated half-reactions have been determined under standard conditions and can be found in listings called "electrochemical series." The potential for a half-reaction is generally called an electrode potential, although it can also be referred to as the oxidation–reduction (redox) potential or the half-reaction or half-cell potential. The electrode potential is, by definition, the electric potential of an electrode (e.g. a piece of metal) in an electrolyte (e.g. water) measured against a reference electrode; it is expressed in volts (V). The potentials of reference electrodes are determined relative to the standard hydrogen electrode (SHE), sometimes called the normal hydrogen electrode (NHE). By convention, the standard hydrogen electrode (constructed by bubbling hydrogen over an inert platinum wire) has a potential of 0 V at pH = 0, temperature = 25°C, and hydrogen pressure = 1 atmosphere (~1 bar).

Electrode potentials can be measured for specific reactions (e.g. oxidation of iron, reduction of oxygen) provided those reactions can be isolated (i.e. there are no other competing reactions). The electrode potentials listed in an electrochemical series are equilibrium potentials (also called standard equilibrium potentials) because they have been determined under equilibrium conditions (i.e. an isolated reaction with no current flowing) and specific (i.e. standard) conditions. The reactions are usually written in the listings as reduction half-reactions (with the electron on the left-hand side), and are called standard equilibrium reduction potentials (E_h^0).

Table 2.1 provides some examples of standard equilibrium reduction potentials from the electrochemical series of Vanýsek (1998). The standard conditions are pure metals in equilibrium with a solution of their own ions at unit activity (approximately 1 mole per litre, 1*M*) at a temperature of 298.15K (25°C) and a pressure of 101.325 kPa (1 atmosphere). The potentials for these single reactions have been determined relative to a standard hydrogen electrode (SHE), which sets the scale.

TABLE 2.1. STANDARD EQUILIBRIUM REDUCTION POTENTIALS

Standard equilibrium reduction half-reactions	Standard equilibrium reduction potentials E_h^0 vs. SHE (V)
$Au^+ + e^- \rightleftarrows Au(s)$	1.692
$O_2(g) + 4H^+ + 4e^- \rightleftarrows 2H_2O$	1.228
$Ag^+ + e^- \rightleftarrows Ag(s)$	0.8
$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	0.771
$Cu^+ + e^- \rightleftarrows Cu(s)$	0.521
$O_2(g) + 2H_2O + 4e^- \rightleftarrows 4OH^-$	0.401
$Cu^{2+} + 2e^- \rightleftarrows Cu(s)$	0.342
$Cu^{2+} + e^- \rightleftarrows Cu^+$	0.153
$2H^+ + 2e^- \rightleftarrows H_2(g)$	0
$Fe^{3+} + 3e^- \rightleftarrows Fe(s)$	–0.037
$Pb^{2+} + 2e^- \rightleftarrows Pb(s)$	–0.126
$Sn^{2+} + 2e^- \rightleftarrows Sn(s)$	–0.138
$Ni^{2+} + 2e^- \rightleftarrows Ni(s)$	–0.257
$Fe^{2+} + 2e^- \rightleftarrows Fe(s)$	–0.447
$Zn^{2+} + 2e^- \rightleftarrows Zn(s)$	–0.762
$Al^{3+} + 3e^- \rightleftarrows Al(s)$	–1.662

Reference material: Skoog et al. (1988); Vanýsek (1998).

EQUILIBRIUM POTENTIAL

When the electrode potential of an isolated half-reaction at equilibrium with no current flowing is determined at non-standard conditions (e.g. other temperatures, other ion concentrations), it is called the equilibrium potential (E_h). Its magnitude can be calculated using the standard equilibrium reduction potential (E_h^0) for the isolated reaction and the Nernst equation (named after German chemist W. Nernst). The Nernst equation can be found in many chemistry textbooks (e.g. Skoog et al. 1988) and it is used to calculate the changes to the equilibrium electrode potential caused by non-standard temperatures, pressures, or ion concentrations. The calculation uses the activities of the species involved. For dilute solutions, the activity of dissolved species is equal to the molar concentration (i.e. moles per litre). For gases, the activity is the partial pressure in atmospheres.

For an electrochemical or corrosion reaction, the cell potential E_{cell} can also be calculated using the equilibrium potentials for the two half-reactions. The sign of the calculated cell potential will predict whether or not the reaction will proceed in the forward (from left to right) direction — which will happen only if E_{cell} is positive. The corrosion of copper can be used as an example.

The corrosion reaction for copper is:

$$Cu(s) + {}^1\!/_2O_2(g) + 2H^+ \rightarrow Cu^{2+} + H_2O$$

This reaction can now be separated into half-reactions and the Nernst equation used to calculate the two half-reaction equilibrium potentials relative to the standard hydrogen electrode (SHE).

The anodic half-reaction is:

$$Cu(s) \rightleftarrows Cu^{2+} + 2e^-$$

and the equilibrium potential for the anodic half-reaction, $E_{h,anode}$, is given by the following Nernst equation:

$$E_{h,anode} = E_h^0 + (0.059/n)\log_{10}[Cu^{2+}]$$

where $E_h^0 = 0.342$ V, $n = 2$ (n is the number of electrons in the reaction), and $[Cu^{2+}]$ is the activity of Cu^{2+} ions.

The cathodic half-reaction is:

$${}^1\!/_2O_2(g) + 2H^+ + 2e^- \rightleftarrows H_2O$$

and the equilibrium potential for the cathodic half-reaction, $E_{h,cathode}$, is:

$$E_{h,cathode} = E_h^0 - (0.0592/n)\log_{10}\{1/([H^+]^2\, p_{O_2}{}^{1/2})\}$$

where $E_h^0 = 1.228$ V, $n = 2$, $[H^+]$ is the activity of H^+ ions, and p_{O_2} is the partial pressure of oxygen gas.

After determining the equilibrium half-reaction potentials, the cell potential can be calculated with the equation:

$$E_{cell} = E_{h,cathode} - E_{h,anode}$$

On the basis of the above equations, if copper is placed in a solution that has a pH = 4 and the dissolved oxygen has a partial pressure (p_{O_2}) = 0.2 atmospheres, then $E_{h,cathode} = 0.98$ V, $E_{h,anode} = 0.16$ V, and $E_{cell} = 0.82$ V (a positive value).

Therefore, the copper corrosion reaction will proceed in the forward direction (i.e. copper will corrode).

Reference material: McNeil and Selwyn (2001); Skoog et al. (1988).

CORROSION BEHAVIOUR

When a metal is placed in contact with an electrolyte (i.e. a corrosive environment), it may or may not corrode, depending on the conditions. It can exhibit one of three types of behaviour: immune, active, or passive, as shown schematically in Figure 2.3 and defined below.

IMMUNE

When a metal is in an immune state, it does not react in the electrolyte and there is no corrosion. When in the immune state the metal is said to be stable. Metals such as gold and platinum are immune to corrosion in most natural environments — which is why they can exist outdoors as pure metals in their natural (or native) state.

ACTIVE

When a metal is in an active state, it reacts with the environment and the resultant corrosion products are soluble enough to diffuse away from the metal surface. Because they leave the surface they do not significantly slow the corrosion reaction and corrosion continues unabated. In conservation, the term "active corrosion" is often used to refer to observations of fresh or new corrosion on an object located in what is normally considered a relatively stable and benign environment. Evidence of active corrosion on museum pieces includes the appearance of powdery corrosion products on an object, or flaking of existing surface corrosion.

PASSIVE

When a metal is in a passive state, it has already reacted with the environment and the resultant corrosion products have formed a relatively insoluble film on the metal surface which significantly decreases the corrosion rate of the metal. The protective qualities of the corrosion layer depend upon the development of an adherent, insoluble corrosion product film.

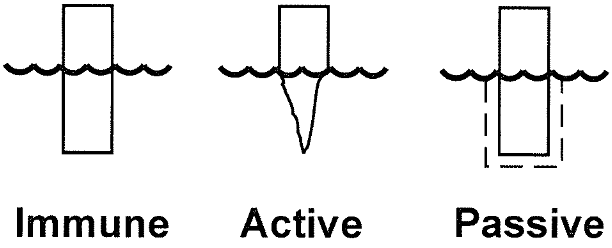

Figure 2.3. A metal in contact with an electrolyte will exhibit one of these three types of behaviour: immune, active, or passive. Adapted from Payer (1992).

Some films, such as metal oxides, are protective (i.e. minimize corrosion) because they provide a strong barrier to the transport of electrons and ions. These films usually re-form easily after being damaged and adhere well to the metal surface. The best passivating films are poor electronic and ionic conductors (e.g. aluminum oxide).

Some films are not protective: they may break down from chemical or mechanical stresses, they may have poor physical characteristics (e.g. poor adhesion to the metal surface), or they may not re-form easily if damaged. These non-protective films leave the metal in the active state. Also, films with high ionic conductivities (e.g. copper sulphides, silver sulphide, many metal chlorides) can support continued oxidation of the underlying metal and therefore do not protect the metal.

Reference material: Canadian Conservation Institute (1997); Garrels and Christ (1990); McNeil and Selwyn (2001); Payer (1992); Payer et al. (1995); Pourbaix (1974).

STABILITY (POURBAIX) DIAGRAMS

Stability diagrams, also known as a Pourbaix or potential-pH diagrams, are theoretical diagrams calculated using thermodynamic information. They can be used to predict the conditions of potential and pH in which a metal will be actively corroding, immune to corrosion, or possibly passivated. These diagrams were originally developed by M. Pourbaix who calculated them for various metals in contact with pure water and then published them in an atlas (Pourbaix 1974).

Stability diagrams are calculated using thermodynamic information for a number of selected chemical species and the possible equilibria between them. Each diagram is calculated for selected fixed conditions (e.g. temperature, pressure, dissolved metal ion concentration) and a selected number of chemical species. If additional chemical species are selected or if other conditions are specified, then a new diagram must be calculated. The calculations and assumptions involved in constructing these diagrams are discussed in modern corrosion textbooks (e.g. Garrels and Christ 1990). There is also a software package

(HSC Chemistry for Windows) developed by Outokumpu Research Oy in Finland which can be used to generate stability diagrams. For more information on this software package, see the Web site for Outokumpu Research Oy (www.outokumpu.com/hsc/index.htm).

Figure 2.4 provides an example of a stability diagram for copper in which the most stable forms of copper are shown to be the metal, a soluble ion, or an insoluble compound. This diagram could also be drawn (see Figure 2.5) to indicate regions where copper is immune (the metal is stable), passive (insoluble compounds are stable), and active (ions are stable) rather than the exact copper species.

These stability diagrams are graphs of equilibrium potential (E_h) on the standard hydrogen electrode (SHE) scale plotted against the logarithmic activity of hydrogen ions (pH). The vertical axis (equilibrium potential) has been explained earlier. The horizontal axis (pH) can be defined as:

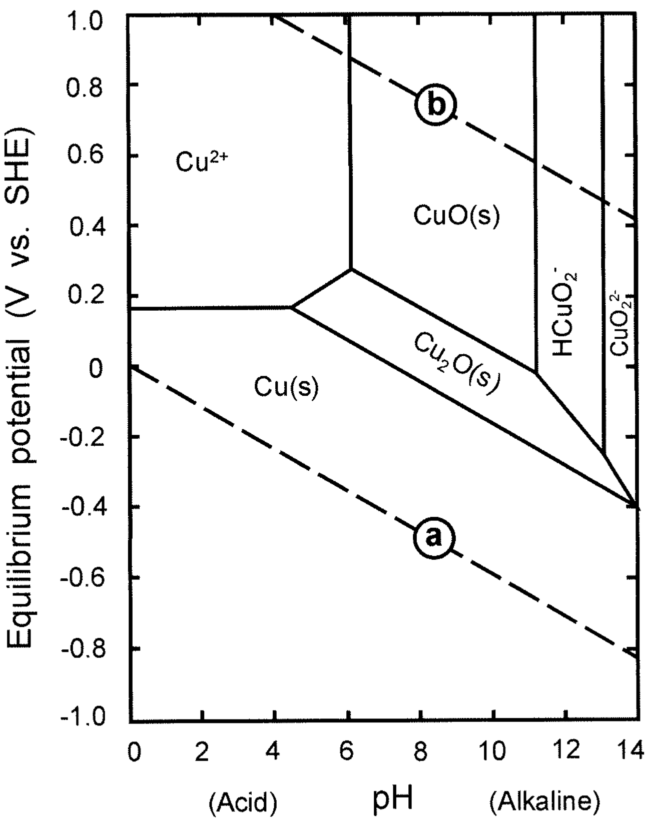

Figure 2.4. A potential-pH (or Pourbaix) diagram for a copper–water system in which the temperature is 25°C, the pressure is 1 atmosphere, and the Cu^+ concentration is 10^{-6} M. Regions are labelled with the species that is the most thermodynamically stable in that area. Water is stable within the boundaries set by the broken lines (a) and (b); it can be oxidized to oxygen gas at or above line (b), and it can be reduced to hydrogen gas at or below line (a). Adapted from McNeil and Selwyn (2001).

$$pH = -\log_{10} [H^+]$$

where $[H^+]$ is the hydrogen ion activity. The pOH of the solution can be defined as:

$$pOH = -\log_{10} [OH^-]$$

where $[OH^-]$ is the hydroxyl ion activity. The pH and pOH are related by:

$$pH + pOH = 14$$

Acid solutions have $pH < 7$ and alkaline solutions have $pH > 7$. The pH of natural environments can vary widely. Pure water is pH 7 (i.e. $[H^+] = [OH^-] = 10^{-7}$ moles $litre^{-1}$). Rainwater and marshy, waterlogged soils are typically acidic (pH 3–6); marine and saline soils are alkaline (seawater is pH ~8; saline soils are pH 10–12).

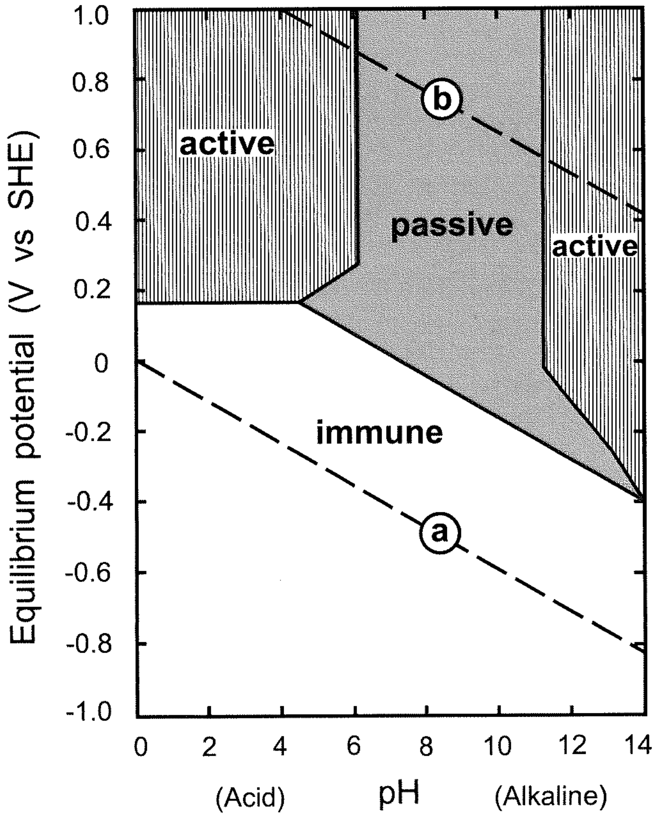

Figure 2.5. The same potential-pH diagram as in Figure 2.4, but this time the regions are labelled as immune, active, or passive. Adapted from McNeil and Selwyn (2001).

The lines on the diagram are calculated using the Nernst equation to determine equilibrium electrode potentials for reactions involving electrons. The calculations also depend on solubility and thermodynamic data for the metal, its ions, and its compounds. Solid lines on the diagram represent equilibrium reactions between adjacent species. The horizontal lines are electrochemical reactions involving electrons (but not H^+ or OH^- ions) and so have a single E_h, independent of pH. The only horizontal line in Figure 2.4 represents the equilibrium potential for the half-reaction $Cu(s) \rightleftharpoons Cu^{2+} + 2e^-$ (calculated in an earlier example):

$$E_h = E_h{}^0 + (0.059/n)\log_{10}[Cu^{2+}]$$

The vertical lines are pure acid–base equilibrium reactions; they do not involve electrons and are at a specific pH, independent of potential. The sloped lines are equilibrium reactions involving both electrons and H^+ ions.

For points on the solid lines, two species or forms co-exist (e.g. copper metal and Cu^{2+} ions on the horizontal line in Figure 2.4). For points not on the line, only one form is stable. Thus the areas on the stability diagram enclosed by solid lines are labelled with the most stable species as determined using the thermodynamics for the specified conditions. In Figure 2.4, for example, the conditions of pH and E_h enclosed by the solid lines in the upper left-hand side of the figure are those where Cu^{2+} ions are stable. In that region, copper metal is unstable and it will corrode and form Cu^{2+} ions.

On stability diagrams, it is standard practice to include the two broken lines (labelled here with "a" and "b") to highlight the region where water is stable. Above the upper broken line, water is unstable and can be oxidized to gaseous oxygen ($2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$). Below the lower broken line, water is also unstable and can be reduced to gaseous hydrogen ($2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$).

The upper broken line (labelled "b" in Figures 2.4 and 2.5) shows the equilibrium half-reaction potential for the reaction $O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$:

$$E_h = 1.228 - 0.059\text{ pH} + 0.015\log_{10} p_{O_2}$$

where p_{O_2} is the partial pressure of oxygen (in atmospheres). In both figures, the broken line labelled "b" was calculated using an oxygen partial pressure of 1 atmosphere. As the partial pressure of oxygen decreases below 1 atmosphere, the equilibrium potential decreases and so the position of the broken line "b" lowers.

The lower broken line (labelled "a" in Figures 2.4 and 2.5) shows the equilibrium half-reaction potential for the reaction $2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-$:

$$E_h = 0.000 - 0.059\text{ pH} - 0.030\log p_{H_2}$$

where p_{H_2} is the partial pressure of hydrogen (in atmospheres). In both figures, the broken line labelled "a" was calculated using a hydrogen partial pressure of 1 atmosphere.

The natural environments in which metals corrode vary from oxidizing to reducing. In porous soils, the conditions are oxidizing (environment can accept electrons) because of the penetration of water carrying dissolved oxygen. Conversely, in poorly drained peat bogs, reducing conditions (environment can donate electrons) are established if the supply of organic matter exceeds that of oxygen.

Reference material: Garrels and Christ (1990); Marek et al. (1987); McNeil and Selwyn (2001); Payer et al. (1995); Pourbaix (1974); Raiswell (2001).

CORROSION POTENTIAL

The corrosion potential (E_c) is the electrode potential of a corroding metal surface in an electrolyte. As mentioned earlier, both anodic and cathodic half-reactions can take place (although at different locations) on the same surface of a single piece of corroding metal. No net current is flowing in or out of the metal because the anodic half-reaction rate is balanced by the cathodic half-reaction rate.

The thermodynamic driving force for corrosion is the difference between the equilibrium potentials for the anodic $E_{h,anode}$ (e.g. metal oxidation) and cathodic $E_{h,cathode}$ (e.g. oxygen reduction) reactions. Because the anodic and cathodic half-reactions are not isolated but are happening on the same metal surface, the resulting corrosion potential of the corroding metal is not an equilibrium potential; rather, it lies somewhere between the equilibrium potentials for the anodic and cathodic half-reactions involved in the corrosion process:

$$E_{h,anode} < E_c < E_{h,cathode}$$

Take, for example, the corrosion potential of a piece of copper immersed in a pH 4 solution. At this pH, it is predicted to lie somewhere between $E_{h,anode}$ and

$E_{h,cathode}$, which were calculated previously (see p. 23) as 0.16 V and 0.98 V, respectively. Therefore:

$$0.16 \text{ V} < E_c < 0.98 \text{ V}$$

The corrosion potential reflects the potential at which the rates of anodic and cathodic half-reactions on the metal surface are equal. The corrosion potential, by itself, does not reflect the corrosion rate of the metal.

To compare the results from corrosion potential measurement with the predicted information on a stability diagram, it is necessary to know the pH of the solution adjacent to the metal surface. (If the metal is immersed in seawater and covered with corrosion and concretion, the pH measurement needs to be determined as close to the metal surface as possible.)

After the corrosion potential and pH of an immersed metal have been measured, the values can be located

MEASURING CORROSION POTENTIALS

The corrosion potential of an immersed metal can be measured relative to a reference electrode (as for any electrode potential measurement). In carrying out a corrosion potential measurement, a platinum electrode (or some other inert electrode) and a reference electrode are connected to a voltmeter. When measuring corrosion potential, convention dictates that the reference electrode is attached to the negative (black) side of a voltmeter and the platinum electrode is attached to the positive (red) side. The platinum electrode is immersed in the solution until it touches the immersed metal and makes electrical contact. Figure 2.6 shows an example of a platinum electrode; more information on making a similar platinum electrode can be found in Selwyn (2001). If the surface of the metal is covered with corrosion products (or concretion if the metal is in seawater), a small area of bare metal must be uncovered to allow for good electrical contact between the platinum electrode and the immersed metal. The reference electrode is also immersed in the solution and held fairly close to the point where the platinum electrode is making contact with the metal. This procedure is represented schematically in Figure 2.7.

If the corrosion potential is measured using a reference electrode other than the SHE, it must be corrected so that it is relative to the SHE scale (the scale used in stability diagrams). One common reference electrode is the saturated calomel electrode (SCE) which contains mercury (Hg), mercury(I) chloride (calomel, Hg_2Cl_2), and a solution saturated with potassium chloride (KCl). It has a known potential of 0.241 V vs. SHE at 25°C; therefore, to convert from a potential versus SCE to one versus SHE, simply add 0.241 V. Another common reference electrode is the saturated mercury/mercurous sulphate electrode (SSE) which contains mercury (Hg), mercury(I) sulphate (Hg_2SO_4), and a saturated solution of potassium sulphate (K_2SO_4). It has a known potential of 0.658 V vs. SHE at 25°C; thus, to convert from a potential versus SSE to one versus SHE, add 0.658 V. Conversion factors for other reference electrodes can be found in ASTM (2001b).

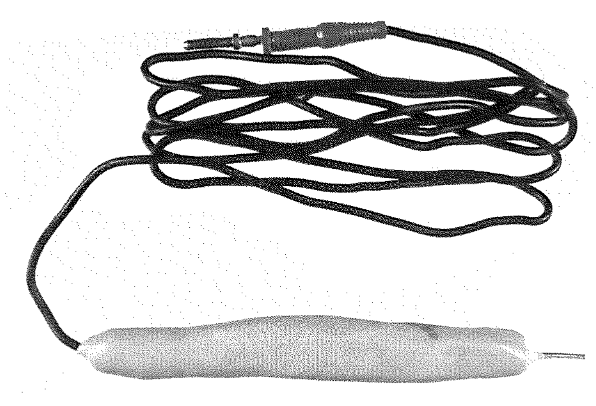

Figure 2.6. This handmade inert electrode is made with a small piece of platinum wire electrode soldered to copper wire and covered with a robust epoxy handle.

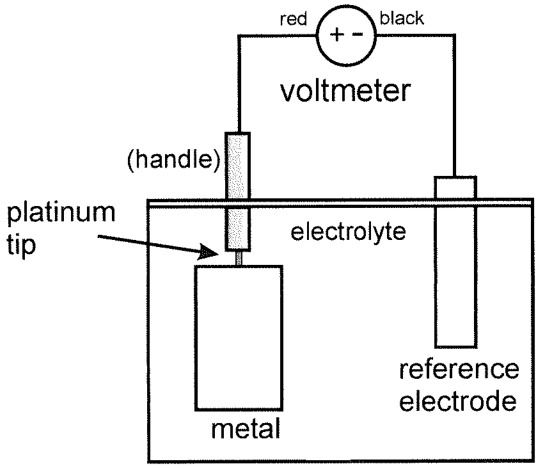

Figure 2.7. Schematic diagram that illustrates the measurement of corrosion potential of a metal using an inert platinum electrode, a voltmeter, and a reference electrode.

on a stability diagram that is appropriate (or close) to the metal and solution being monitored. The position of the corrosion potential and the pH on the stability diagram can be used to predict the surface condition of the metal. For example, if the values lie in a region where ions are the most stable chemical species, then it is likely the metal is freely corroding. However, if they lie in a region where a solid compound is shown to be stable, then it is probable that the solid has formed a protective film on the surface and slowed the corrosion rate.

Reference material: ASTM (2001b); MacLeod (1981); McNeil and Selwyn (2001); Selwyn (2001); Skoog et al. (1988).

GALVANIC CORROSION

As mentioned earlier, corrosion can be described as an electrochemical cell consisting of an anode and cathode in electrical contact in an electrolyte. When the anodic and cathodic sites occur at different areas on the same metal surface, the metal is said to corrode normally. However, when the anodic and cathodic sites occur on two different metals, the corrosion is said to be galvanic.

When two different metals are in electrical contact in the same electrolyte, the more active metal becomes the anode and the less active one becomes the cathode. The resulting galvanic corrosion causes the corrosion of the more active metal to be accelerated relative to its normal rate, while the corrosion of the less active metal is decreased relative to its normal rate. Galvanic corrosion can be prevented if the different metals can be electrically isolated from one another using an insulating material (e.g. Teflon).

GALVANIC SERIES

A galvanic series is a way of ordering metals and other materials with high electronic conductivity according to their electrode potentials in a specific wet environment (electrolyte). The position of a metal in the series indicates its reactivity; the more noble the metal, the less likely it is to corrode. If two materials from this series are connected and immersed in seawater, the one with the lower potential is more active (anodic) and corrodes faster (i.e. suffers from galvanic corrosion) than if it were unconnected and exposed to seawater (i.e. normal corrosion). The one higher on the list is more noble (cathodic) and corrodes more slowly (i.e. galvanic protection) than if it were unconnected and exposed to seawater.

Table 2.2 lists average electrode potentials for various materials in flowing seawater. The numbers are average values taken from LaQue (1975) who lists electrode potentials for metals in seawater measured versus a saturated calomel electrode (SCE). For convenience, the potentials are also listed versus the standard hydrogen electrode (SHE).

TABLE 2.2. GALVANIC SERIES FOR METALS IN SEAWATER

Material	**Average electrode potential in seawater**		**Relative activity**
	vs. SCE† (V)	**vs. SHE‡ (V)**	
graphite	0.25	0.49	noble
platinum	0.21	0.45	(cathodic)
titanium	0.00	0.24	
stainless steel 304*, passive	–0.08	0.16	
silver	–0.13	0.11	
nickel	–0.15	0.09	
lead	–0.22	0.02	
copper–nickels	–0.25	–0.01	
tin bronzes	–0.29	–0.05	
lead–tin solder, 50:50	–0.32	–0.08	
tin	–0.33	–0.09	
copper	–0.34	–0.1	
naval, yellow, and red brass	–0.35	–0.11	
stainless steel 304*, active	–0.52	–0.28	
mild steel, cast iron	–0.66	–0.42	
cadmium	–0.72	–0.48	
aluminum alloys	–0.88	–0.64	
zinc	–1.00	–0.76	active
magnesium	–1.62	–1.38	(anodic)

* UNS S30400.
† Saturated calomel electrode.
‡ Standard hydrogen electrode.

This galvanic series orders the metals such that the more noble ones (e.g. platinum) are at the top and the more active ones (e.g. zinc, aluminum) are at the bottom. Although gold and chromium are not included in this series, they would lie toward the noble end of the series. It should also be noted that stainless steel 304 is listed twice, once as active and once as passive. In general, when stainless steels are protected by an oxide layer (as is commonly found in well-aerated flowing seawater), they have a "passive" potential. However, stainless steels may start actively corroding if they lose their protective layer, as can happen at shielded areas or if the metal is in low velocity or poorly aerated seawater; in such cases the corroding stainless steels have an "active" potential.

The galvanic series in Table 2.2 is for metals in seawater. Although the electrode potential of any given metal is strongly influenced by the composition of the electrolyte, the galvanic series for metals has almost the same order in many electrolytes as it does in seawater (the relative positions of a few metals may change).

The rate of galvanic corrosion of the more active metal is influenced by how far apart the two metals are in the galvanic series (the farther apart the two metals are, the greater the rate of corrosion) and by the ratio of the cathode to anode surfaces (the larger the ratio of the cathode to anode surface areas, the more rapid the corrosion of the anode). The degree of attack is largest at the point of contact, and the effect of corrosion becomes greater if it is concentrated on a small area and less if it is dissipated over a large area. For example, when copper rivets (cathodes) are used on large iron plates (anodes), the effect of the galvanic couple is slight; but when small iron rivets (anodes) are used on large copper plates (cathodes), the rivets deteriorate rapidly. This size effect is illustrated in Figure 2.8.

In some cases a more active metal is intentionally connected to a less active metal to take advantage of galvanic corrosion. The more active metal acts as the anode and corrodes preferentially, which causes the less active metal to corrode at a slower rate. In this situation the active metal is called a sacrificial anode, and the process is known as cathodic protection, galvanic protection, or sacrificial protection. Magnesium is often used in this way to protect certain metallic parts on ships in seawater.

PLATED METALS

Whenever one metal is plated onto another, there is a possibility that galvanic corrosion will occur (and clearly the metals cannot be electrically isolated to eliminate this possibility). As long as the outer plating layer is continuous with no flaws, there will be no galvanic corrosion. The plating layer will act as a physical barrier to protect the underlying metal (preventing water and air from reaching it) and will corrode at its normal corrosion rate. However, if there are breaks, pores, or flaws in the outer layer (that occur naturally or as a result of normal corrosion), galvanic corrosion cells can be established. Once this happens the extent of corrosion of the underlying metal will depend on whether it is more active or less active than the outer plating layer.

Galvanic and physical protection: A plating can provide both galvanic and physical protection to the underlying metal if the plating is the more active metal of the pair. The best-known example of this situation is zinc-coated iron (i.e. galvanized steel); other examples include iron plated with aluminum or cadmium. The effect of these kinds of plating on iron is twofold. As long as the plating layer is present and continuous, it provides a physical barrier that protects the underlying iron by isolating it from the environment and potential electrolytes. (Zinc is particularly good as a physical barrier because its corrosion products help maintain a low corrosion rate.) Second, if the plating does become damaged and the underlying iron is exposed to the environment, the plating (being more active than iron) will preferentially corrode. In other

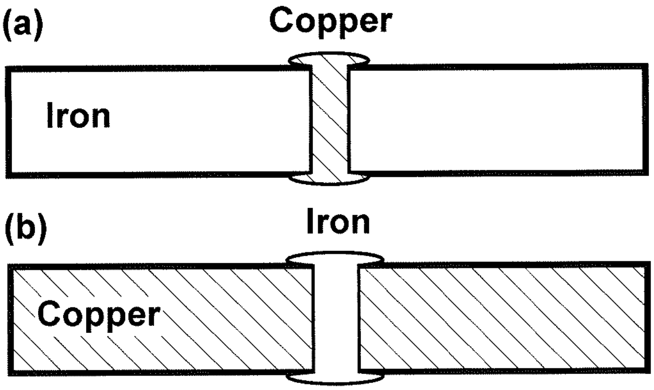

Figure 2.8. Schematic diagram of galvanic corrosion for copper (noble component, cathodic) and iron (active component, anodic) that illustrates the effect of relative size. (a) The effect of the galvanic couple is slight when the cathodic area is small (i.e. copper rivets) and the anodic area is large (i.e. iron plate). (b) The effect of the galvanic couple leads to rapid deterioration of the anodic component when the cathodic area is large (i.e. copper plates) and the anodic area is small (i.e. iron rivets).

words, the outer layer acts as the anode (also called a sacrificial coating) in the galvanic corrosion cell and its accelerated corrosion helps to protect the underlying iron from rusting.

Physical protection: A plating that is more noble than the underlying metal can still provide physical protection as long as it is continuous and adherent, but in this case there will be no galvanic protection. Iron plated with silver, copper, lead, chromium, or nickel falls into this category. If the plating layer becomes damaged, cracked, or porous, the underlying iron will act as the anode in the resulting galvanic corrosion and will suffer accelerated corrosion, which usually shows up as rust staining. Rusting of the underlying iron will also tend to push off the outer plating layer. Figure 2.9 illustrates this phenomenon for chrome-plated iron. When areas of the chromium are lost or become porous enough to allow the electrolyte to reach the underlying iron, it is the iron that becomes the anode and oxidizes (corrodes). Reduction half-reactions (usually reduction of oxygen dissolved in the electrolyte) take place in the electrolyte on the conducting chromium surface.

Galvanic corrosion of plated metals is further complicated by the fact that the relative activity of the two metals can sometimes change, depending on the environment. For example, tin can be more or less active than iron depending on the conditions. For more information, see "Chapter 12. Tin."

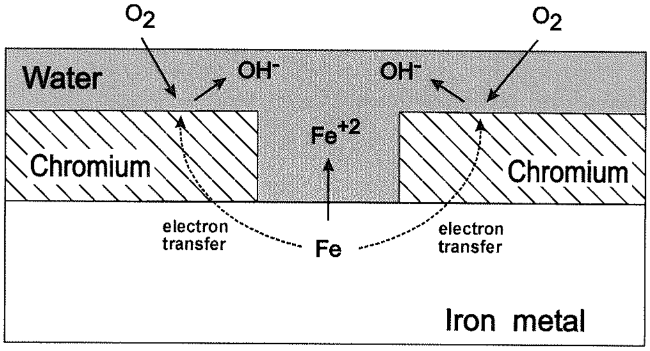

Figure 2.9. Schematic representation of the galvanic corrosion process that can occur on iron that is plated with chrome (i.e. chromium). If porosity or a break in the chromium layer occurs such that the two metals come into contact in the presence of an electrolyte (in this case water), the chromium (the more noble metal) will act as a cathode and the iron (the more active metal) will act as an anode and suffer from accelerated corrosion.

METAL IONS IN SOLUTION

Galvanic corrosion can also occur when a solid metal is placed in a solution containing ions of another metal. If the ions are from a metal that is more noble (less active) than the solid, then it is possible for the ions to be reduced as the solid corrodes. When this happens, a thin layer of the less active metal will plate from the solution onto the surface of the corroding metal. This establishes a true galvanic contact with galvanic corrosion of the more active metal now possible. For example, if copper ions from a corroding bronze statue dissolve in rain and are washed over a stone plinth labelled with lead lettering, the copper may plate onto the lead surface and cause the lead to corrode at an accelerated rate.

Reference material: ASTM (2001c); Baboian (1990); Fontana (1986); LaQue (1975); Revie (2000).

OTHER FORMS OF CORROSION

Galvanic corrosion is only one form of corrosion, and unless intentionally designed to occur as a sacrificial protection measure it should be avoided whenever possible. Other forms of corrosion are discussed below.

UNIFORM CORROSION

Uniform corrosion is a general thinning of the metal without appreciable localized attack such as pitting. Examples include the uniform tarnish layer that forms on silver, and the rust layer that forms on carbon steels outdoors. Weathering steels, such as Cor-Ten steel, corrode more uniformly than carbon steels if subjected to alternating wet and dry weather (weathering steels are low-carbon steels that contain small amounts of other alloying elements such as copper; more information on weathering steels can be found in "Chapter 8. Iron").

Reference material: Fontana (1986); Revie (2000).

PITTING CORROSION

Pitting corrosion is a destructive form of localized corrosion that is usually initiated by chloride ions and can result in holes through a metal. It begins with local dissolution of the metal in areas where there is a discontinuity in the passive surface film — either a mechanical imperfection (such as an inclusion) or a local chemical breakdown. This local dissolution leads to the formation of cavities or pits on the surface. As the metal in the pit corrodes, the oxygen in the area is depleted (because oxygen from the bulk electrolyte cannot diffuse into the pit fast enough to restore the concentration, especially if there is a barrier). This depletion in oxygen concentration sets up a differential aeration cell (also called an oxygen concentration cell): the region inside the pit is anodic and is the site of the oxidation half-reactions; the region outside the pit is cathodic and is the site of the oxygen reduction half-reactions which complete the corrosion cell.

Once a pit has formed, the dissolution of the metal causes the local chemical environment to become substantially more aggressive (i.e. the acidity and the concentration of dissolved metal ions both increase) than the surrounding bulk environment. As the metal dissolves it produces positively charged metal ions (e.g. iron ions, Fe^{2+}) that must be charge-balanced by the migration of negative ions (e.g. chloride ions, Cl^-) into the pit from the surrounding electrolyte. These metal ions undergo hydrolysis in water and decrease the local pH. For example, iron ions hydrolyse in water as follows:

$$Fe^{2+} + H_2O \rightarrow Fe(OH)^+ + H^+$$

The chloride ions (from migration) and the hydrogen ions (from hydrolysis) accelerate the dissolution rate of the metal, which in turn increases the migration and the result is a rapidly accelerating process (sometimes described as an autocatalytic process).

Metals protected by a passive film are particularly prone to pitting corrosion because the protective film is likely to be damaged and/or removed at only a small area, which allows corrosion to be concentrated and a pit to develop. Pitting can be particularly severe if the protective film is an electrical conductor and can act as a cathode to the small area of exposed metal (the anode).

Reference material: Böhni (2000); Fontana (1986); Revie (2000).

CREVICE CORROSION

Crevices are often considered to be large pits, so it follows that crevice corrosion is just a more severe form of pitting. Crevices form under gasketting, biofouling, external deposits, or at metal-to-metal joints, and provide only limited access for oxygen. The lowered concentration of oxygen in the crevice sets up the same conditions as discussed previously for pitting corrosion, i.e. an oxygen concentration cell where the region inside the crevice is anodic (the site of oxidation half-reactions) and the region outside the crevice is cathodic (the site of reduction half-reactions). And so the interior of the crevice corrodes in the same way as a pit.

One common example of crevice corrosion is the staining that can happen to stacked metal sheets after exposure to water (industry refers to this staining as white rust when it occurs on zinc and galvanized steel, as yellow stain when it occurs on tin, and as water or storage stain when it occurs on aluminum and copper alloys). The water is retained between metal surfaces in contact by capillary action. Near the edge of the metal sheets (i.e. where it is in contact with air) the water remains rich in oxygen, but toward the middle the oxygen concentration is reduced. This variation in oxygen content sets up the conditions for a corrosion cell to develop (this is shown schematically in Figure 2.10). The oxygen-rich portions at the outer edges of the water film become cathodic (dissolved oxygen gas is reduced) and the oxygen-poor areas toward the centre become anodic (the metal corrodes). This corrosion results in staining of the metal surface.

Reference material: Böhni (2000); Fontana (1986); Revie (2000).

FILIFORM CORROSION

Filiform corrosion (also called underfilm corrosion) is a specific type of crevice corrosion that can occur on certain metals (e.g. aluminum, iron, magnesium, and possibly silver) when they are covered with an organic coating. The corrosion starts at breaks or defects in the coating and proceeds in relatively straight lines underneath it. It lifts the coating and results in lines that have a hair-like or filamentary appearance. The filiform track is composed of two parts: the head (tip) where moisture is present and corrosion takes place; and the tail (channel) which is filled with dry, porous corrosion products and is inactive. A schematic diagram of a filament is shown in Figure 2.11.

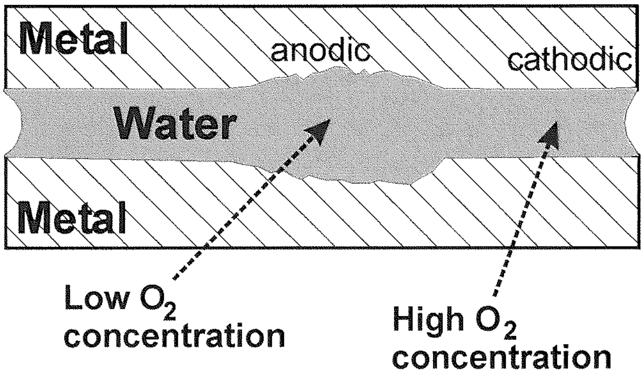

Figure 2.10. Differences in oxygen concentration set up conditions for a corrosion cell to develop. This type of corrosion will lead to staining of metal sheets stacked in a humid environment.

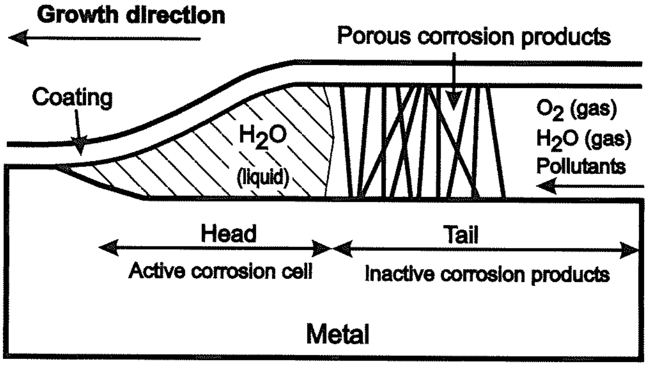

Figure 2.11. Schematic diagram of a cross section through a filament in filiform corrosion, showing the head and the tail. Adapted from Ruggeri and Beck (1983).

The mechanism responsible for filiform corrosion is not fully understood, but probably involves an oxygen concentration cell within the moisture present at the head of the filament. This scenario results in the anodic half-reaction (metal oxidation) taking place at the front of the head where there is little oxygen, and the cathodic half-reaction (oxygen reduction) taking place at the back of the head where there is more oxygen. Corrosion continues as water and oxygen diffuse through the open channel and support reactions at the tip.

Metal surfaces that suffer filiform corrosion have usually been contaminated with salts (e.g. chlorides, sulphates) or other pollutants prior to coating.

Reference material: Fontana (1986); Revie (2000); Ruggeri and Beck (1983).

INTERGRANULAR CORROSION

Intergranular corrosion is caused by preferential corrosion at grain boundaries (or adjacent to them), and can result in the disintegration of an alloy as grains fall out. It occurs when grain boundaries are significantly more reactive than the surrounding material. Such an increase in reactivity can be caused by the precipitation of another phase (e.g. metal carbides, intermetallic phases) at grain boundaries as a result of heating. For example, aluminum alloyed with a small amount of copper is sensitive to intergranular corrosion if intermetallic $CuAl_2$ particles precipitate at grain boundaries. Many stainless steels and die-cast zinc alloys that contain aluminum are also sensitive to intergranular corrosion.

Reference material: Fontana (1986); Revie (2000).

DEALLOYING

This form of corrosion is the selective or preferential removal of one element (usually the least noble) from an alloy, starting at the surface. Dealloying usually occurs in relatively mild conditions when corrosion rates are low. A porous, weak deposit of the more noble constituent is all that remains. Dealloying affects many copper alloys. Copper–zinc alloys (i.e. brasses) containing more than 15 wt% zinc are sensitive to the selective removal of zinc (dezincification). Copper–tin alloys (i.e. bronzes) may suffer from selective removal of tin (destannification). Gray cast iron can also be subject to dealloying in a process known as graphitic corrosion (iron is selectively removed, leaving behind graphite).

Reference material: Fontana (1986); Revie (2000).

STRESS CORROSION CRACKING

Stress corrosion cracking refers to cracks that form in certain alloys when they are simultaneously exposed to stress and corrosive environments. It only occurs when the stress and corrosion are combined; either factor acting alone would not lead to cracking. The stress may be external (e.g. a sudden impact) or internal (e.g. the result of cold-working or welding, or non-uniform cooling after casting). Stress corrosion cracking has been observed in copper–zinc alloys exposed to ammonia and in stainless steels exposed to chloride ions.

Reference material: Fontana (1986); Revie (2000).

MICROBIOLOGICAL CORROSION

Also called microbially induced (or influenced) corrosion (MIC), microbiological corrosion is caused by microorganisms — a wide variety of which (including both aerobic and anaerobic bacteria) are capable of causing metals to corrode. Some microorganisms adhere to the metal surface where they form a biofilm that results in the corrosion of the underlying metal. Others, such as sulphate-reducing bacteria that grow in anaerobic conditions, produce hydrogen sulphide gas that attacks metals and forms metal sulphides.

Reference material: Gu et al. (2000).

CORROSION RATES

The rate of corrosion of a metal is influenced by many factors including the amount of water present as well as its pH, composition, and temperature.

When metals are displayed or stored indoors, the amount of moisture present in the air (i.e. the RH) plays a significant role in their corrosion (because water serves as an electrolyte and provides one of the necessary requirements for corrosion). At RH levels of 65% or above, the water adsorbed on a metal surface is more than three molecules thick and approaches the behaviour of bulk water. This adsorbed water provides enough moisture to support electrochemical reactions on even the cleanest metal surfaces.

Metal surfaces that are not clean may begin to corrode at even lower RH levels. Indoor dust particles often contain salts (e.g. ammonium sulphate); when resting on the surface of metal these salts or other contaminants can absorb moisture from the surrounding air — which can raise the local RH enough to initiate corrosion. A porous corrosion product film that allows water to condense in pores and become trapped can also promote corrosion. Likewise industrial pollution such as sulphur dioxide and soot (carbon) particles can increase the rate of corrosion: when sulphur dioxide dissolves in surface water it forms sulphuric acid which increases the acidity and conductivity of the water, and carbon particles (which are electrical conductors) in direct contact with a metal surface provide cathodic sites for reduction half-reactions. Because so many factors can interact with the RH to increase the rate of corrosion, it is generally recommended that metals be kept in as dry an environment as possible.

Outdoors, corrosion proceeds whenever the RH is high enough for a film of water to condense on the surface (e.g. humid days, rain, fog, mist, dew). Rapid corrosion occurs during the initial stages of wetting and the final stages of drying (because the concentration of corrosive species in a relatively thin water layer is greater than when the water layer is thicker). Shaded and shielded areas that become wet tend to remain wet longer than more exposed areas, and so they experience more severe corrosion.

Rain can be beneficial in the sense that it dilutes corrosive species and rinses away harmful particulates, but it can also be harmful if it contains high levels of chloride ions, e.g. along the coastal regions of North America, particularly in the Atlantic region of Canada. The corrosion rate of a metal outdoors will be influenced not only by the alloy composition and the total amount of rainfall, but also by the location. For example, rural locations are relatively clean, urban locations have high levels of car exhaust, industrial locations have high pollutant levels, and marine locations have high levels of dissolved salts. Table 2.3 gives ranges of corrosion rates for common metals in different kinds of outdoor environments.

TABLE 2.3. CORROSION RATES FOR COMMON METALS OUTDOORS

Metal	Rural (μm yr^{-1})	Urban (μm yr^{-1})	Industrial (μm yr^{-1})	Marine (μm yr^{-1})
aluminum	0–0.1	~1	—	0.4–0.6
copper	~0.5	1–2	2.5	~1
iron	4–65	23–71	26–175	26–104
lead	0.1–1.4	1–2	0.4–2	0.5–2
zinc	0.2–3	2–16	2–16	0.5–8

The pH of the surface water also plays a role in the corrosion rate. In general, metals corrode more quickly in acidic solutions where their corrosion products are more likely to be soluble. In alkaline solutions, the corrosion products are likely to be insoluble and often form a passivating film that slows corrosion. Certain metals corrode under both acidic and basic conditions (their corrosion products are soluble under both acidic and alkaline conditions). These are known as amphoteric metals; examples include aluminum, lead, tin, and zinc.

The effect of pH on the rate of iron (mild steel) corrosion is illustrated in Figure 2.12:

- below pH 4, there is rapid corrosion (cathodic half-reaction is hydrogen ion reduction, $2H^+ + 2e^- \rightarrow H_2(g)$)

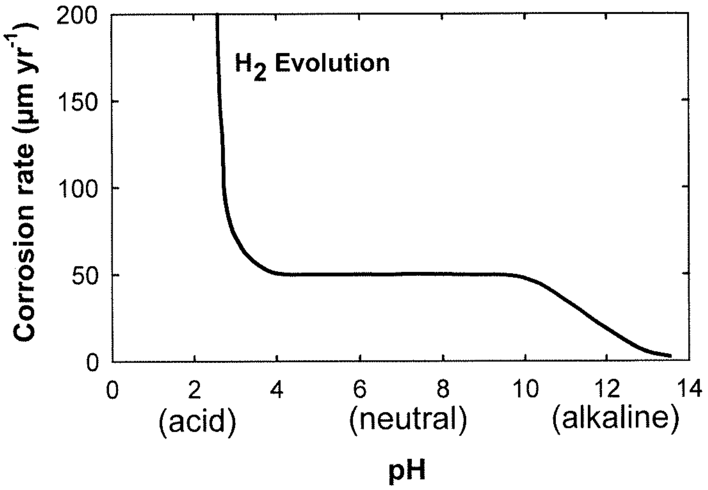

Figure 2.12. This graph illustrates the influence of pH on the rate of corrosion of mild steel. Adapted from Coburn (1978).

- between pH 4 and 9.5, the corrosion rate is relatively uniform (cathodic half-reaction is oxygen reduction, $O_2(g) + 4H^+ + 4e^- \rightarrow H_2O$)
- between pH 9.5 and 14, the corrosion rate is slow because the surface is passivated by insoluble iron hydroxide oxides

Although not shown in the figure, the corrosion rate again increases above pH 14 because of the increased solubility of the iron hydroxide oxides at high pH.

Finally, the rate of corrosion is influenced by temperature — the higher the temperature, the higher the rate of corrosion. As a general rule of thumb, the rate of a reaction is doubled by a temperature rise of 10°C. Although cold temperatures slow the rate of corrosion, they do not stop it entirely (as can be observed for metals exposed to the severe conditions of Antarctica). Furthermore, cold temperatures may turn any trapped water to ice and the expansion of this water as it freezes can cause severe damage such as cracking of cast iron and cast bronzes. It is therefore important for adequate drainage to be incorporated in metal designs (e.g. weep holes in outdoor bronze sculptures).

Reference material: Coburn (1978); Cook and Smith (1982); Hughes (2000); Hughes et al. (2002); Junge and Werby (1958); King (2000); Lobnig et al. (1993); Mattsson (1982); Mattsson and Holm (1982); Payer (1992); Phipps and Rice (1979).

3 SPECIFIC CORROSION PROBLEMS

Various corrosion problems are of particular relevance to metals in museum collections. Several of these are discussed below, along with some tests for identifying materials that are harmful to metals (Appendix 3 on p. 39).

CORROSION AND CORROSION PREVENTION BY VOLATILE ORGANIC COMPOUNDS

VOLATILE ORGANIC ACIDS

Some volatile organic acids can cause corrosion on metals, e.g. acetic acid (ethanoic acid, CH_3COOH) and formic acid (methanoic acid, CHOOH). The most susceptible metal is lead, which starts to corrode at acetic acid levels as low as 0.2 parts per million (ppm). Humans cannot usually smell acetic acid (i.e. vinegar) until it reaches levels of about 1 ppm, so if there is a noticeable vinegar odour the level of acetic acid is high enough to cause the formation of white corrosion products on lead. Other metals susceptible to corrosion when exposed to volatile organic acids include cadmium, copper, iron, and zinc.

Common sources of volatile organic acids in the museum environment include wood, wood products, and other materials that are often used in storage or display areas. Poly(vinyl acetate) adhesives, paints, and sealants may also give off acetic acid as they dry and age. These products can all cause problems for metal artifacts. For example, copper alloys stored in wooden crates or cabinets may become covered with green or blue-green corrosion due to acetic acid emissions.

Plastics made from cellulose acetate can also produce acetic acid when they degrade ("vinegar syndrome"). Examples include sheets used for photographic and cinematographic film and microfiche, and three-dimensional objects (or parts of objects) made to simulate tortoiseshell, ivory, wood, or mother-of-pearl. Cellulose acetate can be identified with a spot test based on the successive application of four pre-mixed reagents (Coxon 1993).

Reference material: Bradley and Thickett (1999); Canadian Conservation Institute (1995); Coxon (1993); Donovan and Stringer (1971); Hatchfield (2002); Tétreault (1994, 1999, 2003); Thickett et al. (1998); Williams (2002).

VAPOUR PHASE INHIBITORS

Although many volatile organic compounds, particularly organic acids, are harmful to metals, others can be used to help slow metal corrosion. These are called vapour phase inhibitors (VPIs) or volatile corrosion inhibitors (VCIs). One well-known example is camphor ($C_{10}H_{16}O$), which prevents silver from tarnishing. These inhibitors evaporate, diffuse throughout the space, and are then adsorbed by metal surfaces. They work best in an enclosed space.

General purpose VPIs are usually salts made of a weak volatile base and a weak volatile acid (the exact chemical compositions of commercially available inhibitors are usually unknown as they are trade secrets). They act as mixed inhibitors because they are adsorbed at both anodic and cathodic regions, slowing both anodic and cathodic processes. The adsorbed inhibitors provide a physical barrier and often a hydrophobic surface, thus helping to isolate the metal surface from surrounding atmospheric moisture. The continued presence of the VPI is necessary to maintain a steady supply of the vapour to the metal surface.

VPIs are not generally used in museum collections because, although they inhibit corrosion on metals, they may be harmful to other materials associated with the metals. Lunning (1980), for example, cites an example of the use of a VPI called Silver Safe where the displayed silver did not tarnish but the paper associated with the display turned yellow.

VPIs may also contain chemicals that are harmful to human health. Before using one, it is important to check the material safety data sheet (MSDS) for each of the chemicals present and follow all indicated safety procedures.

Reference material: Gilberg (1987); Hatchfield (2002); Lunning (1980).

CORROSION BY NON-VOLATILE ORGANIC ACIDS

Non-volatile organic acids can also cause corrosion on metals. Metals in prolonged contact with organic material from animal and vegetable sources (e.g. fats, oils, waxes) can react to form a waxy metal salt (also called a metal soap) in a process known as saponification. Susceptible metals include cadmium, copper, lead, and zinc. One example of this is the green corrosion that is sometimes found on brass saddle tacks. Waxy corrosion products can also be found where metals are in contact with leather, or coated with a wax, fat, or oil. For example, if zinc or galvanized steel (i.e. iron plated with zinc) is coated with an alkyd- or oil-based paint, the zinc can react to form zinc soaps which reduce paint adhesion and cause the paint to peel and flake.

It is the free fatty acids (such as stearic acid, $CH_3(CH_2)_{16}COOH$) in waxes, fats, and oils that cause the metals to corrode. Free fatty acids are usually present in natural plant and animal products (e.g. beeswax, carnauba, lanolin, linseed oil) and can be found in some commercial products (e.g. Neatsfoot Oil used to dress leather is oil extracted from the feet and shin bones of cattle by boiling). They can also be released by degrading organic materials as they undergo hydrolysis or oxidation.

Figure 3.1 illustrates the formation of a green copper soap on a pin inserted through an insect. Other examples (not shown) of objects where metal soaps have been positively identified through analysis include bronze sculptures coated with beeswax, a camera with cadmium plating stored in leather, and paper on crayons coloured with brass flake pigments.

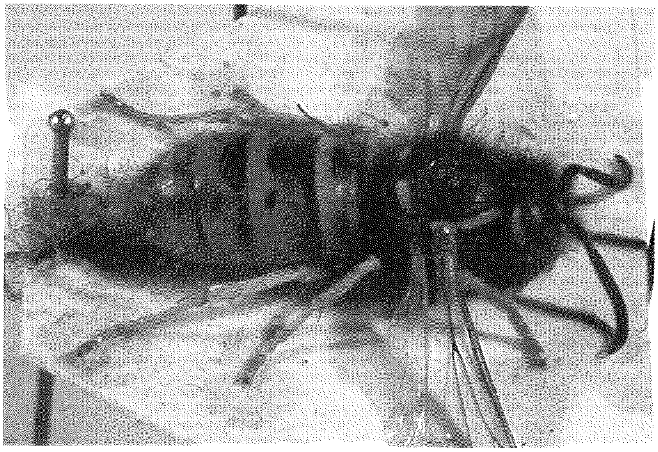

Figure 3.1. Green corrosion (described as verdigris) on a pin where it passes through a bee from the National History Museum, London. The copper and zinc in the pin (made of tin-plated brass) have reacted with free fatty acids from the bee and formed the green corrosion products, identified as copper and zinc salts of fatty acids. (A colour version of Figure 3.1 is available on p. 81.)

Reference material: Burmester and Koller (1987); Helwig et al. (2001); Schrenk (1991, 1994); Sirois and Moffatt (2002); Sirois et al. (2002, 2003); Scott (2002); Tilbrooke (1980).

CORROSION BY REDUCED SULPHUR

The presence of reduced sulphur (i.e. sulphur in a reduced oxidation state) is problematic for various metals. Silver and copper will tarnish when exposed to gases that contain reduced sulphur compounds such as hydrogen sulphide (H_2S), carbonyl sulphide (COS), or elemental sulphur. Levels of hydrogen sulphide as low as parts per trillion will cause a thin film of silver sulphide to form on silver. Other naturally occurring volatile organic sulphides such as carbon disulphide (CS_2), methanethiol (CH_3SH), dimethyl sulphide (CH_3SCH_3), and dimethyl disulphide (CH_3SSCH_3) may also contribute to tarnishing. Sources of sulphur-containing gases include certain foods (e.g. eggs, onions), rubber (see below), protein-based glues, wool, some natural waters, the pulp-and-paper industry, heating fuels based on coal, and other materials (some paints, some modelling clays). Even objects contaminated with reduced sulphur compounds (such as those recovered from anaerobic environments) may be a source of tarnishing gases (e.g. if enclosed inside a display case or storage area along with susceptible metals).

NATURAL RUBBER

Natural rubber is an elastic substance that can be found in elastic materials (e.g. components of clothing, tires) and hard rubbers (e.g. ebonite, vulcanite). It is created by heating the latex of a tropical plant with sulphur to solidify it (this process was discovered by C. Goodyear in 1839, and is known as vulcanization). Hard rubbers have been used in woodwind musical instruments, telephones, gramophones, and a wide range of other manufactured goods. Ebonite and vulcanite are good electrical insulators, and are often found in association with copper alloys in historic scientific instruments, telegraphy, and radio collections.

Hard rubber deteriorates in the presence of air, moisture, and light because its sulphur component (higher in harder rubbers than in the more elastic materials) oxidizes to sulphuric acid. Deteriorating ebonite surfaces have been found to have drops of acidic liquid (pH 1–2) that originate from either sulphuric acid (H_2SO_4, which is hygroscopic even at low RH levels) or other hygroscopic sulphate salts.

If in direct contact with copper alloys (as is often the case, see above), these deterioration products can cause corrosion of the copper alloy. Various copper and zinc sulphates have been identified on copper alloys in association with unstable ebonite. Examples of corrosion products identified include chalcanthite ($CuSO_4 \cdot 5H_2O$), gunningite ($ZnSO_4 \cdot H_2O$), and ammonium zinc sulphate hydrate ($(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$). White crystals of ammonium sulphate ($(NH_4)_2SO_4$) have also been observed on ebonite surfaces. These are probably formed from the reaction of sulphuric acid with ammonium (NH_4^+) ions present in dust.

Reference material: Bacon (1988); Hatchfield (2002); Lobnig et al. (1993); Sirois (1995); Williams (1982, 1988, 1997).

CORROSION BY CHLORIDE IONS

Chloride ions contribute to many corrosion problems associated with museum objects, especially those of archaeological origin. They accumulate on and within archaeological metals during burial, and can cause active corrosion problems on iron (e.g. spalling, flaking, weeping, akaganéite formation) and copper alloys (bronze disease) after excavation. They play an important role in disfiguring pitting on aluminum alloys displayed outdoors (where chlorides can be present from de-icing salts). (More details about these aspects of chloride ions and corrosion are covered in the separate chapters on the various metals.) Chloride contamination can also arise from materials in direct contact or close proximity to metal objects.

Sodium chloride (NaCl) is a major component of human perspiration, and can be transferred to a metal object that is touched with bare hands. The reaction between the sodium chloride and the metal (especially one with a polished surface) may cause fingerprints or other unwanted staining. (In industry, people who cause rapid rusting of iron after touching it are known as "rusters.")

Some modern soldering fluxes contain zinc chloride ($ZnCl_2 \cdot xH_2O$), which is very hygroscopic (picking up moisture at about 10% RH). Because the presence of moisture encourages corrosion, it is dangerous to leave any of this flux as a residue on a metal after soldering.

Chloride ions may also originate from plastics, some of which produce chlorinated acids as they age. For example, hydrochloric acid is one of the degradation products of plastics, gaskets, tubing, adhesives, etc. made from chlorinated polymers such as poly(vinylidene chloride), poly(vinyl chloride) (e.g. certain Tygon tubing), or chlorinated rubbers (e.g. polychloroprene in Neoprene). Chlorinated organic material can be identified with the Beilstein test; copper wire heated in a flame along with the organic material will turn green if chlorine is present (Canadian Conservation Institute 1993). (Aging plastics can also produce harmful non-chlorinated acids; phthalic acid, for example, may be formed by hydrolysis of phthalate ester plasticizers in poly(vinyl chloride).)

Reference material: Bailey and Zaccardi (1983); Canadian Conservation Institute (1993); Hatchfield (2002); Lind (1972); Nagy (1999); Richardson and Malthus (1955); Shashoua (2001); Williams (2002).

CORROSION BY NITROGEN OXIDES

When nitrogen oxide (NO_x) gases come in contact with moist air, they form nitric acid (HNO_3) which is corrosive to many metals. One common source of nitrogen oxide gases is cellulose nitrate (also called celluloid and nitrocellulose), which gives off gases such as NO and NO_2 when it degrades. Nitrate-containing corrosion products have been identified on copper, iron, and zinc located in close proximity to objects containing cellulose nitrate. For example, green copper nitrate corrosion products were identified on a metal necklace (a silver–copper alloy) covered with cellulose nitrate beads (Lee and Thickett 1996c); brown iron(III) nitrate ($Fe(NO_3)_3 \cdot xH_2O$) was identified in corrosion found in a metal laboratory drawer at the Canadian Conservation Institute where cellulose nitrate samples had been stored (Corbeil and Moffatt 1996); and zinc nitrate was identified on a corrosion sample from a belt buckle made of zinc and celluloid (Wypyski 1990).

Cellulose nitrate can be found in lacquers (e.g. Agateen, Frigiline), adhesives (e.g. H.M.G. adhesive), photographic film, and solid objects (e.g. combs, purses, fans) made to imitate natural material such as ivory (imitation called "French ivory"), tortoiseshell, and horn. Its presence can be easily determined with a simple spot test (Williams 1994a); the reagent contains diphenylamine in concentrated sulphuric acid and it turns dark blue in the presence of cellulose nitrate. Likewise the presence of strong acid generated by high concentrations of nitrogen oxides in a closed environment can be detected using indicators such as Cresol Red or Cresol Purple (Fenn 1995).

Reference material: Corbeil and Moffatt (1996); Fenn (1995); Hatchfield (2002); Lee and Thickett (1996c); Lewis (2002); Williams (1994a, 1994b); Wypyski (1990).

DEGRADATION OF ORGANICS BY METAL IONS

In some cases, the deleterious consequences of corrosion extend beyond the effects on the metal. Certain transition metal ions, such as copper and iron ions, are known to accelerate (i.e. catalyse) the decomposition of natural polymeric organic materials such as cellulose and proteins. (Cellulose is the main organic constituent in paper, wood, cotton, and linen; and proteins (e.g. collagen, keratin) are present in materials such as silk, wool, leather, parchment, and skin.) For example, wood often deteriorates in areas adjacent to iron nails or fasteners after exposure to high levels of moisture. Paper degradation known as "foxing" (the discoloration of paper with yellow, brown, or red-brown spots) contains high levels of iron or copper impurities. Parchment and paper suffer damage (e.g. discoloration, loss of support material, perforation) in areas where copper pigments or iron gall inks are present, or where residual iron salts remain (e.g. platinum photographs). Skin and leather experience "black rot" (a type of degradation that shows up as loss of strength, brittleness, and the powdering of fibres) from dyes or mordants that contain transition metal ions (e.g. Cu^{2+}, Fe^{2+}) or from attached metal fittings. And weighted silks (from the late 1800s until about 1950, silks were weighted with metallic salts to increase or replace the weight lost during processing) undergo accelerated degradation due to the metal salts, becoming brittle and easily torn or cracked when handled.

When organic polymers degrade, the polymer chain usually becomes shorter (i.e. the degree of polymerization is reduced) and the material (e.g. paper, silk, leather) becomes fragile, brittle, and easily damaged. This degradation process includes both hydrolysis and oxidation: hydrolysis is the reaction of the polymer with water, and the rate of this reaction is accelerated when the water is acidic or alkaline; oxidation is the reaction of the polymer with oxidizing agents (e.g. oxygen, hydrogen peroxide, free radicals). It is the rate of this oxidation reaction that can be accelerated by the presence of transition metal ions under humid conditions.

In the presence of moisture and acidity, transition metals (either in the metallic state or in metal compounds) dissolve as ions. These transition metal ions then participate in reactions with molecular oxygen and organic molecules to produce free radicals (e.g. $HO\bullet$, $HO_2\bullet$, $R\bullet$, $RO_2\bullet$ where R represents an organic molecule) and hydrogen peroxide (H_2O_2). These react with organic polymers — causing their accelerated degradation. In particular, the formation of the hydroxyl free radical $HO\bullet$ by the reaction of Fe^{2+} with hydrogen peroxide (the Fenton reaction, $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^-$) is thought to play an important role in polymer degradation (i.e. oxidation) because the hydroxyl free radical is an extremely powerful oxidizing agent.

One well-known example of the degradation of organic material by transition metal ions occurs in paper that has been written or drawn on with iron gall inks. Such inks are formulated by mixing aqueous solutions of iron(II) sulphate ($FeSO_4$) and tannin-containing extracts of gall nuts, and they can be relatively acidic (e.g. pH 2–3.7). Their dark blue-black colour develops when they are exposed to air (the Fe^{2+} ions are oxidized to Fe^{3+} ions, which then react with the tannins and precipitate as dark iron(III) tannate complexes). Over time, the black colour of the ink fades and the paper supporting the ink shows signs of deterioration such as blurred lines, holes, and eventual loss. The Fe^{2+} ions are thought to play an important role in this degradation by means of the Fenton reaction, which produces Fe^{3+} ions and powerful hydroxyl free radicals that attack and degrade the cellulose in the paper. As the cellulose decomposes, some of the organic decomposition products are capable of reducing Fe^{3+} ions back to Fe^{2+} ions, which allow the Fenton reaction and subsequent cellulose degradation to continue. This regeneration of Fe^{2+} ions is so effective that old iron gall ink lines on paper may still contain substantial amounts of them. Their existence can be determined with a non-bleeding indicator paper (developed by H. Neevel at the Netherlands Institute for Cultural Heritage) that turns magenta if Fe^{2+} ions are present (see www.preservationequipment.com for information on this commercially available test).

Reference material: Banik (1997); Banik et al. (1982); Bicchieri and Pepa (1996); Daniels and Leese (1995); Deasy (1967); Dignard and Gordon (1999); Emery and Schroeder (1974); Gent and Rees (1994); Graf et al. (1984); Mairinger et al. (1980); Miller and Reagan (1989); Neevel (1995); Reissland (1999); Scott (2002); Scott et al. (2001); Tang (1978); Williams et al. (1977).

APPENDIX 3: TESTING FOR THE PRESENCE OF HARMFUL MATERIALS

As the above examples demonstrate, many materials can cause metals to corrode. To circumvent these problems, it is important to identify the presence of any harmful materials. A number of tests are available for this purpose.

ACCELERATED CORROSION TEST ("ODDY TEST") FOR HARMFUL MATERIALS

Accelerated corrosion tests can be used to identify potentially dangerous materials. Often referred to as "Oddy tests" (after A. Oddy who first published a description of them), they have proven simple, relatively fast, and effective in detecting materials that may be unsuitable for use in museum storage or display. In accelerated corrosion tests, copper, lead, and silver are used to identify materials (e.g. polymers, foams, gaskets, tubing, adhesives, fabrics) that may be harmful to museum objects. To conduct a test, place a sample of the material to be tested and some water into each of three containers. Add copper foil (high purity foil, at least 99 wt% pure, about 0.1 mm thick) to the first container, lead foil to the second, and silver foil to the third. Heat the containers for 28 days at 60°C. If any of the metal foils are affected (i.e. tarnished or corroded), the material should not be used.

Reference material: Bamberger et al. (1999); Green and Thickett (1995); Lee and Thickett (1996a); Oddy (1973, 1975); Williams (2002).

TEST FOR REDUCED SULPHUR

A simple spot test can be used to identify materials that are capable of producing reduced sulphur gases (e.g. hydrogen sulphide, carbonyl sulphide). (Note: Because the chemicals used in this test may be harmful (sodium azide, in particular, is toxic and may explode if heated), their material safety data sheets (MSDS) should be consulted for health and safety information before proceeding.) To conduct the test, place a small sample of the material in question on a microscope slide and add a cover. Apply a few drops of an aqueous solution containing potassium iodide (KI), iodine (I_2), and sodium azide (NaN_3) so that it is wicked under the cover and wets the sample (see reference material cited below for exact concentrations and more detailed instructions). The presence of reduced sulphur (e.g. inorganic sulphides, organic thioketones (R=S, where R is an organic chain), organic mercaptans (R-SH)) will be indicated by the formation of nitrogen (N_2) bubbles. The bubbles form due to the following reaction, which is catalysed by reduced sulphur.

$$2Na^+ + 2N_3^- + I_2(g) \rightarrow 3N_2(g) + 2Na^+ + 2I^-$$

This reaction can be observed by testing a sample of your own hair or a fibre from a wool sweater (the proteins in hair and in wool contain reduced sulphur). A preliminary test on hair or wool will also serve to determine whether or not the azide solution is still good.

Reference material: Daniels and Ward (1982); Lee and Thickett (1996b).

TEST FOR CHLORIDE IONS IN SOLUTION

A qualitative test based on silver nitrate ($AgNO_3$) can be used to identify the presence of chloride ions (Cl^-) in aqueous solutions. This test is simple and fast. Simply add dilute silver nitrate (e.g. 0.2*M*) to a sample of the test solution. The formation of a cloudy white precipitate of silver chloride (AgCl) indicates the presence of chlorides.

$$Cl^- + Ag^+ + NO_3^- \rightarrow AgCl(s) + NO_3^-$$

Note: This test will work only if the solution is acidic; therefore test solutions should first be acidified with a few drops of nitric acid (HNO_3). Alkaline solutions will form a brown precipitate of silver oxide (Ag_2O) when $AgNO_3$ is added.

This test is often used to monitor the presence of chloride ions in treatment solutions for archaeological iron. It is sensitive to low levels of Cl^- ions, with a cloudy white precipitate clearly visible at Cl^- concentrations of 5 ppm (5 mg L^{-1}). If a more accurate determination of dissolved Cl^- ions is necessary, quantitative methods based on the use of specific-ion electrodes are available.

Reference material: Odegaard et al. (2000); Selwyn (2001); Semczak (1977).

4

INTRODUCTION TO SPECIFIC METALS

The following chapters are devoted to the alloys and corrosion properties of the nine metals most commonly found in museum collections:

- aluminum
- copper
- gold
- iron
- lead
- nickel
- silver
- tin
- zinc

PROPERTIES

Each chapter begins with a table of the following properties of the metal and a general description of it:

- principal oxidation number(s)
- atomic weight (g mol^{-1})
- density at 20°C (g cm^{-3})
- melting point (°C)
- boiling point (°C)
- linear expansivity ($°C^{-1}$)
- UNS range for alloys

Reference material: CRC Press (1998).

LINEAR EXPANSIVITY

Metals respond to changes in temperature by expanding or contracting — a phenomenon that is important whenever the metal is in close contact with other materials. If allowances are not made for this change in size, severe stresses occur whenever the object is exposed to temperature fluctuations.

The change in the length of a piece of metal (ΔL) in response to a change in temperature (ΔT) is defined as:

$$\Delta L = \alpha \, \Delta T \, L$$

where α is the coefficient of linear expansion (also known as linear expansivity).

For example, lead is known to have a linear expansivity of 28.9×10^{-6} $°C^{-1}$. Therefore, if a lead bar with a length (L) of 1 m at 20°C is heated to 30°C (i.e. $\Delta T = 10°C$), the bar's change in length (ΔL) will be $\alpha \, \Delta T \, L = (28.9 \times 10^{-6}\ °C^{-1}) \times (10°C) \times (1\ m) = 2.9 \times 10^{-4}$ m. In other words, the bar that is 1 m long at 20°C will expand to 1.00029 m at 30°C.

CORROSION PRODUCTS

Most chapters include a table that contains information about the metal's common corrosion products. For each compound, the chemical name, chemical formula, mineral name, and colour are provided. (Note: The listed colours are approximate and are included only as a general guide. The exact colour of corrosion products depends on the particle size, particle shape, and the presence of contaminants. For example, some products may be transparent and almost colourless when they consist of large crystals, but appear white or some other colour when formed as tiny particles. Corrosion products may also change colour if stained by trace amounts of coloured contaminants.) More information about minerals, including a "sound bite" for the correct pronunciation of mineral names, can be found in the Mineralogy Database (www.webmineral.com).

PHASE DIAGRAMS

Phase diagrams (adapted from ASM International 1992) are provided in each chapter for the alloys under discussion. In all cases the top scale indicates the amount of the element in atomic percent and the bottom scale gives its amount in weight percent. More information on phase diagrams can be found on the phase diagram tutorial Web site provided by the Interactive Learning Centre, University of Southampton, UK (www.soton.ac.uk/~pasr1/index.htm).

To better understand the concepts of atomic and weight percentage, and how they are related, consider a mixture of two elements. The first element has an atomic weight x, a weight percentage w_x, and an atomic percentage a_x; the other has an atomic weight y, a weight percentage w_y, and an atomic percentage a_y.

The atomic and weight percentages of each individual element are related as follows:

$$a_x = \frac{100}{1 + (x/y)[(100/w_x) - 1]}$$

$$w_x = \frac{100}{1 + (x/y)[(100/a_x) - 1]}$$

The atomic and weight percentages of the two elements are related by:

$$w_y = 100 - w_x$$

$$a_y = 100 - a_x$$

All of the phase diagrams in the following chapters are annotated in the same way:

- the liquid phase is labelled simply as "Liquid" when it is the only phase that exists, and as "L" if the liquid is present along with a solid phase in a two-phase region
- regions where only one solid phase exists are labelled with a symbol representing that phase, often a Greek letter (see Table 4.1 for a list of the letters used)
- regions where two solid phases co-exist are labelled with symbols representing the two phases
- magnetic transitions and uncertain boundaries are shown as broken lines

TABLE 4.1. GREEK LETTERS

Name	Greek symbol (lower case)	Greek symbol (upper case)
alpha	α	A
beta	β	B
gamma	γ	Γ
delta	δ	Δ
epsilon	ε	E
zeta	ζ	Z
eta	η	H
theta	θ	Θ

Reference material: ASM International (1992); Scott (1991); Wanhill (2001).

EQUATIONS

In many cases chemical reactions are written in equation form. Within these equations, the phase of each chemical formula is identified as solid (s), liquid (l) (except where the liquid is water in which case only H_2O is used), or gas (g). When the chemical species is in the ionic form and labelled with a charge (e.g. Cl^- or H^+), it is assumed to be dissolved in a liquid.

TOXICITY

The metals discussed in this publication range in toxicity from relatively harmless (e.g. iron) to seriously toxic (e.g. lead). For a few metals, mention of the toxicity is made at the end of the chapter. More information about the hazards of various materials encountered in conservation can be found in Rossol (2002) (an excellent reference that is highly recommended).

Reference material: Rossol (2002).

5

ALUMINUM (Al)

Principal oxidation number(s)	Atomic weight (g mol^{-1})	Density at 20°C (g cm^{-3})	Melting point (°C)	Boiling point (°C)	Linear expansivity (°C^{-1})	UNS range for alloys
Al^{3+} (aluminic)	26.98	2.70	660	2519	23.1×10^{-6}	A00001– A99999

GENERAL DESCRIPTION

Pure aluminum is a highly reflective, silvery-white metal that is light and can be easily formed, machined, and cast. It is non-magnetic and has high thermal and electrical conductivity. Its corrosion products are colourless or white, and they form a passivating protective oxide film that renders aluminum resistant to further corrosion. Because pure aluminum is soft and has relatively little strength, small amounts of other elements are added to make stronger, harder alloys.

Further information on aluminum is available in the reference material and on the Web site of the Aluminum Association (www.aluminum.org).

Reference material: Aluminum Association (1983); Ghali (2000); Zahner (1995a).

ORIGIN

Aluminum is not found naturally in a pure state. Rather, it is present as an oxide and mixed with other minerals in an ore. The principle aluminum-bearing ore is bauxite, in which aluminum oxide is present mainly as the minerals gibbsite and boehmite.

The first attempt to recover aluminum occurred in 1807, when Sir H. Davy tried unsuccessfully to isolate a new metal he called "alumium." Impure aluminum was isolated in 1825 by H.C. Oersted, and finally, in 1827, pure aluminum was isolated by F. Wohler. However, it was not used widely until after 1886, when C.M. Hall and P.L.T. Heroult independently discovered an electrolytic process that made producing aluminum easier and more affordable (today this procedure is known as the Hall-Heroult process, signifying their joint discovery). Many aluminum alloys were developed between 1914 and 1918 due to the growing need for lightweight high-strength materials during World War I.

Canada (with its abundance of the hydroelectric power necessary to reduce aluminum oxide to aluminum metal) is a major producer of aluminum.

Today aluminum is also easily recycled, and remelting aluminum scrap requires only 5% of the energy needed to produce aluminum from its ore.

Reference material: Hammond (1998); Kelley (1995).

USE

One of the earliest examples of the use of aluminum can be found in the Washington Monument (its pyramidal aluminum cap was cast — at great expense — in 1884). Another example is the cast figure of *Eros* on the Shaftesbury Memorial in Piccadilly Circus, London (unveiled 1893). Today aluminum has many uses: in aircraft and automotive components; as siding, roofing, and decorative metalwork in modern buildings; in cans; and even in modern coins. Buckminster Fuller used aluminum to build his Dymaxion House, a prototype for mass-produced affordable housing (that never caught on).

Reference material: Aluminum Association (1983); Gayle and Look (1992); Krause and Mishler (1991); Waite (1992); Zahner (1995a).

ALLOYS AND PLATING

Small quantities of various elements can be added to aluminum to produce alloys with special properties, e.g. greater strength or hardness, improved casting characteristics, increased corrosion resistance. Certain alloying elements (e.g. manganese, copper, zinc) increase strength while others (e.g. magnesium, silicon) increase corrosion resistance. The aluminum industry divides aluminum alloys into two categories according to how they will be formed:

- wrought aluminum alloys — which are designed to be formed by a wide variety of processes (e.g. into sheet, plate, foil, extrusions, bars, wire, etc.)
- cast aluminum alloys — which are specially formulated to flow

The Aluminum Association (AA) has assigned a unique AA number (and a corresponding UNS number) to commercially available wrought and cast aluminum alloys, depending on their composition. The first digit in the AA number is assigned according to the major alloying elements, as shown in the following two tables. (The *x*'s indicate numbers between zero and nine.) For example, the designation AA 7075 (UNS A97075) has been assigned to a wrought aluminum–zinc alloy that is one of the highest-strength aluminum alloys in use today.

WROUGHT ALUMINUM ALLOYS

Some of the common wrought aluminum alloys are listed in Table 5.1, along with their series designations according to the Aluminum Association (AA) and their corresponding UNS numbers.

Wrought aluminum alloys are used in building construction (e.g. roofing, siding, flashing) and to make aluminum cans.

Reference material: ASM International (1992); Cayless (1990); Doyle (1985); Duncan (1988); Ghali (2000); Hollingsworth et al. (1989); King (1985); Staley (1989); Young (1985); Zahner (1995a).

CAST ALUMINUM ALLOYS

The main elements added to aluminum to make cast alloys are silicon, copper, and magnesium (either alone or in combination). Some modern cast aluminum alloys are listed in Table 5.2, along with their series designations according to the Aluminum Association (AA) and their corresponding UNS numbers.

TABLE 5.1. WROUGHT ALUMINUM ALLOYS

Wrought aluminum alloys	Concentration range	AA number	UNS number
aluminum	≥99.00 wt% aluminum	1xxx	A91xxx
aluminum + copper	1–6 wt% copper	2xxx	A92xxx
aluminum + manganese	0.5–1.5 wt% manganese	3xxx	A93xxx
aluminum + silicon	5–12 wt% silicon	4xxx	A94xxx
aluminum + magnesium	0.5–5 wt% magnesium	5xxx	A95xxx
aluminum + (magnesium and silicon)	0.5–1.5 wt% magnesium 0.5–1.5 wt% silicon	6xxx	A96xxx
aluminum + zinc	3–7 wt% zinc	7xxx	A97xxx

TABLE 5.2. CAST ALUMINUM ALLOYS

Cast aluminum alloys	Concentration range	AA number	UNS number
aluminum	≥99.00 wt% aluminum	1xx.x	A01xxx
aluminum + copper	4–8 wt% copper	2xx.x	A02xxx
aluminum + silicon + (copper or magnesium)	5–22 wt% silicon 0.5–4.5 wt% copper 0.3–1.0 wt% magnesium	3xx.x	A03xxx
aluminum + silicon	5–12 wt% silicon	4xx.x	A04xxx
aluminum + magnesium	4–10 wt% magnesium	5xx.x	A05xxx
aluminum + zinc	3–7 wt% zinc	7xx.x	A07xxx
aluminum + tin	6 wt% tin	8xx.x	A08xxx

Cast aluminum alloys are used in the cylinder blocks and wheels of many of today's cars.

Reference material: Cayless (1990); Duncan (1988); Ghali (2000); Hollingsworth et al. (1989); Young (1985); Zahner (1995a).

TEMPER

The degree of hardness and strength of aluminum alloys (achieved by either mechanical working or heat treatment, or both) is designated by its temper. In North America, there is a temper designation system for aluminum alloys (both wrought and cast). This system is based on the sequences of mechanical or thermal treatments, or both, used to produce the various tempers. The temper designation is usually listed after the UNS or AA alloy designation and consists of a capital letter for the basic temper designation followed by one or more digits for the subdivision. Some basic temper designations include "F" for as-fabricated, "O" for annealed, "H" for work-hardened, and "T" for heat-treated.

Aluminum alloys (both wrought and cast) can be further categorized on the basis of whether or not they are heat-treatable.

Non-heat-treatable: Some aluminum alloys cannot be hardened by heat treatment. However, these alloys are still harder than pure aluminum because of the presence of the alloying elements; this type of hardening is referred to as solid solution hardening. They can also be hardened by cold-working.

Heat-treatable: Other aluminum alloys can be hardened by heat treatment; this type of hardening is referred to as age-hardening or precipitation hardening and results from the formation of intermetallic compounds. Among the first of these heat-treatable aluminum alloys was Duralumin, developed by A. Wilm and first produced in Germany in 1908. Wilm discovered that the addition of a small amount of copper to aluminum caused an increase in its hardness. Since then, many heat-treatable aluminum alloys have been developed.

Heat treatment involves several steps. Take, for example, a copper–aluminum alloy containing 4 wt% copper. First the solid alloy is heated to a temperature of about 500°C to dissolve all the copper in the aluminum (this is shown in the partial phase diagram for aluminum and copper in Figure 5.1). Next it is cooled rapidly (quenched) to room temperature where the solubility of copper in aluminum is less than 0.5 wt% copper. Finally the alloy is aged at a temperature below 200°C, which causes the precipitation of the intermetallic compound $CuAl_2$ (which corresponds to the θ phase in the phase diagram). This hardening happens naturally over a period of a few days if the alloy is left at room temperature, but controlled heating below 200°C produces the optimum size and distribution of $CuAl_2$. Different alloys produce different intermetallic compounds as a result of heat treatment, e.g. when aluminum alloys that contain magnesium and silicon (series 6xxx) are heat-treated, the intermetallic compound Mg_2Si precipitates.

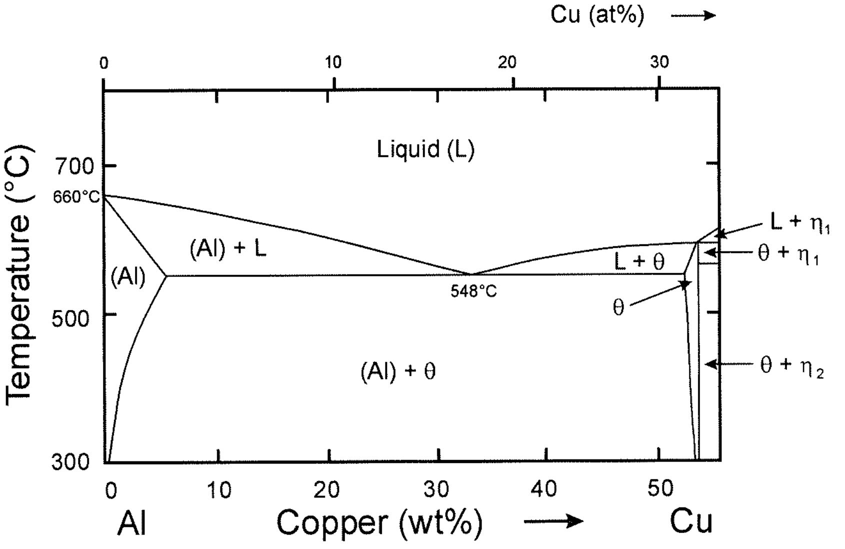

Figure 5.1. Partial equilibrium phase diagram for aluminum and copper. The bottom scale is weight percent and the top scale is atomic percent. The phase labelled θ is the intermetallic phase with an approximate composition of $CuAl_2$. Adapted from ASM International (1992).

Reference material: Cayless (1990); Ghali (2000); Hollingsworth et al. (1989); Zahner (1995a).

ALCLAD PLATING

The term "alclad" refers to wrought aluminum products (e.g. sheets, tubes, wires) with a layered or sandwich structure. Alclad material consists of an aluminum alloy core which has an outer layer (cladding) of a more corrosion-resistant material (either pure aluminum or another aluminum alloy) on one or both sides. The outer layer is applied by spraying molten aluminum, and tends to be soft and easily scratched. The core alloy is chosen for its mechanical properties, usually strength.

Reference material: Ghali (2000); Hollingsworth et al. (1989); Zahner (1995a).

ALUMINUM-PLATED IRON

Iron or steel can be coated with aluminum using a hot-dipping process that was developed in the 1940s. During the 1970s, the aluminum in this process was replaced with various aluminum–zinc alloys (e.g. trade names Aluzink, Galfan, Galvalume, Zincalume). This type of "aluminized" steel is often used for roofing. More information on aluminum-plated iron can be found in "Chapter 8. Iron."

Reference material: Zahner (1995b).

CORROSION

Various aluminum compounds mentioned in this chapter are listed in Table 5.3.

SOLUTION CHEMISTRY

The principal oxidation state of aluminum is +3 (Al^{3+}). When immersed in water with a pH between 4 and 9, it corrodes slowly (reacts with dissolved oxygen gas) in accordance with the reactions below:

Anodic half-reaction: $Al(s) \rightarrow Al^{3+} + 3e^-$
Cathodic half-reaction: $\frac{3}{4}O_2(g) + 1\frac{1}{2}H_2O + 3e^- \rightarrow 3OH^-$
Net reaction: $Al(s) + \frac{3}{4}O_2(g) + \frac{1}{2}H_2O \rightarrow Al^{3+} + 3OH^-$

Initially, an amorphous aluminum hydroxide gel forms, followed by crystallization into one of the aluminum hydroxides bayerite or gibbsite or the aluminum hydroxide oxide boehmite. As these corrosion products cover the surface of the aluminum, they passivate it and slow corrosion.

Aluminum is considered an amphoteric metal because its corrosion products dissolve in either acid or alkaline conditions, allowing for uniform corrosion of the exposed metal. (When the pH is less than 4 (i.e. acid conditions), aluminum dissolves as the Al^{3+} ion; when the pH is greater than 9 (i.e. alkaline conditions), aluminum dissolves as the AlO_2^- ion.) Therefore, aluminum corrodes if exposed to acidic solutions and also if in contact with alkaline material such as sodium hydroxide, concrete, or mortar.

Reference material: Ghali (2000); Graedel (1989); Hollingsworth et al. (1989); Staley and Haupin (1992).

TABLE 5.3. ALUMINUM MINERALS AND CORROSION PRODUCTS

Chemical name	Mineral name	Chemical formula	Colour
aluminum(III) oxide (also called alumina)	—	γ-Al_2O_3	white
aluminum(III) hydroxide	bayerite*	$Al(OH)_3$	white
aluminum(III) hydroxide	gibbsite (also known as hydrargillite)*	$Al(OH)_3$	white
aluminum(III) hydroxide oxide	boehmite†	$AlO(OH)$	white
aluminum(III) chloride hexahydrate	chloraluminite	$AlCl_3 \cdot 6H_2O$	white

* The chemical formula for bayerite and gibbsite is sometimes written as $Al_2O_3 \cdot 3H_2O$.
† The chemical formula for boehmite is sometimes written as $Al_2O_3 \cdot H_2O$.

ANODIZING

Anodizing is an electrolytic process that produces a thick oxide layer on aluminum (thicker than would result from normal corrosion). The process is accomplished by making aluminum the anode in an electrochemical cell and forcing it to corrode. As the aluminum corrodes, the aluminum oxide grows and thickens into a hard, non-conductive layer that increases the aluminum's resistance to atmospheric corrosion and abrasion. Dyes or other coloured compounds can be incorporated into the open structure of freshly formed aluminum oxide, and then trapped by exposing the aluminum to boiling water (which causes the formation of aluminum hydroxide oxide boehmite). Various dyes can be used to colour the anodized layer, but some are more susceptible to fading than others. Anodizing was first used commercially to produce an industrial finish in the 1920s.

Reference material: Child (1993); Duncan (1988); Ghali (2000); Hollingsworth et al. (1989); Zahner (1995a).

INDOOR EXPOSURE

Aluminum and its alloys are generally resistant to corrosion in clean air due to the presence of a thin film (about 25Å) of aluminum oxide. This film forms rapidly when new aluminum (after extraction from its ore) is initially exposed to the oxygen in air (so even if aluminum is scratched it quickly forms a new oxide film). This film is protective in clean air (i.e. free of dust, pollutants, salts, etc.) as long as the RH levels remain below about 70%, and it helps polished aluminum maintain a bright reflective surface.

However, it is hard to maintain a mirror finish on polished aluminum because most air contains contaminants (e.g. dust, pollutants, salts) that promote corrosion (especially above 70% RH), which slowly dulls the aluminum. Indoor pollutants that contribute to aluminum corrosion include acidic organic gases such as formic acid (methanoic acid) and dust particles contaminated with chlorides or sulphates. As aluminum corrodes it becomes covered with a thin layer of white corrosion products that tend to be amorphous and difficult to identify by X-ray diffraction.

Reference material: Duncan (1988); Ghali (2000); Graedel (1989); Green and Thickett (1993); Staley and Haupin (1992); Zahner (1995a).

OUTDOOR EXPOSURE

Aluminum that is allowed to weather naturally outdoors slowly turns gray — with the shade ranging from light to dark, often with variations in colour over the surface. The surface becomes covered with various aluminum oxides and hydroxides oxides: alumina forms first, followed by boehmite, and finally the aluminum hydroxides (e.g. bayerite or gibbsite). Rain has a cleaning effect that can help to keep more openly exposed surfaces on outdoor aluminum less corroded than sheltered areas (where moisture and corrosive particles tend to accumulate). Figure 5.2 shows an example of the build-up of a thicker layer of white aluminum corrosion products in a less exposed area. When exposed outdoors, aluminum usually corrodes more slowly than metals such as carbon steel, zinc, and copper.

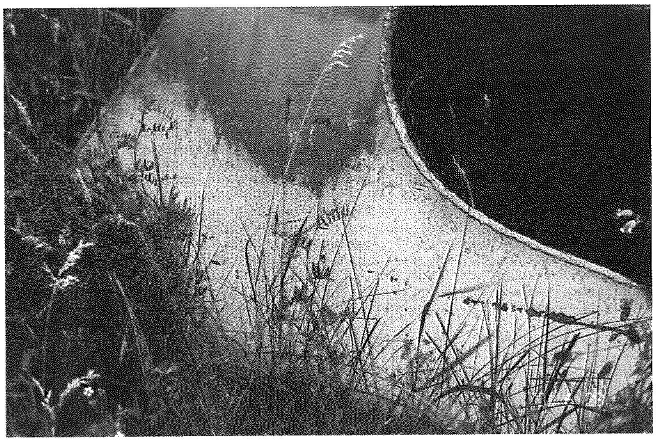

Figure 5.2. White corrosion has formed close to the ground on an aluminum support for an outdoor aluminum sculpture.

The corrosion rate of aluminum is increased in the presence of chloride ions (e.g. marine locations) and sulphate ions (e.g. urban locations), which become incorporated into the corrosion layer as aluminum hydroxide sulphates and aluminum chloride hydroxides. These corrosion products are amorphous and difficult to identify by X-ray diffraction. Airports usually avoid using chloride-containing de-icing salts because of the severe corrosion the chlorides may cause to aluminum aircraft; instead they use salts such as sodium formate (sodium methanoate) and potassium acetate (potassium ethanoate) which are less damaging to aluminum and are considered environmentally friendly.

Reference material: Ghali (2000); Graedel (1989); Hollingsworth et al. (1989); MacLeod (1983).

CORROSION DURING BURIAL

During burial (whether in soil, freshwater, or seawater), the surface of aluminum becomes covered with a gradually thickening layer of aluminum hydroxides or aluminum hydroxide oxide. These may be amorphous or crystalline. The aluminum hydroxides bayerite and gibbsite are favoured at room temperature. Bayerite has been identified on aluminum immersed in a freshwater lake for 50 years. The corrosion rate of aluminum is slow in deaerated water and increases as the amount of dissolved oxygen increases.

Many aluminum alloys are fairly resistant to corrosion in unpolluted seawater, although they can suffer from pitting corrosion due to the presence of chloride ions. Some aluminum alloys (particularly those that contain copper) suffer more serious corrosion during burial due to galvanic corrosion; this is especially true if intermetallic compounds such as $CuAl_2$ are present in the alloy. (For more information, see the sections below on chloride ions and galvanic corrosion.)

Reference material: Corbeil et al. (1995); Degrigny (1993, 1995); Hallam et al. (1997); MacLeod (1983).

CORROSION BY CHLORIDE IONS

Aluminum corrosion is enhanced in the presence of chloride ions.

As aluminum first begins to corrode, it releases Al^{3+} ions at the anodic sites. The Al^{3+} ions react with water in the electrolyte, and cause the anodic region to become acidic:

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3(s) + 3H^+$$

This influx of positively charged ions upsets the charge balance in the region surrounding the anodic site. Therefore, to maintain charge balance, the Al^{3+} and H^+ ions attract counter (negatively charged) ions. When chloride ions (Cl^-) are present in the electrolyte, they are preferentially attracted (because they have high mobility) and concentrate at the anodic regions where they form soluble aluminum chlorides (e.g. $AlCl_3$, $AlCl_4^-$). The reaction of the Al^{3+} ions that are released by the aluminum in the presence of Cl^- ions can therefore be described as:

$$Al^{3+} + 3Cl^- + 3H_2O \rightarrow Al(OH)_3(s) + 3H^+ + 3Cl^-$$

The HCl that is produced in this reaction then attacks any remaining solid aluminum:

$$Al(s) + 3H^+ + 3Cl^- \rightarrow Al^{3+} + 3Cl^- + 1^1/_2\ H_2(g)$$

which produces more Al^{3+} ions and causes a continuing corrosion cycle. The ongoing corrosion eventually causes extensive pitting on the aluminum.

Note: When the pH < 4, the cathodic half-reaction is the reduction of hydrogen ions and not the reduction of dissolved oxygen gas.

Reference material: Duncan (1988); Ghali (2000); Graedel (1989); Green and Thickett (1993); Hollingsworth et al. (1989); Holroyd (2001); Staley and Haupin (1992).

GALVANIC CORROSION

Aluminum is a relatively active metal compared to most others (see the section on galvanic series in "Chapter 2. Corrosion"). As such, it is usually the metal that corrodes preferentially when galvanically coupled to other metals (see the example in Figure 5.3). The galvanic attack is more severe when aluminum is in contact with copper or copper-based alloys than when it is in contact with most other metals. Only magnesium and zinc are more anodic than aluminum (at least in seawater) and corrode to protect it.

Alclad alloys: In alclad materials, the coating alloys are selected for their high inherent corrosion resistance combined with their electrochemical characteristics (i.e. the coating alloy is more anodic than the core alloy in most natural environments). This structure protects the inner core in two ways. First, as long as the outer aluminum layer is present and continuous, it provides a physical barrier (with a low corrosion rate) that prevents the underlying alloy from corroding. Second, even if the outer layer is not continuous (e.g. it has cut edges, rivet holes, or scratches), it corrodes preferentially — thus still protecting the inner layer. In this sense the corrosion behaviour of alclad alloys is similar to galvanized steel, which has an outer layer of zinc (active metal that corrodes preferentially) and an inner layer of steel (noble metal that is protected).

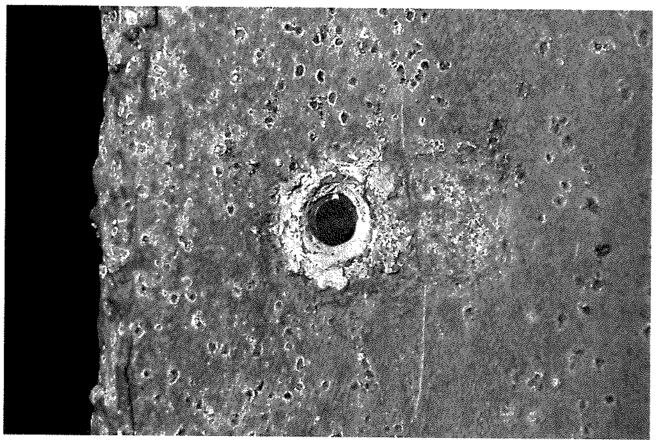

Figure 5.3. White corrosion on aluminum adjacent to a copper alloy bolt is evidence of galvanic corrosion caused by one metal (aluminum) being more active than another metal (a copper alloy) with which it is in direct contact.

Reference material: Ghali (2000); Hollingsworth et al. (1989); Zahner (1995a).

Intermetallic compounds: Some aluminum alloys, especially those alloyed with copper (2xxx series) or zinc (7xxx series), are susceptible to galvanic corrosion on a microscopic scale due to the presence of intermetallic particles. These compounds are formed by the interaction of aluminum with alloying elements such as copper, magnesium, lithium, and zinc. Because intermetallic compounds have electrode potentials that differ from those of aluminum or the solid solutions in which they have formed, they create local corrosion cells when they precipitate at grain boundaries (e.g. during aging treatments). For example, the precipitation of intermetallic $CuAl_2$ in aluminum–copper alloys causes the areas around the grain boundaries to become depleted in copper. The grain boundaries then become more anodic (more reactive) than the $CuAl_2$ particles and corrode preferentially, resulting in intergranular corrosion.

Exfoliation: Also called layer or lamellar corrosion, exfoliation is an extreme form of galvanic corrosion that occurs mainly in copper-containing wrought aluminum alloys (predominantly in relatively thin pieces with highly cold-worked, elongated grain structures, i.e. rolled or extruded pieces). It is characterized by alternating layers of thin, relatively uncorroded metal and thicker corrosion layers. This selective attack usually occurs along grain boundaries and proceeds along multiple narrow paths parallel to the surface; delamination happens as a result of the expansion that occurs as the corrosion products form. The intensity of exfoliation increases in slightly acidic environments. Figures 5.4 and 5.5 provide an example of exfoliation corrosion on a copper-containing aluminum alloy used in a space glove disconnect.

Metal ions in solution: If aluminum is exposed to a solution that already contains other dissolved metal

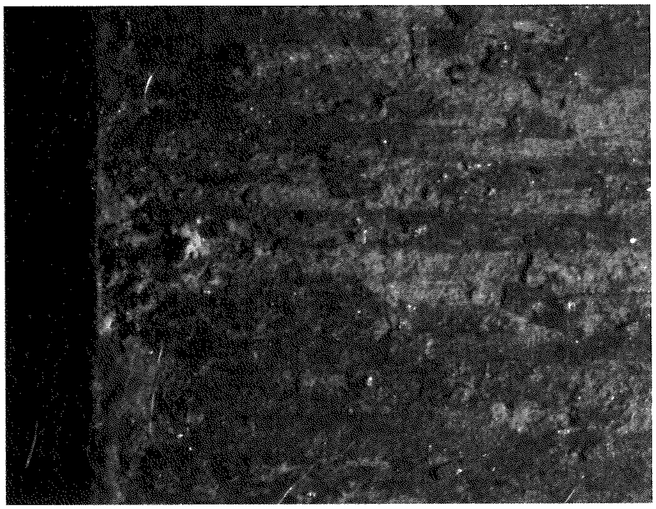

Figure 5.4. A photomacrograph of whitish accretions and flaking metal on the surface of aluminum suffering from exfoliation corrosion. The piece of aluminum is from the inside surface of the disconnect section of a Gemini space glove (D1973-0835) belonging to the National Air and Space Museum, Smithsonian Institution. Photo: CCI. (A colour version of Figure 5.4 is available on p. 81.)

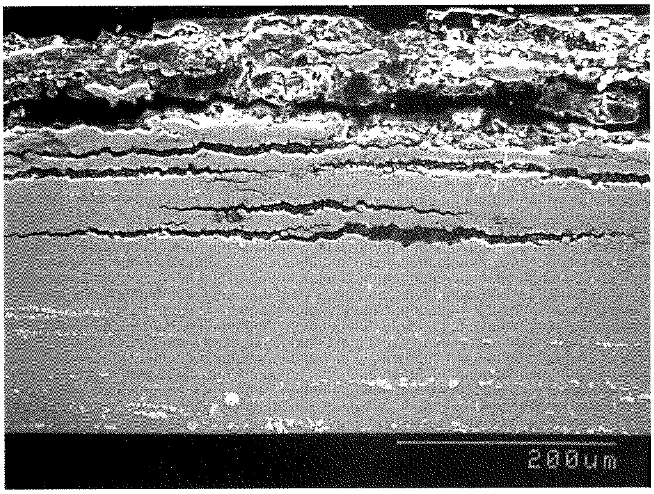

Figure 5.5. A backscatter electron image of a piece of aluminum suffering from exfoliation corrosion. The bright grains in the metal are areas rich in copper, manganese, and iron. The piece of aluminum is from the inside surface of the disconnect section of a Gemini space glove (D1973-0835) belonging to the National Air and Space Museum, Smithsonian Institution. Photo: CCI.

ions, these metal ions may be reduced to solid metal and plate onto the aluminum. Once in contact with the aluminum they provide local corrosion cells that can accelerate aluminum corrosion, usually as pitting. For example, if rain runs over a copper alloy surface and then over an aluminum surface, the aluminum surface will become stained as the dissolved copper ions plate out as copper metal. This will set up a galvanic cell in which the aluminum corrodes preferentially, and eventually pitting will occur in the aluminum as it corrodes. Dissolved copper, cobalt, lead, mercury, nickel, and tin ions can all plate onto aluminum. Mercury has been known to cause severe corrosion on aluminum if present in solution at more than a few parts per billion.

Reference material: Duncan (1988); Ghali (2000); Hollingsworth et al. (1989); Holroyd (2001); Sirois et al. (2002); Staley and Haupin (1992).

STAINING

Staining can occur in stacked sheets of aluminum if water is present in the restricted space between the layers. Because the oxygen concentration of the water becomes reduced near the centre of the sheets, this area becomes anodic and the aluminum corrodes. The resulting stain patterns range in colour from gray to brown to black and are referred to as water staining.

Reference material: Ghali (2000); Hollingsworth et al. (1989); Zahner (1995a).

CHEMICAL CONVERSION COATINGS

Aluminum alloys must be pretreated (e.g. chemical etching, chemical conversion coatings) to remove or alter surface oxides before they are painted. Chemical conversion coatings are created by applying a solution to the aluminum surface that reacts with it to form a well-adhered corrosion layer. This layer increases the corrosion resistance of aluminum and promotes the adhesion of paint to the surface. The solutions are traditionally based on chromates or phosphates, and can be either alkaline or weakly acidic. The resulting corrosion layer contains a complex mixture of compounds (e.g. oxides, chromates, phosphates), and can range in colour from nearly colourless or slightly iridescent to green, yellow, or brown. The first chemical conversion coating for aluminum was an alkaline type developed by Bauer and Vogel in 1915; later alkaline coatings include modified Bauer Vogel, Erftwek, Alrok, and Pylumin. The acid-based processes were not developed until the 1940s; some modern commercially available conversion coatings include Alocrom, Alodine, Bonderite, Chromicoat, Iridite.

Reference material: Adams and Hallam (1993); Burns and Bradley (1967); Duncan (1988).

FILIFORM CORROSION

Filiform corrosion occurs when painted aluminum alloys corrode underneath the paint coating. Corrosion starts at breaks in the coating and proceeds underneath it in relatively straight lines that have a hair-like or filamentary appearance. As water and oxygen diffuse through this channel, further corrosion is supported at the tip in a mechanism that is thought to involve an oxygen concentration cell (the anodic half-reaction (aluminum oxidation) takes place at the tip and the cathodic half-reaction (oxygen reduction) takes place at the back). Residues of chemicals used to pretreat aluminum alloys prior to painting may contribute to filiform corrosion.

Reference material: Ghali (2000);
Leth-Olsen and Nisancioglu (1998);
Ruggeri and Beck (1983); Steele (1994).

CATHODIC CORROSION

"Cathodic corrosion" refers to the corrosion process that is observed on aluminum alloys when they are subject to cathodic polarization, i.e. the aluminum is attached to a power supply such that it becomes the cathode in an electrochemical circuit. It occurs when a cathodic half-reaction results in the corrosion of aluminum (an anodic process). In this case the cathodic half-reaction is the reduction of water to hydroxyl ions and hydrogen gas ($2H_2O + 2e^- \rightarrow 2OH^- + H_2$) that usually takes place at cathodic material (e.g. impurities, intermetallic compounds) in the aluminum alloy surface. This increases the local alkalinity, which in turn dissolves the protective aluminum oxide film on nearby aluminum and allows it to corrode. The process eventually leads to pitting on the aluminum surface.

Reference material: Degrigny (1993, 1995);
Hallam et al. (1997).

6

COPPER (Cu)

Principal oxidation number(s)	Atomic weight (g mol^{-1})	Density at 20°C (g cm^{-3})	Melting point (°C)	Boiling point (°C)	Linear expansivity (°C^{-1})	UNS range for alloys
Cu^{1+} (cuprous) Cu^{2+} (cupric)	63.55	8.96	1085	2562	16.5×10^{-6}	C00001–C99999

GENERAL DESCRIPTION

Pure copper is light red or salmon pink in colour, ductile (can be drawn in wire), and malleable (can be hammered into sheet). It is non-magnetic, has high thermal and electrical conductivity (making it useful for cooking pots and electrical wiring), and can be easily soldered and brazed — although welding is more difficult and requires special equipment. Because it is soft, it is often alloyed with other elements to make it harder, e.g. brass is an alloy of copper and zinc, bronze is an alloy of copper and tin, and nickel silver (German silver) is an alloy of copper, nickel, and zinc.

For more information on copper, see the Web sites for the Canadian Copper and Brass Development Association (www.ccbda.org) and the Copper Development Association (www.copper.org).

Reference material: Gettens and Fitzhugh (1993a, 1993b); Kühn (1993); Scott et al. (2001); Scott (2002).

ORIGIN

Copper is the only common metal found naturally in the metallic state. Copper deposits can be found on most continents around the world (with the possible exception of Antarctica), and it was mined by some of the earliest civilizations. Large deposits of native copper were "discovered" in Michigan by the state geologist in 1841, although Native Americans had been using it since 5000 B.C. The native copper, known as float copper*, had been torn from rock by a glacier which carried the copper along and eventually deposited it elsewhere as the glacier melted. (*It was called float copper because early scientists thought that it floated on or in the glacier.)

In the past, it was relatively easy to reduce copper(I) oxide to copper metal using reducing conditions created with carbon monoxide and a temperature of about 200°C. Today, the important minerals from which copper is obtained are sulphide ores (e.g. bornite, chalcopyrite, covellite, chalcocite). Many countries around the world currently have copper mines, with the largest producers being South America (Chile and Peru) and the United States. In Canada, which is also among the world's leading producers of copper, the bulk of it is mined in British Columbia, Ontario, Quebec, and Manitoba.

Reference material: George (1993); McDonnell (2001).

USE

Copper is one of the earliest metals to be used by humans — the first recorded use being about 8500 B.C. in what is now northern Iraq. Over the years it has found many applications.

Copper minerals have been used as pigments for greens (malachite, neutral verdigris) and blues (azurite, basic verdigris). Copper sheets have been hammered into various shapes (a technique known as repoussé) and used for works of art (e.g. Statue of Liberty in New York City). Copper can also be found as a support material for paintings.

Copper has been used extensively for coins. From 1953 to 1997, Canadian 1-cent coins were made of relatively pure copper (98 wt% copper, 1.75 wt% zinc, 0.25 wt% other metals). From 1997 until 2000, they were made from zinc plated with copper. Today, the coin is made of copper-plated steel. For more information on Canadian coins, see the Web site for the Royal Canadian Mint (www.rcmint.ca).

Copper alloys such as brasses (copper mixed with zinc) and bronzes (copper mixed with tin) can be found in a wide variety of items: brasses in military hardware (e.g. guns, cartridges), utilitarian objects (e.g. bed frames, lamps), and jewelry; and bronzes as casting alloys for statues, bells, etc. White copper–nickel alloys have been used for coins and as substitutes for silver.

Reference material: Baboian et al. (1990); Craddock (1998); Gayle and Look (1992a); Hayden and Despont (1986); Scott (2002); Waite (1992); Weaver (1993); Zahner (1995a).

ROOFING

Sheets of relatively pure copper have been used for roofing and other architectural purposes. The sheets are joined together with special seams (e.g. batten, standing, flat) designed to accommodate copper's high coefficient of linear thermal expansion and prevent buckling and tearing. More information on copper roofing can be found on the Web site for the Copper Development Association (www.copper.org).

Reference material: Ashurst and Ashurst (1988); Gayle and Look (1992a); Waite (1992); Weaver (1993); Zahner (1995a).

MIRRORS

Mirrors made with silvery-white "speculum metal" (high-tin bronzes) were first used by the Romans and ancient Chinese. This practice continued among many cultures until about 1300, when better tin amalgam mirrors became available. (For more information on tin amalgam mirrors, see "Chapter 12. Tin.") In the mid 1500s, high-tin copper alloys were again used as mirrors in the ongoing search for reflecting metal surfaces. In 1671, Sir Isaac Newton used a high-tin bronze to make mirrors for the earliest reflecting telescopes.

Reference material: Habashi (1998).

POLYCHROME DESIGNS

A number of early cultures used a combination of contrasting precious metals inlaid into a background metal surface to create elaborate polychrome designs or pictures. The Japanese, for example, used contrasting precious metals to decorate tsubas (hand guards mounted on Japanese swords). The background metal surface could be either patinated or brightly polished. These cultures discovered that certain copper alloys, usually those containing gold (called shakudo in Japan), silver (called shibuichi in Japan), or arsenic, were useful for backgrounds because they could be patinated to a deep black colour that could be polished to a high shine. This lustrous black finish contrasted well with the other coloured precious metals used in the design.

Reference material: Craddock and Giumlia-Mair (1993); La Niece (1991); Murakami (1993).

ALLOYS AND PLATING

Copper can be alloyed with other elements to provide materials with a broad range of mechanical, physical, and chemical properties. One of the earliest alloys was created by adding 2 wt% arsenic to copper. Known as arsenical copper (also called arsenical bronze), this alloy melted more easily, was harder, and could be more soundly cast than pure copper. In general, the addition of alloying elements to copper increases its strength, decreases its electrical conductivity, and changes its colour (from the typical pink of pure copper to various shades of yellow until, at high enough levels of zinc or tin, the alloys become white).

The ternary diagram in Figure 6.1 is provided here to help illustrate the traditional copper alloy names and the general relationship between name and overall composition. For more details about interpreting such ternary diagrams, see "Chapter 7. Gold."

There are no hard and fast divisions between the different copper alloys. However, in general:

- brass describes copper alloys that contain zinc as the principal alloying element
- bronze describes copper alloys in which the major alloying element is not zinc or nickel (although in ancient times, the term "bronze" described copper alloys with tin as the principal alloying element)
- gunmetal describes copper alloys that contain both zinc and tin

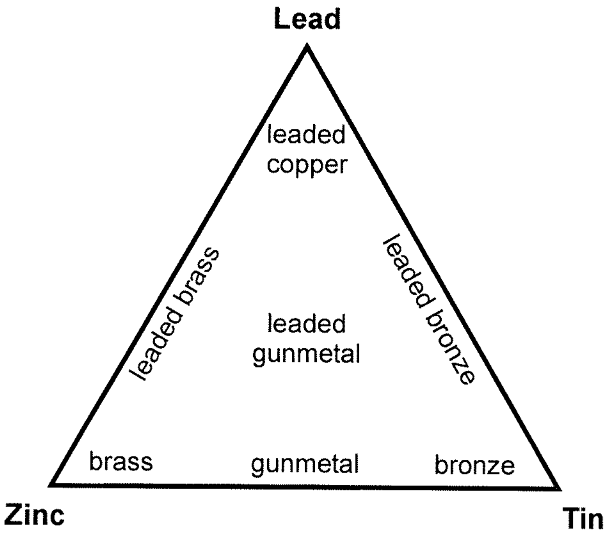

Figure 6.1. Schematic triangular diagram for copper alloyed with lead, zinc, and/or tin illustrating the names of traditional copper alloys and the general relationship between name and overall composition. Adapted from Bayley (1998).

Some brass, bronze, and gunmetal alloys may also contain lead (i.e. be "leaded"), the addition of which improves their machineability. However, due to increasing concern about lead toxicity, modern alloys are more likely to contain alloying elements such as bismuth for this purpose. Because the solubility of lead in copper alloys is negligibly small, when lead is present in copper alloys it normally appears as separate microscopic globules.

Modern copper and copper alloys are classified in a systematic way in the Unified Numbering System (UNS) for metals and alloys. Wrought alloys are numbered C10000–C79999 and cast materials are C80000–C99999. Unfortunately, sometimes the modern trade names do not reflect the traditional uses of the terms bronze and brass, and can lead to confusion. For example, the modern trade name for UNS alloy C22000 is "commercial bronze" but it contains 90 wt% copper and 10 wt% zinc and falls under the category of wrought brass. The term gunmetal is also used as a modern commercial trade name for the casting alloy C90500 that contains about 88 wt% copper, 10 wt% tin, and 2 wt% zinc.

Reference material: Bayley (1998); Copper Development Association (2001); Gayle and Look (1992a); Lambert (1997).

COPPER METAL

The UNS numbers for modern wrought and cast copper are listed in Tables 6.1 and 6.2.

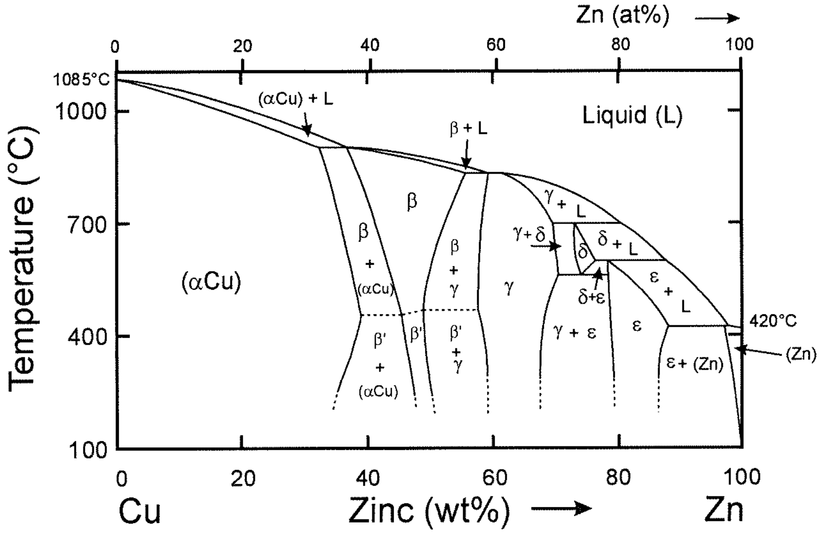

Figure 6.2. Equilibrium phase diagram for copper and zinc. The bottom scale is weight percent and the top scale is atomic percent. Adapted from ASM International (1992).

TABLE 6.1. WROUGHT COPPER ALLOYS

Wrought copper alloys	Alloying elements	UNS numbers
coppers	≥99.3 wt% copper	C10100–C15815
high-copper alloys	>96 wt% copper	C16200–C19900

TABLE 6.2. CAST COPPER ALLOYS

Cast copper alloys	Alloying elements	UNS numbers
coppers	≥99.3 wt% copper	C80100–C81200
high-copper alloys	>94 wt% copper	C81400–C82800

Relatively pure copper is obtained using modern electrolytic reduction techniques. The electrodeposited copper recovered from reduction is called electrolytic tough pitch copper (ETP) and it ranges in purity from 99.94 to 99.96 wt%. The electrical industry uses high-purity copper because of its high electrical conductivity.

Reference material: Breedis and Caron (1993); Copper Development Association (2001); George (1993).

BRASS (COPPER–ZINC AND RELATED ALLOYS)

Alloys made of copper and zinc have traditionally been described as brasses. They range in colour from a red similar to pure copper through a pleasing yellow to white (above about 45 wt% zinc). The ancient Romans prepared brass by the calamine process and used it for coinage and ornamental trimmings. Crushed zinc ore was mixed with powdered charcoal and grains of copper and then heated in a covered crucible to about 1000°C. The zinc vapour that was created diffused into the heated copper and formed brass. This process was used into the 19th century when it was replaced by the melting together of zinc and copper metals.

Reference material: Barclay (1992, 1993); Day (1991); Dutrizac and O'Reilly (1984).

Copper–zinc phase diagram: The phase diagram for copper and zinc is shown in Figure 6.2, and the phases relevant to brasses are in the region with the lower zinc content. Modern brasses are copper alloys that contain between 5 and 40 wt% zinc, and involve the α and β phases.

The α brasses are single-phase copper–zinc alloys that contain up to about 38 wt% zinc (labelled αCu in the phase diagram). They have generally good workability, although those with high zinc concentrations are easily work-hardened and must be annealed frequently during working to keep them soft. As the zinc content of α brasses increases, the colour of the alloy gradually changes from red to yellow. The yellowest brasses are the single-phase α brasses with the highest amount of zinc.

As the zinc content increases above 38 wt%, copper–zinc alloys become a mixture of both α and β phases. They remain a mixture of two phases until the zinc content reaches about 45 wt%, at which time they again become single-phase (in this case β phase). The β phase is white in colour and copper–zinc alloys containing mainly this phase are referred to as "white brass." Because the β phase is brittle, alloys containing this phase are extremely difficult to work.

Reference material: ASM International (1992); Zahner (1995b).

Wrought brasses: In the Unified Numbering System, the wrought brasses have been grouped into different categories, as listed in Table 6.3.

TABLE 6.3. WROUGHT BRASSES

Wrought brasses	UNS family names	UNS numbers
brasses	copper–zinc alloys	C21000–C28000
leaded brasses	copper–zinc–lead alloys	C31200–C38500
tin brasses	copper–zinc–tin alloys	C40400–C48600

Several common wrought brasses are listed in Table 6.4.

TABLE 6.4. COMMON WROUGHT BRASSES

Common or trade name for wrought brasses	Copper content (wt%)	Zinc content (wt%)	UNS number
gilding brass	95	5	C21000
commercial bronze	90	10	C22000
jewelry bronze	87.5	12.5	C22600
red brass	85	15	C23000
cartridge brass	70	30	C26000
yellow brass	65	35	C27000
Muntz metal	60	40	C28000

Copper–zinc alloys containing small amounts of zinc (typically less than 9 wt%) were called gilding brass because they were often used as a base metal for gilding with gold leaf or by electroplating. A modern example is C21000 (95 wt% copper, 5 wt% zinc), which is a single-phase α brass with a colour similar to the red of pure copper.

Copper–zinc alloys with about 15 wt% zinc are similar in colour to gold, e.g. the modern alloy C22600 (87.5 wt% copper, 12.5 wt% zinc) resembles 14 kt gold. Gold-coloured brasses became popular as cheap gold substitutes in Europe in the 18th century when metallic zinc became more readily available and the alloy content could be more easily controlled. These alloys were used for imitation gold jewelry, snuff boxes, watches, and buttons. The most famous was called Pinchbeck, invented in 1725 by watchmaker C. Pinchbeck. Other names for gold-coloured brasses in the 18th century included Tombac, Prince Rupert's Metal, Prince's Metal, Mannheim Gold, Bath Metal, and Similor. In 1942 and 1943, Canada issued 5-cent coins made of 88 wt% copper and 12 wt% zinc, an alloy referred to as tombac.

Several common names used to describe modern copper–zinc alloys are listed below.

- Cartridge brass (C26000, 70 wt% copper, 30 wt% zinc) is one of the best known and most used of the modern brasses. It is yellow in colour and has traditionally been used in the munitions industry for making shell cartridges. It is easy to polish, plate, and patinate. The relatively high zinc content of this alloy makes it sensitive to dezincification (i.e. corrosion resulting in loss of zinc).

- Yellow brass (e.g. C27000, 65 wt% copper, 35 wt% zinc) contains close to the maximum amount of zinc that can be added to copper while still maintaining a single-phase (α) alloy. Care must be taken during processing of this alloy to avoid the formation of the β phase.

- Muntz metal (C28000, 60 wt% copper, 40 wt% zinc, also known as 60-40 brass) is named after G.F. Muntz who promoted the use of this alloy for the lining of ships' hulls in the 1830s. It is a two-phase alloy with a golden yellow colour. Muntz metal and similar alloys that contain between 35 and 45 wt% zinc are usually two-phase (α + β) alloys, the number of phases depending on their heat treatment.

Leaded brasses are copper–zinc alloys that contain a small amount (a few wt%) of lead. The use of leaded brasses increased in the mid 19th century when it became apparent that these alloys were easier to machine than common brasses.

Tin brasses are copper–zinc alloys (typically containing greater than 15 wt% zinc) to which about 1 wt% tin is added. These tin brasses are significantly more resistant to dezincification (i.e. loss of zinc) than the same alloys without tin. Two specific tin brasses were popular for use in seawater until World War II (when better alloys were developed): Admiralty metal (or Admiralty brass), made by adding 1 wt% tin to cartridge brass (70 wt% copper, 30 wt% zinc); and naval brass, made by adding 1 wt% tin to Muntz metal (60 wt% copper, 40 wt% zinc). Today, the corrosion resistance of tin brasses can be increased even more by adding small amounts (typically 0.05–0.1 wt%) of arsenic, antimony, or phosphorus (e.g. C44300, C44400, C44500).

Reference material: Breedis and Caron (1993); Child (1988); Copper Development Association (2001); Sequeira (2000); Temple (1985); Thornton (2000); Zahner (1995b).

Cast brasses: The range of modern cast brasses is listed in Table 6.5.

One of the most popular modern cast brasses is C83600 (85 wt% copper, 5 wt% tin, 5 wt% zinc, 5 wt% lead), also known as 85-5-5-5 alloy, 85-3-5 metal, three-fives metal, red bronze, compositional bronze, and ounce metal. This alloy was used to cast a set of some 50 copies of *The Hiker* (a statue sculpted by T.A.R. Kitson), which are now located throughout the United States. Another popular cast brass for sculptures is C87300 (95 wt% copper, 4 wt% silicon, 1 wt% manganese).

TABLE 6.5. CAST BRASSES

Cast brasses	UNS family names	UNS numbers
red and leaded red brasses	copper–tin–zinc and copper–tin–zinc–lead alloys	C83300–C83810
semi-red and leaded semi-red brasses	copper–tin–zinc and copper–tin–zinc–lead alloys	C84200–C84800
yellow and leaded yellow brasses	copper–zinc and copper–zinc–lead alloys	C85200–C85800
high-strength and leaded high-strength yellow brasses	manganese bronze and leaded manganese bronze alloys	C86100–C86800
silicon bronzes and silicon brasses	copper–silicon alloys	C87300–C87900

Reference material: Breedis and Caron (1993); Copper Development Association (2001); Meakin et al. (1992); Zahner (1995b).

BRONZE (COPPER–TIN AND RELATED ALLOYS)

Alloys containing copper and tin are known as bronzes, and have been around since at least 3500 B.C. Copper–tin alloys with a low tin content (<10 wt% tin) are reddish, those with 10–20 wt% tin are more orange-yellow, and those with >20 wt% tin are usually white. Copper–tin alloys used in antiquities are generally classified as either low-tin bronze (up to about 14 wt% tin) or high-tin bronze (about 19–27 wt% tin). As mentioned earlier, the modern use of the term bronze is for copper alloys with elements other than zinc or nickel.

Reference material: Dutrizac and Reilly (1984); Meeks (1993b); Zahner (1995b).

Copper–tin phase diagram: The phase diagram for copper and tin is shown in Figure 6.3. Copper–tin alloys containing up to about 14 wt% tin are usually a single phase (the copper-rich α phase indicated as αCu in the phase diagram), and they can be shaped by hammering. The low-tin bronzes of antiquity are typically single-phase alloys.

When copper–tin alloys containing more than about 14 wt% tin are cooled, they usually contain two phases — a copper-rich α phase and a silvery-white δ phase (a hard intermetallic compound with composition $Cu_{31}Sn_8$). (In practice, copper–tin alloys cool relatively quickly and do not normally form the equilibrium room temperature phases (i.e. α and ε) predicted in the diagram.) Copper–tin alloys that contain more than about 14 wt% tin are brittle, hard, and have a bright, highly reflective silver colour when polished.

When copper alloys are tinned by hot-dipping in molten tin, the copper surface reacts with the tin to form two hard, white-coloured intermetallic compounds. A layer of the ε phase (Cu_3Sn) forms next to the copper surface, and an outer layer of the η phase (Cu_6Sn_5) forms over the ε phase.

Reference material: ASM International (1992); Meeks (1986, 1993a, 1993b).

Wrought bronzes: The UNS numbers for a variety of wrought bronzes are listed in Table 6.6.

Modern wrought bronzes of commercial importance are single-phase (α phase) alloys containing 1–10 wt% tin.

Brazing alloys consist of copper alloyed mainly with either silver and phosphorus, or just phosphorus. Brazing is, by definition, the joining of two metals at an elevated temperature (above about 450°C). (When conducted at lower temperatures, this process is called soldering.) A brazed join is generally stronger and more stable than a soldered join. Copper and its alloys are readily brazed, usually with copper-based brazing alloys. As with soldering, brazing is done at a temperature above the melting point of the brazing (filler) alloy and below that of the alloy being joined. The filler or brazing metal is placed in or near the joining surfaces in the form of a strip, wire, or powder. When heat is applied the filler melts, fills the gap (by capillary action), and forms a metallurgical bond between the joining surfaces. The surfaces must be cleaned prior to brazing, and during brazing a flux is needed to prevent oxidation.

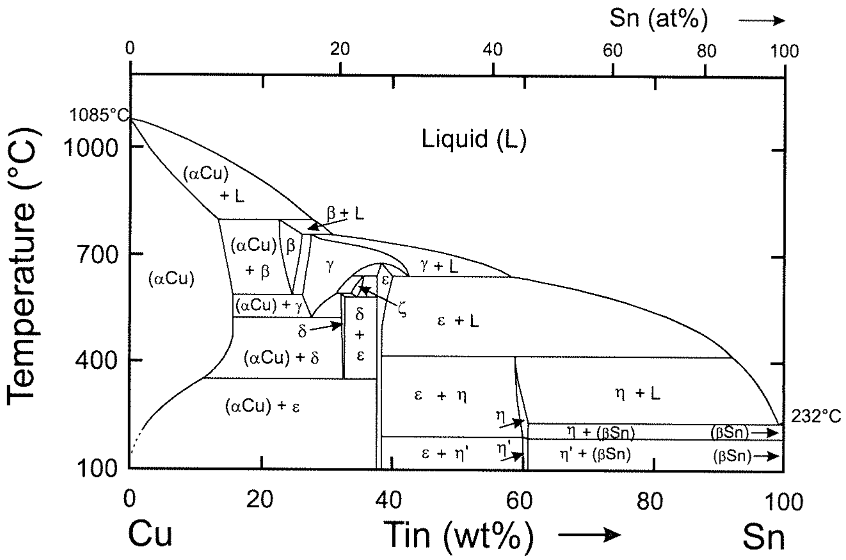

Figure 6.3. Equilibrium phase diagram for copper and tin. The bottom scale is weight percent and the top scale is atomic percent. The ε phase contains the intermetallic compound Cu_3Sn, the δ phase contains $Cu_{31}Sn_8$, and the η phase contains Cu_6Sn_5. Adapted from ASM International (1992).

Aluminum bronzes are copper alloyed with 2–15 wt% aluminum. They have good corrosion resistance due to the formation of an adherent aluminum oxide film that protects the surface from further oxidation. The presence of this film makes these alloys more corrosion-resistant than other copper alloys in seawater. The aluminum bronze alloy C61550 is similar to gold in colour. The Canadian 2-dollar coin, introduced in 1996, contains an inner core of aluminum bronze (92 wt% copper, 6 wt% aluminum, 2 wt% nickel) and an outer ring of nickel.

Silicon bronzes are made of copper alloyed with up to 4 wt% silicon. These alloys have high strength and can be used outdoors for architectural purposes. Sheets and plates of alloy C65500, for example, are particularly popular because they can be cold-worked without becoming brittle.

Reference material: Breedis and Caron (1993); Copper Development Association (2001); Sequeira (2000); Zahner (1995b).

Cast bronzes: The UNS numbers for a variety of modern cast bronzes are listed in Table 6.7.

TABLE 6.6. WROUGHT BRONZES

Wrought bronzes	UNS family names	UNS numbers
phosphor bronzes	copper–tin–phosphorus alloys	C50100–C52480
leaded phosphor bronzes	copper–tin–lead–phosphorus alloys	C53400–C55284
brazing alloys	copper–phosphorus and copper–silver–phosphorus alloys	C55180–C55284
—	copper–silver–zinc alloys	C56000
aluminum bronzes	copper–aluminum alloys	C60800–C64210
silicon bronzes	copper–silicon alloys	C64700–C66100
—	other copper–zinc alloys	C66200–C69710

Modern cast bronzes are used for casting statuary (e.g. C93200, 83 wt% copper, 7 wt% tin, 7 wt% lead, 3 wt% zinc) and for bearings (e.g. C93700, 80 wt% copper, 10 wt% tin, 10 wt% lead).

Copper alloys that contain tin and zinc are often referred to as gunmetal (such alloys were traditionally used as yellow casting metal for cannons, hence the name). Admiralty gunmetal was a standard alloy for pumps

TABLE 6.7. CAST BRONZES

Cast bronzes	UNS family names	UNS numbers
tin bronzes	copper–tin alloys	C90200–C91700
leaded tin bronzes	copper–tin–lead alloys	C92200–C92900
high-leaded tin bronzes	copper–tin–lead alloys	C93100–C94500
tin–nickel bronzes	copper–tin–nickel alloys	C94700–C94900
aluminum bronzes	copper–aluminum–iron and copper–aluminum–iron–nickel alloys	C95200–C95900

and valve parts in marine use, and it is still available as a modern gunmetal alloy (e.g. C90500, 88 wt% copper, 10 wt% tin, 2 wt% zinc). Around 1920, when tin became expensive, zinc and lead became widely used as substitutes. This led to the popular casting alloy C83600 (85 wt% copper, 5 wt% tin, 5 wt% zinc, 5 wt% lead), known as "three-fives" alloy.

Bell metals are tin-rich copper alloys (containing 15–25 wt% tin) that are used to cast bells, the first of which appeared in European churches in the 8th century. The quality of the sound of such bells is affected by the tin content of the alloy, with 25 wt% tin considered optimum. During casting, the formation of tin oxides is minimized (to avoid disagreeable sounds) by adding phosphorus or some other deoxidizer. One of the most famous examples of a "bell metal" bell is the huge (13 760 kg) bell of Westminster in London (known as "Big Ben") which was cast at the Whitechapel Bell Foundry in 1858. For more information on this bell, see the Web site for the Whitechapel Bell Foundry (www.whitechapelbellfoundry.co.uk).

Silvery-white copper alloys that contain a high concentration of tin are referred to as "speculum metal." The high-tin bronzes of antiquity contained 19–27 wt% tin and often lead as well. The Romans and ancient Chinese used them to make highly polished mirrors (although the Romans also made mirrors of copper alloyed with low concentrations of tin that were finished by surface tinning).

Reference material: Breedis and Caron (1993); Copper Development Association (2001); Day (1991); Habashi (1998); Meeks (1993b); Sequeira (2000); Temple (1985); Twarog (1993).

COPPER–NICKEL ALLOYS

Copper and nickel are completely soluble in one another, so copper–nickel alloys are single phase across the entire composition range (the copper–nickel phase diagram is provided in Figure 10.1 on p. 126). These alloys, also called cupronickels, are noted for their resistance to tarnishing and corrosion. When the nickel content is more than 12 wt%, they are white.

Modern alloys: Commercial copper–nickel alloys contain 5–20 wt% nickel. The UNS numbers for modern wrought and cast copper–nickel alloys are listed in Tables 6.8 and 6.9.

TABLE 6.8. WROUGHT COPPER–NICKELS

Wrought copper–nickels	UNS family names	UNS numbers
copper–nickels	copper–nickel alloys	C70100–C72950
nickel silvers	copper–nickel–zinc alloys	C73500–C79830

TABLE 6.9. CAST COPPER–NICKELS

Cast copper–nickels	UNS family names	UNS numbers
copper–nickels	copper–nickel–iron alloys	C96200–C96950
nickel silvers	copper–nickel–zinc alloys	C97300–C97800

The modern copper–nickel alloys with the best corrosion resistance under immersion conditions are C70600 (90 wt% copper, 10 wt% nickel) and C71500 (70 wt% copper, 30 wt% nickel). Corrosion resistance can be improved by adding small amounts of iron and manganese.

Reference material: Breedis and Caron (1993); Copper Development Association (2001).

Coins: The alloy C71300 (75 wt% copper, 25 wt% nickel) has very good tarnish resistance and is used extensively for coinage. In Canada, for example, the 5-cent coin was made from this white copper–nickel alloy between 1982 and 2000.

Reference material: Breedis and Caron (1993).

Nickel silvers: Nickel silvers are copper-rich alloys that contain nickel and zinc, and are usually white in colour. The name nickel silver is misleading (because these alloys contain no silver and at most 30 wt% nickel), but resulted from the silvery-white colour of the alloy, its ability to take a high polish, and early trade names such as "German silver."

Modern nickel silvers contain copper alloyed with 4–25 wt% nickel and 3–30 wt% zinc (for the alloy to be silvery-white, the nickel content must be at least 20 wt% and the zinc content moderate). Two examples of common modern nickel silvers are C75200 (65 wt% copper, 17 wt% zinc, 18 wt% nickel) and C77000 (55 wt% copper, 27 wt% zinc, 18 wt% nickel). The high nickel content in these alloys makes them resistant to dezincification (i.e. loss of zinc), and the high nickel and zinc contents give them good resistance to corrosion.

The precursors of modern nickel silvers were the silvery-white alloys (known as "paktong") used by the ancient Chinese. By the mid 1820s, Germany began producing alloys that resembled the Chinese paktong, names for which included "neusilber" (new silver) and "argentan." When neusilber was exported to Sheffield, England, in 1830, it became known as German silver — a name that was used until after World War I, when it was replaced with the generic term nickel silver. The use of nickel silver for architectural decorative and structural elements in the Art Deco style became popular during the early 1900s. Nickel silver continued to be used in architectural design elements until the mid 1950s, when stainless steel and aluminum became a lower cost alternative for nickel silver and other white metals.

Nickel silvers can also be found in ornamental objects as an underlying base metal that is electroplated with silver or nickel. Silver-plated nickel silvers were very popular in the Art Deco period, and chrome plating (i.e. chromium plating) became common in the 1920s. Such items were typically marked with EPNS (to indicate electroplated nickel silver) or CPNS (to indicate chrome-plated nickel silver).

Reference material: Breedis and Caron (1993); Child (1993); Cowden (1995); Gayle and Look (1992b); Sequeira (2000); Temple (1985); Tundermann et al. (1996); Zahner (1995b).

COPPER–GOLD AND COPPER–SILVER ALLOYS

"Shakudo" is the Japanese name for copper–gold alloys that can be patinated to a rich purple-black colour. These copper–gold alloys typically contain 4–5 wt% gold, although the concentration can be as low as 1 wt%. The unpatinated alloys resemble pure copper in colour. Before patination, the alloy is polished to a mirror finish with abrasives followed by careful degreasing. The black patina is created by boiling the alloy in an aqueous solution of copper sulphate, copper acetate (copper ethanoate), and possibly other compounds. After boiling for about 30 minutes, the copper–gold alloy turns a rich purple-black colour. The same treatment applied to pure copper turns it reddish-brown. Analysis of the black patina has identified cuprite filled with fine particles of metallic gold. Similar black patinated surfaces on copper–gold alloys have been identified in China, Egypt, and other early cultures. In addition to gold, these alloys may contain small amounts of silver and arsenic.

"Shibuichi" is the Japanese name for copper–silver alloys that can be patinated by boiling in the same chemical process as shakudo. The copper–silver alloys typically contain about 25 wt% silver, although the concentration can vary from 10 to 50 wt%. The colour of patinated shibuichi changes from brownish-gray to whitish-gray with increasing silver content.

Reference material: Craddock and Giumlia-Mair (1993); La Niece (1991); Murakami (1993); Notis (1988); Scott (2002); Wayman and Craddock (1993).

GOLD-PLATED COPPER ALLOYS

There are several ways to gild a copper alloy. One method is to apply a gold amalgam (fire gilding); the best-known examples of fire-gilded copper sculptures are the four gilded horses from the Basilica of St. Mark in Venice. Gold can also be added as gold leaf, applied either by burnishing as was done to gild the statue of Marcus Aurelius in Rome, or by glueing as was done to regild the flame on the Statue of Liberty in New York City. For more information about various gilding methods, see "Chapter 7. Gold."

Reference material: Alunno-Rossetti and Marabelli (1976); Gohard (1990); Selwyn (2000); Vaccaro (1992).

SILVER-PLATED COPPER ALLOYS

There are also many methods to apply a layer of silver to copper alloys. Silver plating first became popular in the 1800s with the development of close plating, Sheffield plating, and electroplating — which provided an economical way to produce a thin silver deposit on many different metals. Copper objects that have been electroplated with silver are usually stamped with EP copper (electroplated copper). Methods for silver plating are discussed in detail in "Chapter 11. Silver."

Reference material: Birnie (1993); La Niece (1990, 1993).

TIN-PLATED COPPER ALLOYS

In ancient times, copper alloy cooking vessels were often tinned to prevent the tainting of food. Traditionally, only copper, low-tin bronzes, and some brasses were tinned (high-tin bronzes were not normally tinned because they were naturally silvery when polished). The tinning created a silver-coloured, durable, and corrosion-resistant surface that could take a good polish. The deliberate application of a layer of tin was usually done by wiping, hot-dipping, or mercury amalgam tinning. The modern method of tinning is electroplating. For more information on these plating methods, see "Chapter 12. Tin."

Reference material: Meeks (1986, 1993a, 1993b).

Tin sweat: This term refers to the silver-coloured layer of tin-rich material that is sometimes observed on the surface of cast copper–tin alloys containing up to about 14 wt% tin (i.e. low-tin bronzes). Similar in appearance to deliberate tinning, it forms during the cooling of cast copper–tin alloys and contains a mixture of the copper-rich α phase and the white intermetallic δ phase. The copper-rich α phase solidifies first, enriching the tin content of the remaining molten alloy. Tin sweat forms as the last remaining molten alloy is squeezed from the core of the cooling metal onto its surface, especially if a gap has formed between the mould and the casting metal as the cooling metal shrinks. Shrinkage can also cause internal pressure which forces molten material to the surface. The last remaining liquid contains about 25.5 wt% tin and solidifies with a white colour.

If the casting alloy also contains lead, globules of lead may be squeezed onto the surface (i.e. lead sweat) by the same process as tin sweat.

Reference material: Oddy and Bimson (1985); Meeks (1986, 1993a, 1993b).

LEAD-COATED AND TERNE-COATED COPPER

Copper can be coated with lead–tin alloys either by hot-dipping the copper in the molten alloy or by electroplating. Lead-coated copper refers to copper that has been coated with a lead–tin alloy containing about 4 wt% tin, and terne-coated copper is copper that has been coated with a lead–tin alloy (terne) containing more than 5 wt% tin (typically 15–20 wt%), the finish of which is a dull gray. The lead–tin alloy coating slows the corrosion rate of the copper and helps minimize copper staining of associated materials (e.g. stone). Terne-coated copper was recently identified on the roof of the Library of Parliament in Ottawa. For more information on terne-coated copper, see "Chapter 9. Lead."

Reference material: Cser et al. (2000); Gayle and Look (1992c).

COPPER-PLATED ZINC

Zinc was a popular metal for creating cast sculptures between about 1850 and 1920. Inexpensive compared to bronze, it was usually finished to imitate other more expensive materials. For example, zinc sculptures could be plated with copper and then artificially patinated with chemicals to resemble bronze sculptures. However, these did not survive well outdoors because of galvanic corrosion problems. For more information on zinc sculptures, see "Chapter 13. Zinc."

Reference material: Grissom (1994).

COPPER-PLATED IRON

Early techniques for applying copper to iron included mechanical attachment of foils and dipping in molten copper alloys (e.g. hot-dipping). However, modern methods are more likely to involve electroplating techniques that make it possible to plate two or more metals simultaneously. For example, copper–tin and copper–zinc alloys can now be electroplated onto iron using an electrolyte containing copper along with tin or zinc salts.

Reference material: Child (1993); Corfield (1993).

ELECTROFORMING (ELECTROTYPING)

The development of electroplating techniques in the 1840s made it relatively easy to create reproductions of objects. These reproductions are called electroforms or electrotypes, and copper is one of the metals commonly used to make them. For more information on electroforming, see "Chapter 1. Metals."

Reference material: Child (1993); Larsen (1984).

CORROSION

Most copper(I) compounds and complexes are almost colourless, with the exception of the coloured cuprite (which is red) and chalcocite (which is black). Most copper(II) compounds and complexes are coloured, usually in various shades of green or blue. Many of the copper minerals and corrosion products discussed in this chapter are listed in Table 6.10.

TABLE 6.10. COPPER MINERALS AND CORROSION PRODUCTS

Chemical name	Mineral name	Chemical formula	Colour
copper(I) oxide	cuprite	Cu_2O	red
copper(II) oxide	tenorite	CuO	black
copper(II) hydroxide	spertiniite	$Cu(OH)_2$	blue
copper(II) carbonate hydroxide[1]	malachite	$Cu_2CO_3(OH)_2$	green
copper(II) carbonate hydroxide	georgeite	$Cu_2CO_3(OH)_2$	blue
copper(II) carbonate hydroxide	azurite	$Cu_3(CO_3)_2(OH)_2$	blue
copper(II) sodium carbonate trihydrate	chalconatronite	$CuNa_2(CO_3)_2 \cdot 3H_2O$	blue
sodium carbonate decahydrate	natron	$Na_2CO_3 \cdot 10H_2O$	white
copper(II) sodium acetate carbonate	—	$\sim CuNa(CH_3CO_2)(CO_3)$	pale blue
sodium acetate trihydrate	—	$Na(CH_3CO_2) \cdot 3H_2O$	white
copper(II) acetate monohydrate[2]	—	$Cu(CH_3CO_2)_2 \cdot H_2O$	green
copper(II) acetate hydroxide pentahydrate[3]	—	$Cu_3(CH_3CO_2)_4(OH)_2 \cdot 5H_2O$	blue
copper(I) chloride	nantokite	$CuCl$	pale gray
copper(II) chloride dihydrate	eriochalcite	$CuCl_2 \cdot 2H_2O$	blue-green
copper(II) chloride hydroxide[4]	atacamite	$Cu_2Cl(OH)_3$	green
copper(II) chloride hydroxide	clinoatacamite	$Cu_2Cl(OH)_3$	green
copper(II) chloride hydroxide	paratacamite	$Cu_2Cl(OH)_3$	green
copper(II) chloride hydroxide	botallackite	$Cu_2Cl(OH)_3$	green
copper(I) sulphide	chalcocite	Cu_2S	black
copper iron(II) sulphide	chalcopyrite	$CuFeS_2$	yellow
iron(II) sulphide	pyrite	FeS_2	yellow
copper iron(II) sulphide	bornite	Cu_5FeS_4	red-brown
copper(I,II) sulphide	geerite	$Cu_{1.6}S$	black
copper(I,II) sulphide	digenite	$Cu_{1.8}S$	blue-black
copper(I,II) sulphide	djurleite	$Cu_{1.96}S$	black
copper(I,II) sulphide	covellite	CuS	dark blue
copper(II) sulphate pentahydrate	chalcanthite	$CuSO_4 \cdot 5H_2O$	blue
copper(II) hydroxide sulphate[5]	brochantite	$Cu_4(OH)_6SO_4$	green
copper(II) hydroxide sulphate	antlerite	$Cu_3(OH)_4SO_4$	green
copper(II) hydroxide sulphate monohydrate	posnjakite	$Cu_4(OH)_6SO_4 \cdot H_2O$	light blue
copper(II) iron(III) hydroxide sulphate tetrahydrate	guildite	$CuFe(OH)(SO_4)_2 \cdot 4H_2O$	yellow-brown
calcium copper(II) sodium chloride phosphate pentahydrate	sampleite	$CaCu_5NaCl(PO_4)_4 \cdot 5H_2O$	blue-green
copper(II) hydroxide phosphate	libethenite	$Cu_2(OH)(PO_4)$	green
copper(II) chloride hydroxide sulphate trihydrate	connellite	$Cu_{19}Cl_4(OH)_{32}(SO_4) \cdot 3H_2O$	blue
copper(II) hydroxide nitrate[6]	gerhardtite	$Cu_2NO_3(OH)_3$	green

1. Copper carbonate hydroxides are also called basic copper carbonates.
2. Copper acetate monohydrate is also known as neutral verdigris.
3. Copper acetate hydroxide pentahydrate is also known as basic verdigris.
4. There are several polymorphs of copper chloride hydroxide. Polymorphs are compounds with the same chemical formula, but with different crystal structures. Three examples of these polymorphs are clinoatacamite (monoclinic), atacamite (orthorhombic), and paratacamite (rhombohedral). Recent work by Jambor et al. (1996) has shown that the X-ray diffraction reference pattern PDF 25-1427 corresponds to a monoclinic crystal structure, newly named clinoatacamite. The pattern had been incorrectly assigned to paratacamite which has a rhombohedral crystal structure. They also point out that for rhombohedral paratacamite to be stable, a small amount of zinc or nickel must replace some of the copper. Previous reports of paratacamite on copper alloys, with identification based on matching an experimental X-ray diffraction pattern to PDF 25-1427, should probably be assigned to clinoatacamite. Further work may be needed to distinguish between clinoatacamite and paratacamite, especially if zinc is present in the copper alloy. Copper chloride hydroxides are also called basic copper chlorides.
5. Copper hydroxide sulphates are also called basic copper sulphates.
6. Copper hydroxide nitrates are also called basic copper nitrates.

Reference material: Jambor et al. (1996); Massey (1973); Richardson (1993); Scott (2000a, 2002).

SOLUTION CHEMISTRY

The principal oxidation states of copper are +1 (Cu^+) and +2 (Cu^{2+}). The initial anodic and cathodic half-reactions are usually given by:

Anodic half-reaction: $Cu(s) \rightarrow Cu^+ + e^-$
Cathodic half-reaction: $^1/_4O_2(g) + {}^1/_2H_2O + e^- \rightarrow OH^-$
Net reaction: $Cu(s) + {}^1/_4O_2(g) + {}^1/_2H_2O \rightarrow Cu^+ + OH^-$

The pH of the solution and assorted other factors determine which copper(I) compounds form. When the pH of the water is above about 5, solid cuprite can precipitate from solution. When the pH is low (acidic conditions), the oxygen content is low, and chloride ions are present, nantokite can precipitate. Two copper(I) ions (Cu^+) can also react with one another in a process known as "disproportionation" (one ion is reduced to copper metal and the other ion is oxidized to a copper(II) ion (Cu^{2+})), as given by:

$$2Cu^+ \rightarrow Cu(s) + Cu^{2+}$$

This disproportionation reaction can be prevented if the Cu(I) oxidation state is stabilized with a complexing agent. For example, the copper(I) ions form soluble complex ions with chloride ions, ammonia, cyanide ions, and acetonitrile (ethanenitrile).

Copper(II) ions are stable in aqueous solutions. Solutions containing these ions tend to be acidic because the ions hydrolyse in water as follows:

$$Cu^{2+} + H_2O \rightarrow CuOH^+ + H^+$$

When the pH of a solution containing copper(II) ions is increased above 4, the ions precipitate as tenorite or spertiniite. The copper(II) ions also form soluble complex ions in aqueous solutions with ammonia (the most stable ones), carbonates, hydroxides, chlorides, and tartrates.

The precipitation of copper(II) salts is usually determined by the relative concentrations of dissolved species making up the local water chemistry: copper hydroxide sulphates precipitate when the level of sulphate ions is high, copper chloride hydroxides when the level of chloride ions is high, and copper carbonate hydroxides when the level of carbonate ions is high. These copper(II) salts have low solubility in neutral solutions, but their solubility increases with increasing solution acidity. If the local chemistry changes, it is possible for these copper(II) salts to convert from one phase to another by a process of partial or complete dissolution of the original phase followed by precipitation of a new phase.

Reference material: MacLeod (1987a); Richardson (1993); Woods and Garrels (1986a, 1986b).

PATINATION

Almost all bronze statuary is patinated, and the range of colours that can appear varies widely (the colour of the patination depends on the various chemicals to which the bronze is exposed). The compounds that make up an artificial patina are similar to the corrosion products found in natural patinas formed in the outdoor environment (e.g. copper sulphides, copper chloride hydroxides, copper hydroxide sulphates). The recipes for artificial patination are usually mixtures of several chemicals (e.g. salts, acids or bases, oxidizing agents) which are applied hot, although in some cases they can also be applied cold. Dark brown and black finishes are generally formed using aqueous sulphide solutions such as ammonium sulphide, sodium sulphide, or potassium sulphide. One exception is the dark finish created on copper alloys in some scientific instruments using exotic chemicals (e.g. solutions containing platinum, arsenic, or mercury). Green finishes are produced with aqueous solutions of sulphates (e.g. ammonium sulphate or copper sulphate), chlorides (e.g. ammonium chloride or copper chloride), or nitrates (e.g. copper nitrate). Reddish-brown colours can be formed using ferric nitrate. One compound present in artificial patinas but rare on outdoor bronzes is the copper hydroxide nitrate (gerhardtite).

Care must be taken during artificial patination as overapplication of patination solutions or attempts to speed up the process tend to build up superficial layers of non-adherent, dried-on chemicals. If this loose and excess unreacted material is not removed, residual chemicals can stimulate corrosion. For example, if the local RH becomes high, the residual, unreacted chemicals can dissolve in surface moisture and form an electrolyte, promoting additional corrosion. Hughes (1992) and Otieno-Alego et al. (1998) note that an artificial patina on bronze does not offer any significant corrosion protection to the base metal.

Reference material: Birnie (1993); Hughes and Rowe (1982); Hughes (1992, 1993); Otieno-Alego et al. (1998); Scott (2002); Shearman (1976); Young (2000); Young and Fennell (1980).

INDOOR EXPOSURE

When copper and copper alloys are exposed to a clean atmosphere at room temperature, they become coated with an oxide film that is composed mainly of cuprite. This oxide layer grows rapidly on initial exposure. However, the rate of growth slows over time and the film remains thin — too thin to be visible. Only if the copper is heated does the oxide layer become thick enough to become coloured by the interference of light.

Reference material: Mattsson and Holm (1982).

Tarnishing: Copper and copper alloys tarnish when exposed to air containing sulphur in a reduced oxidation state (e.g. hydrogen sulphide, carbonyl sulphide, elemental sulphur). Sources of reduced sulphur compounds include display or storage materials (e.g. rubber vulcanized with sulphur), pollution (e.g. hydrogen sulphide), and objects (e.g. wood) recovered from anaerobic environments that are contaminated with reduced sulphur compounds produced by sulphate-reducing bacteria. The copper reacts with these sulphur-containing gases to form a tarnish layer of dark-coloured copper sulphides such as chalcocite.

There are several reported cases of mould-like spots forming on copper alloy objects on display or in storage. Some have been "black spots" while other three-dimensional growths have been reddish-brown or golden in colour. However, when these "spots" were analysed, various copper sulphides (e.g. digenite, covellite, chalcocite) were identified. The spots were likely formed by copper in reaction with reduced-sulphur compounds in the air and did not result from microbiological attack as originally thought.

Reference material: Eggert and Sobottka-Braun (1999); Graedel et al. (1987a); Hjelm-Hansen (1984); Kammlott et al. (1984); Lee and Thickett (1996); Mattsson and Holm (1982); Scott (2002); Weisser (1990).

Local contamination: Perspiration or other residues left on copper alloy objects after handling can result in fingerprints, dark stains, and local green corrosion — which can be very visible and distracting on highly polished pieces. Chloride contamination may arise from materials in direct contact with or located close to copper alloy objects. For example, hydrochloric acid may be given off as a degradation product from items made of poly(vinyl chloride) (e.g. certain Tygon tubings) or polychloroprene (e.g. Neoprene rubber). Aging plastics may also produce non-chlorinated acids that can cause copper corrosion and the formation of green spots in areas of direct contact; phthalic acid, for example, may be formed by hydrolysis of phthalate ester plasticizers in poly(vinyl chloride). Dust contaminated with ammonium sulphate particles can also cause the formation of green spots (e.g. posnjakite, antlerite, brochantite) on copper alloys.

Reference material: Bailey and Zaccardi (1983); Lobnig et al. (2003); Nagy (1999); Shashoua (2001).

Volatile organic acids: Wood products, some paints, construction materials in display or storage units, and the degradation of organic material can all give off volatile gases that can cause corrosion on copper alloys. For example, following exposure to volatile organic acids such as acetic acid (ethanoic acid) or formic acid (methanoic acid), white, green, and blue-green copper corrosion products have been noted on copper alloys, white lead carbonate hydroxide (white lead) has been found on lead-containing copper alloys, and white zinc formate hydrate has been identified on a zinc-rich copper alloy. Likewise, green and blue-green corrosion products have been noted on copper alloys stored in wooden crates or cabinets. In one analysis, green copper acetate monohydrate (copper ethanoate monohydrate, neutral verdigris) was identified.

The response of copper to volatile organic acids can sometimes be used to advantage. In the past, green and blue copper acetates that were used as pigments in paint were prepared by exposing copper plates to acetic acid vapours. The copper corrosion products that were produced were mixtures of the green neutral verdigris and the blue basic verdigris (copper acetate hydroxide pentahydrate).

Note that although the term "verdigris" is mostly used to describe copper acetates of varying chemical composition that range in colour from green to blue, it can also be used in a more general sense to describe undesirable and disfiguring green corrosion products on copper alloys that are not necessarily copper acetates.

Reference material: Kühn (1993); Lang (1996); Lee and Thickett (1996); Oddy and Bradley (1993); Paterakis (1998, 2003); Scott et al. (2001); Scott (2002); Trentelman et al. (2002); Wilthew (1993).

OUTDOOR EXPOSURE

Freshly exposed copper alloys corrode rapidly. The water-soluble corrosion products that initially form (e.g. copper(II) sulphate or copper(II) chloride) can be easily washed off by rain, leading to green staining on adjacent surfaces, especially porous stone or concrete. As corrosion proceeds during the first year of outdoor exposure, the surface of copper alloys gradually becomes covered with a layer of insoluble cuprite and possibly copper sulphides. As this film thickens, purple and blue interference colours develop and the colour of the surface darkens. This darkening will be familiar to anyone who has had the opportunity to see the installation of a new copper roof, an example of which is shown in Figure 6.4.

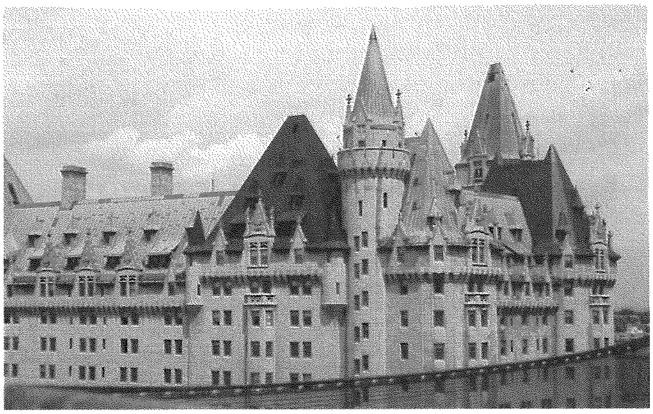

Figure 6.4. Original and recent replacement pieces of copper roofing on the Château Laurier Hotel in Ottawa. The green areas are original (dating to ~1912) and the darker areas are recent replacements (1990 and 1991). This photograph was taken in 1993. (A colour version of Figure 6.4 is available on p. 82.)

With continued outdoor exposure (several years), the corrosion rate of copper alloys gradually slows as insoluble corrosion products adhere to the surface. These form a roughly layered structure, with one layer of copper(I) oxide adjacent to the metal surface and another layer of mainly green copper(II) compounds on top.

The corrosion products on large flat areas of copper (e.g. copper roofing) form a layer of fairly uniform thickness and even green colour. This can be seen on the Web site for the Copper Development Association (www.copper.org), which has a weathering chart illustrating how the colour on copper roofing changes with time (architecture.copper.org/weathering-chart.html). But the situation is different for three-dimensional copper objects (e.g. bronze sculptures), where corrosion products tend to have varying thickness, colour (black to light green), and patterns (patchy areas, streaking). There are sometimes small "islands" of black crusts standing above lower green areas. Areas readily washed by rain tend to be an overall light green, whereas areas sheltered from rain tend to be black, in part because of the accumulation of extraneous material such as debris, soot, pollutants, and other material. Any soluble or hygroscopic salts present in this extraneous material can promote additional corrosion during periods of high RH.

Atmospheric pollutants (e.g. sulphur dioxide, nitrogen dioxide, ozone) increase the corrosion rate of copper alloys outdoors. Laboratory studies have shown that nitrogen dioxide or ozone in combination with sulphur dioxide strongly increases the corrosion rate of copper in humid air.

The green rain-washed areas of copper alloys outdoors are predominantly brochantite over cuprite. The darker rain-sheltered areas often contain mixtures of several compounds, often dark particulate matter (e.g. quartz, soot, dust) mixed with green copper(II) salts such as brochantite or one of the copper(II) chloride hydroxides (atacamite, clinoatacamite, paratacamite) over cuprite. White accretions of gypsum (calcium sulphate dihydrate) sometimes develop on the outside of sculptures when residual casting material on the inside is dissolved and redeposited on the outside after seeping through cracks and pores in the casting. Bird droppings can also damage copper alloys either by direct reaction with the components of urine or as a result of fungal growth: bird urine contains varying amounts of ammonia, uric acid, and phosphates, and has a pH that ranges from 5 to 8; and bird excrement can support fungal growth which lowers the pH (e.g. from 7 to less than 4).

Reference material: Cowden (1995); Graedel (1987a, 1987b); Graedel et al. (1987b); Lins and Power (1994); Richardson (1993); Robbiola et al. (1993); Scott (2002); Selwyn et al. (1996); Strandberg (1998a, 1998b, 1998c); Strandberg and Johansson (1997, 1998); Strandberg et al. (1996); Zahner (1995a).

Sulphates: When copper alloys are exposed to outdoor air that is polluted with sulphur dioxide, the sulphur dioxide can dissolve in surface water and react with the copper to form copper(II) hydroxide sulphates. The most common copper hydroxide sulphate on outdoor bronze sculptures is brochantite, which is usually found in the green rain-washed areas. Antlerite is less common, but can often be detected in sheltered areas that favour the accumulation of debris. It precipitates under more acidic conditions than does brochantite, and is thought to be favoured in the presence of chloride ions. Laboratory studies have shown that antlerite can form in environments containing sodium chloride and sulphur dioxide.

Other copper(II) sulphates have occasionally been identified on outdoor copper alloys such as posnjakite and the readily soluble chalcanthite. These sulphates are considered transitory or intermediate compounds that indicate recent copper corrosion. They are either washed away by rainwater or converted to more stable copper(II) hydroxide sulphates such as brochantite.

Reference material: Graedel et al. (1987b); McNeil and Mohr (1992b); Robbiola et al. (1993); Selwyn et al. (1996); Strandberg (1998a, 1998b, 1998c); Strandberg and Johansson (1998); Strandberg et al. (1996); Woods and Garrels (1986a).

Chlorides: When the surface of outdoor copper alloys is contaminated with high levels of chloride ions (e.g. from marine environments, nearby use of de-icing salts, air pollution), copper(II) chloride hydroxides can form. For example, atacamite and paratacamite (or possibly clinoatacamite instead) have been identified on copper alloys exposed outdoors. On occasion, the copper(I) chloride nantokite has also been identified.

Reference material: Graedel et al. (1987b); Jambor et al. (1996); Robbiola et al. (1993); Selwyn et al. (1996); Strandberg (1998a, 1998b, 1998c); Strandberg and Johansson (1998); Strandberg et al. (1996); Woods and Garrels (1986a).

Carbonates: Copper carbonates and copper carbonate hydroxides form on copper alloys when carbon dioxide gas dissolves in water and reacts with the underlying metal. Malachite and chalconatronite have been identified on outdoor bronze statues, but only rarely — likely because any that form are converted to copper hydroxide sulphates due to the presence of sulphur dioxide.

Reference material: Bullard et al. (1998); Graedel et al. (1987b); Meakin et al. (1992); Römich (1996); Scott (2002); Sirois et al. (2003b); Strandberg and Johansson (1998); Woods and Garrels (1986a).

Sulphides: Several copper sulphides (e.g. chalcocite, djurleite, geerite) have been identified on outdoor copper alloys. These may have been formed by reaction with patination chemicals such as ammonium, potassium, or sodium sulphides, or they may have originated from the reaction of the copper alloy with hydrogen sulphide, especially if the copper alloys are close to pulp-and-paper mills.

Reference material: Hughes and Rowe (1982); Selwyn et al. (1996); Van Zelst and Lachevre (1983).

CORROSION DURING BURIAL

The surface layer of buried copper alloys may become coarse and covered with a fairly thick layer of copper corrosion products. There is usually an inner layer, next to the metal surface, of copper(I) compounds — mainly red cuprite (the colour of which changes from yellow through orange and red to purple as the crystal size increases). The copper(I) chloride nantokite may also be present if chloride ions are present in the burial environment. Covering these copper(I) compounds are outer layers of green or blue copper(II) compounds, consisting of one or more copper(II) salts. The predominant corrosion products identified on copper alloys recovered from soils are cuprite and malachite. The "original surface" or shape of an archaeological object may be preserved in a cuprite layer beneath the outer layers of copper(II) compounds.

Recent studies in Sweden on archaeological bronzes have shown that moisture-retaining conditions around objects as well as high concentrations of soot (carbon) or phosphate in the soil accelerate corrosion during burial. Furthermore, recently excavated bronzes are more deteriorated than earlier finds, possibly due to increased atmospheric pollution and proximity to roads where de-icing salts are used.

Reference material: Fjaestad et al. (1996, 1998); Gettens (1970); MacLeod (1991); Scott (2002).

Copper–tin alloys: When buried Chinese high-tin bronzes and other archaeological copper–tin alloys are excavated, their surfaces can range from a beautiful smooth patina to a thick rough surface more typical of buried copper alloys. This variation results from the fact that copper–tin alloys may suffer preferential corrosion of the copper (decuprification) or preferential corrosion of the tin (destannification). On some recovered tin-rich copper artifacts, the surface is covered by a thin layer of tin oxides and there is still enough of the δ phase left to impart a silver colour to the object. On others, the surface has a black patina of thicker tin oxides. These patinas are often beautiful and highly valued.

Reference material: Chase (1994); Gettens (1970); Meeks (1986, 1993a); Robbiola et al. (1993, 1998a, 1998b); Scott (2002); Strandberg et al. (1997).

Carbonates: The presence of carbon dioxide in the burial environment can lead to the formation of copper(II) carbonate hydroxides such as green malachite and blue azurite, which have been identified on archaeological copper alloys recovered from the humid, closed spaces of underground tombs where the oxidation of organic material can generate high levels of carbon dioxide. Malachite tends to form on copper alloys in contact with ground waters containing dissolved carbon dioxide, and azurite is favoured under drier conditions with high carbon dioxide levels. Other copper carbonates that can form during burial include metastable georgeite which may form temporarily on copper alloys before being converted to malachite, and chalconatronite which has been identified on copper alloys from Egypt where the soil is rich in various salts due to evaporation. An example of the turquoise-blue colour of chalconatronite is shown in Figure 6.5.

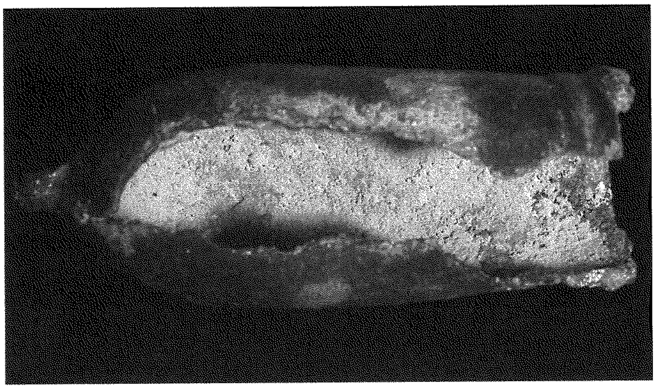

Figure 6.5. A copper alloy Egyptian situla (ROM 976.151.45) covered with a turquoise-blue corrosion product identified as chalconatronite. With permission of the Royal Ontario Museum © ROM. (A colour version of Figure 6.5 is available on p. 82.)

Reference material: Gettens (1970); Gettens and Frondel (1955); MacLeod (1991); Pollard et al. (1990, 1991); Scott (2002); Sirois (2003); Woods and Garrels (1986a).

Chlorides: Various chloride-containing compounds have been identified on archaeological copper alloys, the main ones being the waxy copper(I) chloride nantokite and the green copper(II) chloride hydroxides atacamite, clinoatacamite, paratacamite, and (rarely) botallackite. The blue-green copper(II) chloride dihydrate eriochalcite has also been identified on a copper alloy object from Egypt.

When buried copper alloys are exposed to chlorides, the corroding copper attracts chloride ions from the surrounding local environment towards the interface between the metal and corrosion. Under low oxygen (i.e. reducing) and acidic conditions, the copper(I) ions and chloride ions precipitate as CuCl (nantokite) adjacent to the metal surface, either within or below the cuprite layer, and below the outer layer of various copper(II) salts. The process that leads to the precipitation of nantokite is a form of pitting corrosion where the anodic region (corroding copper) is isolated beneath a conducting film (e.g. cuprite, gilding, carbon) and the balancing cathodic region (oxygen reduction) occurs above the conducting film. This separation of anodic and cathodic regions provides a mechanism by which chloride ions are concentrated at anodic sites, encouraging the formation of insoluble CuCl and soluble copper(I) chloride complex ions. It is soft, has a grayish appearance like paraffin wax, and can be stained green. The accumulation of nantokite within the corrosion layers on archaeological copper alloys can result in a corrosion problem known as bronze disease after excavation (more details about bronze disease are given below in the section on corrosion after excavation).

Reference material: Brock (2001); Fabrizi and Scott (1987); Gettens (1970); Jambor et al. (1996); MacLeod (1991); McNeil and Little (1991); Paterakis (2000); Scott (2000a, 2002).

Phosphates: Two copper(II) phosphate salts have been identified on archaeological copper alloys: libethenite and sampleite. The source of phosphate ions in the burial environment may be bones or phosphate-rich soils (e.g. in Egypt).

Reference material: Fabrizi and Scott (1987); Fabrizi et al. (1989); Gettens (1970); Griffin (2000); Scott (2000b, 2002).

Hydroxides: The copper(II) hydroxide spertiniite has been identified on a completely mineralized copper object, and possibly on an object recovered from a marine environment. With a colour that can be described as duck-egg blue or turquoise-blue, this rare hydroxide is unstable in the presence of carbon dioxide and water (although it does exist in nature as the mineral spertiniite, first identified from a mine in Quebec).

Reference material: Grice and Gasparrini (1981); MacLeod (1991); Paterakis (1999, 2003); Richardson (1993); Scott (1997, 2002).

Sulphides: Sulphate-reducing bacteria thrive in anaerobic conditions (e.g. underwater, in waterlogged soils) and can generate high levels of hydrogen sulphide and/or elemental sulphur. Copper alloys that are buried in anaerobic conditions are therefore exposed to hydrogen sulphide or elemental sulphur, and can form copper sulphides as they corrode. Several different copper sulphides (chalcocite, covellite, digenite, djurleite, geerite) have been identified on copper alloys recovered from anaerobic burial environments, but chalcocite is the most common one.

The iron-containing copper sulphides chalcopyrite and bornite have also been identified on copper alloy objects recovered from anaerobic burial conditions. Chalcopyrite often has a golden yellow colour (although it can sometimes be brown, or iridescent blue and purple), and it can resemble gilding when it precipitates on the outer surface of an object. In fact, the term pseudogilding is sometimes used to describe these gold-like layers of chalcopyrite (or pyrite, an iron sulphide) on copper alloys. It can be difficult to tell if the sulphides have been intentionally applied (deliberate pseudogilding) or deposited during burial (microbiological pseudogilding).

Chalcopyrite is unstable above about 60% RH. When exposed to moister air, the sulphide can be oxidized to sulphates (e.g. antlerite or guildite), and possibly to sulphuric acid. The formation of sulphuric acid is particularly dangerous because it can cause further damage to metals and other associated materials. Therefore, if chalcopyrite is present on an excavated object, the object must not be exposed to high humidity.

Reference material: Clydesdale (1993); Duncan and Ganiaris (1987); Eggert and Kutzke (2002); Gettens (1970); Howie (1992); MacLeod (1991); McNeil and Little (1999); McNeil and Mohr (1993); McNeil et al. (1991); Schweizer (1994); Scott (2002); Sequeira (2000).

Sulphates: Although copper(II) sulphates are rarely found on buried copper objects, the complex copper salt connellite has been identified.

Reference material: Gettens (1970); MacLeod (1991); McNeil and Mohr (1992b).

CORROSION AFTER EXCAVATION (BRONZE DISEASE)

The term "bronze disease" has long been used to describe the appearance of powdery light green spots on the surface of archaeological copper alloys (an example is shown in Figure 6.6). Objects exhibiting this form of corrosion were once said to be diseased or sick, and the cause was attributed to bacterial or fungal infection. However, it is now known that this corrosion is caused by chloride contamination. D.A. Scott defines bronze disease as "the process of interaction of chloride-containing species within the bronze patina with moisture and air" (1990) and also as "a progressive deterioration of ancient copper alloys caused by the existence of cuprous chloride (nantokite) in close proximity to whatever metallic surface may remain" (2002).

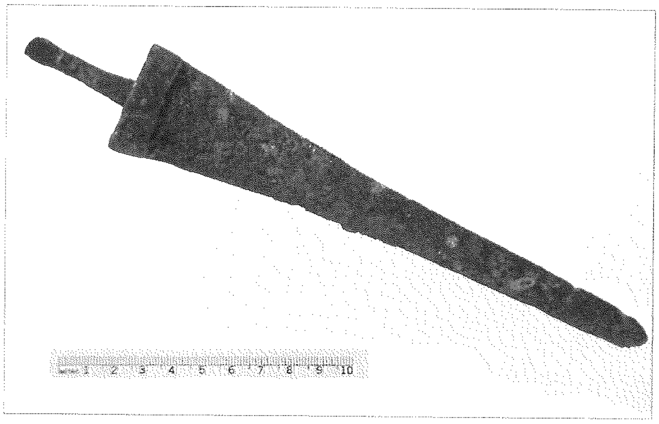

Figure 6.6. These bright green spots of corrosion (copper chloride hydroxides) on an archaeological copper alloy blade are symptoms of bronze disease. (A colour version of Figure 6.6 is available on p. 82.)

The main source of chloride-containing species within the corrosion layer on archaeological copper alloys is the copper(I) chloride nantokite, a waxy material with a gray colour (see the example in Figure 6.7). As long as the nantokite is isolated from the surrounding air by the outer layers of corrosion, it remains unreacted. However, if the protective outer material covering the nantokite is cracked, damaged, or even removed, the nantokite is exposed to the surrounding environment. Once exposed in this manner it can react with moisture in the air to form copper chloride hydroxides — the symptoms of bronze disease. A schematic diagram of bronze disease is shown in Figure 6.8.

Figure 6.7. The pale gray area on this elbow fibula (ROM 959.91.22) is nantokite, the main cause of bronze disease on archaeological copper alloys. Surrounding the large gray area are small reddish areas of cuprite and bright green areas typical of copper chloride hydroxides. Photograph by S. Stock. With permission of the Royal Ontario Museum © ROM. (A colour version of Figure 6.7 is available on p. 83.)

Scott (1990) proposed the following reaction for the oxidation and hydrolysis of nantokite:

$$4CuCl(s) + O_2(g) + 4H_2O \rightarrow 2Cu_2Cl(OH)_3(s) + 2H^+ + 2Cl^-$$

This reaction produces green copper(II) chloride hydroxides that appear as powdery green spots characteristic of bronze disease. When the corrosion products in these spots are analysed, one or more of the copper chloride hydroxides (e.g. atacamite, clinoatacamite, paratacamite) may be identified (these copper chloride hydroxides have similar thermodynamic stabilities and local conditions influence which one forms). The formation of hydrochloric acid (HCl) is thought to promote further corrosion of the remaining metal, possibly by the following reaction:

$$2Cu(s) + 2H^+ + 2Cl^- \rightarrow 2CuCl(s) + H_2(g)$$

which generates more nantokite (CuCl).

Strandberg and Johansson (1998) proposed a different reaction for the oxidation and hydrolysis of nantokite:

$$6CuCl(s) + 1^1/_2O_2(g) + 3H_2O \rightarrow 2Cu_2Cl(OH)_3(s) + 2Cu^{2+} + 4Cl^-$$

The reaction products are the copper(II) chloride hydroxides and the soluble copper(II) chloride $CuCl_2$ which can react with remaining copper metal as follows:

$$2Cu(s) + 2Cu^{2+} + 4Cl^- \rightarrow 4CuCl(s)$$

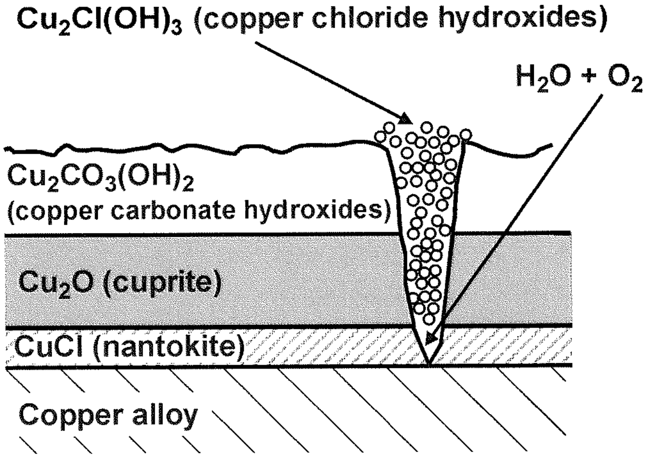

Figure 6.8. Schematic diagram of bronze disease on archaeological copper alloys. Adapted from Organ (1970).

The reaction product is again more nantokite (CuCl).

In either of the proposed corrosion reactions, the chloride ions are gradually removed as they become bound in the solid copper(II) chloride hydroxides. If only a small amount of nantokite is present, it is possible that the corrosion will stop once the chloride ions have been incorporated into solid copper(II) chloride hydroxide. However, if there is a thick layer of nantokite on archaeological copper alloys, it may be enough to cause the corrosion of all of the remaining metal and totally destroy the object.

Reference material: Gilberg (1988); McNeil and Mohr (1992a); McNeil and Selwyn (2001); Organ (1970); Pollard et al. (1989, 1992); Richardson (1993); Scott (1990, 2000a, 2002); Strandberg and Johansson (1998).

NON-TRADITIONAL BRONZE DISEASE

Bronze disease has traditionally been associated with archaeological copper alloys, the accumulation of nantokite during burial, and the formation of copper chloride hydroxides following oxidation and hydrolysis of nantokite after excavation. However, chloride ions can also cause copper corrosion and produce symptoms of "bronze disease" on non-archaeological copper alloys located either indoors or out. This type of corrosion results from exposure to an electrolyte containing dissolved chloride ions, and nantokite may form as an intermediate in the process.

Copper alloys (e.g. bronze sculptures) that are placed outdoors are often exposed to solutions containing chloride ions (e.g. seawater or de-icing salts), and it is not uncommon for copper chloride hydroxides (the symptoms (i.e. the reaction products) of bronze disease) to be identified on them. Although these copper chloride hydroxides could have been formed through the original patination process, it is more likely that they have resulted from copper corrosion in the presence of environmental chloride ions. The occasional identification of nantokite on these objects demonstrates that the overlying corrosion layers have isolated it from moist air.

Copper alloys that are kept indoors are not normally exposed to chloride-containing solutions. In spite of this, copper chloride hydroxides are often identified in the patina and in local corrosion spots on them (although the identification of nantokite is much less common). This can be explained by the fact that copper alloy sculptures are usually chemically patinated, and often with chloride-containing solutions. If a chloride-based patination recipe was used, the patina may contain nantokite next to the metal surface or it may contain trapped residual unreacted solution. As long as the nantokite and residual chemicals are isolated from moist air they remain unreacted, but any change that exposes them to moist air can allow new corrosion processes to proceed. This could result from accidental exposure to high humidity, or from damage to (or cracking of) the surface patina followed by exposure to moist air. One example of "bronze disease" on a modern indoor sculpture can be found on R. Lippold's *The Sun* at the Metropolitan Museum of Art in New York City. This piece was made with gilded bronze wire. Over time, the wire became covered with disfiguring green pustules and the wires started breaking. Nantokite and paratacamite (probably clinoatacamite) were identified in the corrosion.

Reference material: Flotte and Dommermuth (2000); Robbiola et al. (1993); Selwyn et al. (1996); Strandberg (1998a); Weisser (1987); Woods and Garrels (1986b).

CORROSION CAUSED BY SODIUM CONTAMINATION

In some cases, unusual and sometimes unexpected sodium-containing corrosion, either blue to bluish-green or white in colour, can be noticed on copper alloy objects during storage or while on display in museums.

The blue corrosion products may be residual material from the burial environment. Egyptian soils, for example, are rich in hydrated sodium carbonates (e.g. the mineral natron), and one of the first identifications of the rare mineral chalconatronite was on an Egyptian copper alloy. However, these sodium-containing corrosion products may also arise from sources of sodium ions other than those found within a burial environment, e.g. residual treatment chemicals or associated material in a composite object. Sodium ions may be present because a previous sodium-based treatment was not rinsed from the copper alloy object: examples of sodium-based treatments include soaking in sodium carbonate or sodium sesquicarbonate (equimolar sodium carbonate and sodium hydrogen carbonate); electrochemical reduction in an electrolyte of sodium hydroxide; and stripping in alkaline glycerol (sodium hydroxide plus glycerine), alkaline Rochelle salt (sodium hydroxide plus sodium potassium tartrate), or Calgon (sodium hexametaphosphate). Sodium ions may also be released from unstable material in contact with a copper alloy. Unstable glass, for example, can become covered with a sodium or potassium hydroxide solution as uncombined alkali ions (e.g. Na^+, K^+) within the glass exchange with H^+ ions in water.

Any residual sodium ions can react with moisture in the air to form sodium hydroxide, or with other gases in the air (e.g. carbon dioxide, acetic acid) to form powdery white efflorescence (e.g. sodium carbonate, sodium acetate trihydrate). Sodium hydroxide is extremely hygroscopic, absorbing moisture at room temperature whenever the RH is above about 10%. Sodium hydroxide solutions can rapidly absorb carbon dioxide from the air and precipitate sodium carbonate. Sodium hydroxide solutions can also absorb acetic acid (e.g. from any wood in proximity) and precipitate sodium acetate (sodium ethanoate).

Residual sodium ions can also react with copper ions to form new corrosion products in various shades of blue. Two such sodium–copper compounds have been identified on copper alloys. One is blue or bluish-green chalconatronite and local spots of this light blue corrosion, typical of active corrosion, have been mistaken for bronze disease. The formation of chalconatronite may be linked to the presence of the copper(II) carbonate complex ion $[Cu(CO_3)_2]^{2-}$ that turns solutions containing it a deep blue colour. The other blue compound is a pale blue or turquoise colour, and it is associated with storage or display in an environment contaminated with acetic (ethanoic) acid. Work is still being done to fully characterize this material, but it is described as a copper sodium acetate carbonate (copper sodium carbonate ethanoate) with an approximate formula $CuNa(CH_3CO_2)(CO_3)$.

Reference material: Bradley and Thickett (1999); Franzon (2000); Gettens and Frondel (1955); Horie and Vint (1982); MacLeod (1987a, 1987b); Merk (1978); Newton and Davison (1989); Oddy and Hughes (1970); Organ (1963); Paterakis (1999, 2003); Pollard et al. (1990); Strahan (1986); Tennent and Baird (1992); Thickett and Odlyha (2000); Thickett et al. (1998); Waller (1992); Weisser (1987).

CORROSION ASSOCIATED WITH HARD RUBBER (EBONITE, VULCANITE) DETERIORATION

Historic scientific instruments and objects associated with telegraphy and radio may contain copper alloy components in association with hard rubber. When the hard rubber deteriorates, the sulphur component can be oxidized to sulphuric acid which can cause the copper to corrode. For more information on corrosion problems associated with hard rubber deterioration, see "Chapter 3. Specific Corrosion Problems."

Reference material: Bacon (1988).

CORROSION CAUSED BY FATTY ACIDS

Copper soaps can form when copper alloys are in contact with free fatty acids. These soaps have been found on copper alloys in contact with leather, bronze sculptures coated with beeswax, and on the brass flake pigments colouring the paper around crayons (zinc soaps were also detected on these brass flakes). For more information on metal soap formation, see "Chapter 3. Specific Corrosion Problems."

Reference material: Burmester and Koller (1987); Helwig et al. (2001); Robinet and Corbeil (2003); Schrenk (1991, 1994); Sirois et al. (2002, 2003a); Tilbrooke (1980).

AMMONIA AND STRESS CORROSION CRACKING

Ammonia is harmful to copper alloys because it can cause uniform corrosion and, for certain alloys, stress corrosion cracking. In the presence of oxygen and moisture, copper and its alloys react with ammonia to form soluble copper(I) ammonia and copper(II) ammonia complex ions. Many copper(I) and copper(II) compounds, even those only slightly soluble in water, are dissolved by aqueous ammonia because of the stability of these complexes. Contact between copper alloys and solutions containing ammonia should therefore be avoided. This includes the many commercial products that contain ammonia, such as cleaning solutions, polishes for copper and brass, and acrylic-based adhesives and sealants (which are usually stabilized with ammonia).

Stress corrosion cracking is a corrosion process in which cracks form in certain alloys, particularly brasses, under stress (an example of stress corrosion cracking in a bugle is shown in Figure 6.9). The copper alloys that are susceptible to stress cracking tend to be the same ones that are susceptible to dealloying. For example, the α phase copper–zinc alloys (α brasses) that contain more than about 15 wt% zinc are susceptible, with susceptibility increasing as the zinc content increases up to 40 wt%. The copper alloys that are most resistant to stress corrosion cracking are the copper–nickel ones.

Ammonia promotes stress corrosion cracking because it forms soluble complexes with copper(I) and copper(II) ions. When copper is exposed to aqueous solutions that contain ammonia, any dissolved oxygen reacts with the copper to form

Figure 6.9. Stress corrosion cracking in a brass bugle by Snow of London (Bate Collection, University of Oxford, No. 70). Photo courtesy of the University of Oxford.

copper(I) ions which then react with ammonia to form the copper(I) ammonia complex:

$$2Cu(s) + {}^1\!/_2O_2(g) + H_2O + 4NH_3(g) \rightarrow 2[Cu(NH_3)_2]^+ + 2OH^-$$

Dissolved oxygen can then oxidize copper(I) complexes to copper(II) complexes:

$$2[Cu(NH_3)_2]^+ + {}^1\!/_2O_2(g) + H_2O + 4NH_3(g) \rightarrow 2[Cu(NH_3)_4]^{2+} + 2OH^-$$

The copper(II) complex can now be reduced to the copper(I) complex by reaction with remaining copper metal:

$$[Cu(NH_3)_4]^{2+} + Cu(s) \rightarrow 2[Cu(NH_3)_2]^+$$

This reduction reaction supports continued corrosion. The overall process is considered to be autocatalytic in that the reduction reaction of the copper(II) ammonia complex generates more copper(I) ions in solution, which are subsequently oxidized to copper(II) ions, which in turn accelerate the rate of corrosion. Other solutions may also cause stress corrosion cracking in copper alloys (e.g. citrates, tartrates, nitrites, carbonates, phosphates, and amines).

Reference material: Breedis and Caron (1993); Brock (2001); Mattsson and Holm (1982); Sequeira (2000); Zahner (1995b).

DEALLOYING

Dealloying is the selective or preferential removal of the more chemically active constituent of an alloy, leaving a porous, weak deposit of the more noble constituent. This process affects many of the copper alloys, e.g. selective loss of aluminum from copper–aluminum alloys (known as dealuminification) and selective loss of nickel from copper–nickel alloys (known as denickelification). Copper–tin alloys, depending on the relative concentrations of copper and tin, can undergo selective removal of the copper (decuprification) or selective removal of the tin (destannification). The mechanism is complicated and the reference material should be consulted for more detail.

Reference material: Chase (1994); Gettens (1970); Meeks (1986, 1993a); Robbiola et al. (1993, 1998a, 1998b); Scott (2002); Strandberg et al. (1997).

Dezincification: Corrosion of copper–zinc alloys (brasses) that contain more than 15 wt% zinc can result in selective removal of the zinc (i.e. dezincification). When dezincified, polished yellow brass changes colour from the yellow of the copper–zinc alloy to the pink of residual copper.

Single-phase α brasses that contain less than 15 wt% zinc are resistant to dezincification, but those with more than 15 wt% zinc are susceptible — and the susceptibility increases as the zinc content rises. In these α brasses, the loss of zinc occurs uniformly over the entire surface and is known as "layer-type" dezincification. A dezincified object remains unaltered in size and shape, but the metal is less dense. The surface appears porous or spongy, and has the characteristic salmon-pink colour of copper metal (although this may be obscured by corrosion products). Dezincification (i.e. pink areas) can sometimes be seen on polished yellow brass kickplates on doors regularly splashed during the winter with salty water from de-icing. This layer-type dezincification can be inhibited by the addition of low levels of tin (~1 wt%) as well as small amounts (~0.04 wt%) of arsenic, phosphorus, or antimony; this inhibitory effect led to the development of the Admiralty brasses.

In two-phase copper–zinc alloys (those containing both α and β phases), the β phase is the more active phase and it is preferentially attacked. As a result, the corroded metal contains discrete regions where penetration has occurred, leaving plugs of porous copper. This type of attack is termed "plug" dezincification. The addition of 1 wt% tin is effective in preventing dealloying of the β phase; this inhibitory effect led to the development of naval brass.

Because of the potential for dezincification, it is important to identify the presence of zinc in copper alloy objects before starting conservation treatments with long immersion times. Such treatments, which may have been developed for copper–tin alloys, could cause problems if used on copper–zinc alloys.

Reference material: Breedis and Caron (1993); Brock (2001); Hughes (1993); Scott (2002); Sequeira (2000); Weisser (1975).

GALVANIC CORROSION

Copper and its alloys are usually noble with respect to other common metals (e.g. aluminum, iron, lead, tin, zinc) used in industry and architecture. Large sheets of copper in direct contact with small fasteners made of more active metals (e.g. iron, aluminum, galvanized steel) will therefore increase the rate of corrosion of the fasteners, and the copper will be cathodically protected. For this reason, industry avoids using iron, aluminum, or galvanized steel fasteners on copper roofing.

On outdoor bronze sculptures, galvanic corrosion resulting from direct contact between the copper alloy and iron can cause disfiguring iron staining and severe rusting. In the past, it was common to use iron fittings to attach sculptures to their base and as internal supports (e.g. the Statue of Liberty in New York City). However, severe rusting of internal iron armatures can damage the surrounding copper alloy, especially if the rusting occurs in a restricted area. The formation of rust exerts huge destructive forces on surrounding material and can crack adjacent bronze metal. Severe rusting of the iron bolts can dangerously weaken attachments, as observed in Philadelphia on the heavy (24 489 kg) and tall (11 m) statue of William Penn located on top of City Hall. If direct contact between metals cannot be avoided (e.g. iron armatures in bronze sculptures), galvanic corrosion can be minimized by replacing iron with a metal close to the copper alloy in the galvanic series (e.g stainless steel type 316L, UNS S31603). For more information on the galvanic series, see "Chapter 2. Corrosion."

Dissolved copper ions can also cause accelerated corrosion of less noble metals. For example, if a solution containing copper ions flows over a less noble metal, the copper ions can be reduced to copper metal while the less noble metal corrodes and its ions go into solution. This can happen when rainwater flows first over a bronze sculpture and then over lead letters set in the stone below; the direct contact between the plated copper metal and the lead creates local galvanic cells and accelerates the corrosion of the lead. The use of steel wool and steel brushes on copper alloys can also lead to problems. In addition to the harder steel scratching the softer copper alloy surface, tiny pieces of iron can become trapped in the copper alloy and residual iron will rust, causing ugly brown stains on the copper.

Reference material: Baboian (1990); Lins (1985); Sequeira (2000); Zahner (1995a).

STORAGE OR WATER STAINS

Water staining can occur on freshly cleaned copper alloys that have not been fully dried, or under water drops that are the last to evaporate. Staining can also occur on stacked pieces of copper alloys if water has condensed between them (this staining is called storage stain). Water stains can have interference colours ranging from yellow to purple, and can have a mottled appearance. Sometimes there can even be black spots. For more information on staining, see "Chapter 2. Corrosion."

Reference material: Brock (2001); Mattsson and Holm (1982); Zahner (1995a).

TOXICITY

Copper is an essential element for humans and most other forms of life, although it is toxic to most fungi, algae, and certain bacteria in exceedingly low amounts. For this reason, copper metal is often used to cover the hulls of boats to prevent the growth of algae, barnacles, and other aquatic organisms. Copper compounds are also used in marine antifouling paints, and copper sulphate is a common algicide.

Although not considered a serious health hazard to humans, copper and copper compounds can be harmful in high doses. Accidental ingestion of large amounts of copper salts can cause poisoning, as was noted during the 18th century when people were poisoned by food contaminated by verdigris. Inhalation of copper fumes can cause metal fume fever as can the inhalation of zinc fumes. In plumbing systems, the leaching of lead from lead-containing copper alloys or from lead–tin solder may be of concern. Toxic copper compounds have also been used as wood preservatives (e.g. chromated copper arsenate, copper naphthenate).

Reference material: George (1993); Scott (2002); Zahner (1995a, 1995b).

7

GOLD (Au)

Principal oxidation number(s)	Atomic weight (g mol^{-1})	Density at 20°C (g cm^{-3})	Melting point (°C)	Boiling point (°C)	Linear expansivity (°C^{-1})	UNS range for alloys
Au^{1+} (aurous) Au^{3+} (auric)	196.97	19.3	1064	2856	14.2 x 10^{-6}	P00001–P00999

GENERAL DESCRIPTION

Gold is one of eight precious metals (the other seven are silver (Ag), and the six platinum metals — platinum (Pt), ruthenium (Ru), osmium (Os), rhodium (Rh), iridium (Ir), and palladium (Pd)), and in its pure form is yellow in colour and non-magnetic. It is soft, easy to work, does not tarnish, and is resistant to corrosion under most conditions. To make it harder and more useful, it is commonly alloyed with copper or silver.

More information on gold is available on the Web site of the World Gold Council (www.gold.org).

Reference material: Grimwade (1985).

ORIGIN

Gold occurs in nature in relatively pure form. (The earliest chemists tried unsuccessfully to find the "Philosopher's Stone" which was said to be able to convert non-precious metals to gold.) Over the years, major gold rushes have taken place in California (1849), Australia (1851), and the Yukon (1898). Today, South Africa is the main source of gold. The first discovery of native gold (placer gold) in Canada was in the streams of Quebec's Beauce region in 1823. It was later found in Nova Scotia, British Columbia, Ontario, and the Yukon.

Reference material: Grimwade (1985).

USE

Early civilizations associated the bright yellow colour of gold with the sun and, because it kept its original colour, made use of it for adornments. Being very scarce, gold soon became regarded as a symbol of power and wealth. It was eventually used as money and also to gild other objects made of less valuable materials. Today it can be found in jewelry, ornaments, coins, gilding (e.g. gold leaf on picture frames, gold electroplated onto sterling silver or copper alloys), dental applications (e.g. crowns, fillings), electronic devices (e.g. circuit boards), architecture and engineering (e.g. gold films on windows or firefighters' masks), and medicine.

Reference material: Selwyn (2000).

ALLOYS AND PLATING

Gold is usually alloyed with other elements (mostly silver and copper) to make it harder. Ancient gold–silver alloys were referred to as electrum or white gold; these alloys were generally pale green or silvery in colour and contained more than 30 wt% silver. Today the term white gold is used to describe alloys that are based primarily on gold mixed with copper or silver to which enough nickel or palladium has been added to bleach out the yellow colour; these modern alloys are white in colour and were developed as substitutes for platinum. Gold alloys that contain 10–90 wt% copper are known as tumbaga alloys; these are usually associated with gold objects from early South American cultures.

Reference material: Cretu and van der Lingen (1999); Drost and Haußelt (1992); Scott (1983).

COLOUR

Naturally occurring gold usually contains silver (5–45 wt%) and copper (0.1–5 wt%), and is yellow in colour. Gold alloys vary in colour depending on the amount of each alloying element. Jewellers distinguish these different colours as "red gold" (gold–copper alloys), "green gold" (gold–silver alloys), "yellow gold" (gold–copper–silver alloys), and "white gold" (gold–copper–silver alloys with additional nickel or palladium), and often take advantage of the different shades in their designs (see Figure 7.1).

The range of colours of gold alloys made by adding silver or copper is illustrated in the triangular or ternary diagram in Figure 7.2. Each corner represents a pure metal, and each axis along the sides of the triangle defines the concentrations of mixtures of just two elements. For example, the line along the left side of the triangle (joining the corners labelled Au and Ag) represents mixtures with varying concentrations of silver and gold. Along this axis, the concentrations are labelled as wt% silver. As silver is added to gold, the colour changes progressively from yellow through shades of green-yellow to the white of pure silver. As copper is added to gold, the colour changes progressively from yellow to the pinkish-red of pure copper.

Figure 7.1. A gold ring with red, white, and yellow bands of 18 kt gold. Photo courtesy of Alyea's Jewellers in Ottawa (Canada). (A colour version of Figure 7.1 is available on p. 83.)

Each point within the triangle corresponds to a different alloy composition. Figure 7.3 shows an example of the location of an alloy with composition 20 wt% silver, 30 wt% copper, and 50 wt% gold. The gold composition at any given point within the triangle can be determined by following the line that runs parallel to the corner labelled Au and reading off the gold content from either axis. In this diagram, the line connecting the gold and copper corners is labelled with the wt% gold. The other line (connecting the gold and silver corners) is labelled with the wt% silver (so the concentration of gold is 100 minus the wt% silver).

Reference material: Cretu and van der Lingen (1999); Drost and Haußelt (1992); Wise (1964).

AMOUNT OF GOLD IN AN ALLOY

The proportion (weight percentage) of gold in a gold-containing alloy can be expressed in terms of karats or fineness. Both systems indicate only the gold content; neither specifies what other alloying elements are present.

Karat: The karat (kt) is an expression of the weight fraction of gold in a gold-containing alloy in parts

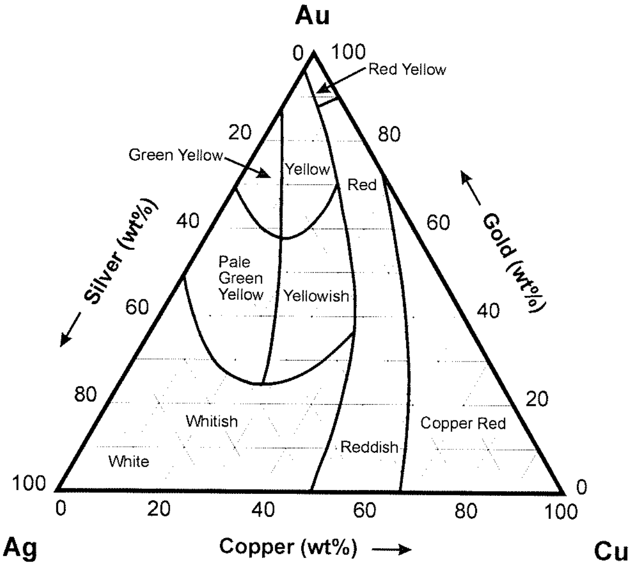

Figure 7.2. The composition ranges for various colours in gold–silver–copper alloys. The weight percentage concentrations for gold, silver, and copper are defined along the sides of the triangle. Adapted from Wise (1964).

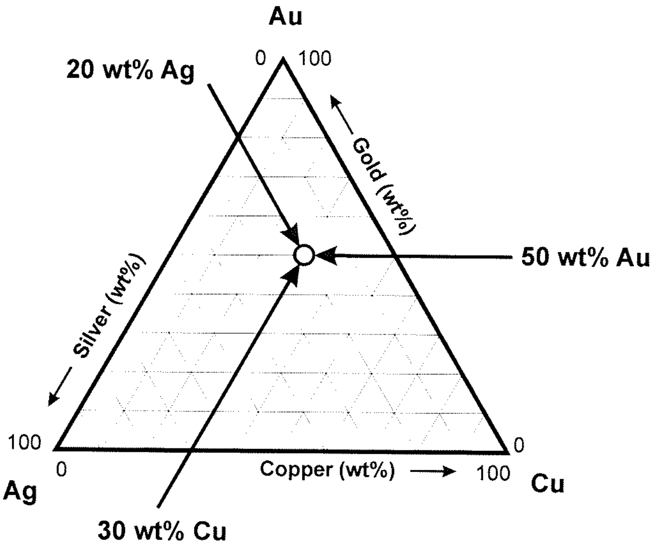

Figure 7.3. The point in this concentration triangle identifies an alloy with 20 wt% silver, 30 wt% copper, and 50 wt% gold. Adapted from Selwyn (2000).

per 24. For example, pure gold contains only gold; it is therefore 24 parts gold per 24 parts (24/24 or 1.00) and is termed 24 kt. Similarly an alloy that contains 18 parts gold per 24 parts (18/24 or 0.75) is 18 kt. Expressed in terms of weight percentage, 24 kt gold is 100 wt% gold and 18 kt gold is 75 wt% gold. Figure 7.4 highlights the concentration ranges of 18 kt and 12 kt gold. In general, the higher the karat, the softer the metal.

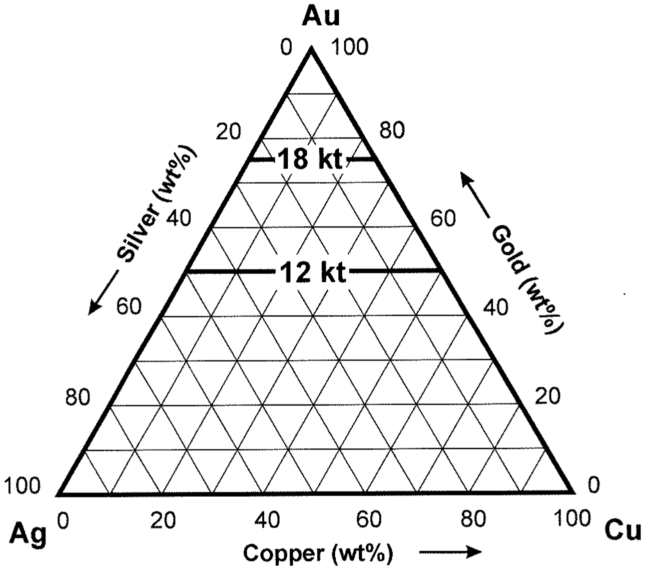

Figure 7.4. The solid lines across this concentration triangle show the locations of 18 kt and 12 kt gold alloys. Adapted from Selwyn (2000).

Because this system does not differentiate on the basis of what alloying elements are present, alloys with the same amount of gold may be different colours. For example, the colour of 18 kt gold can vary from red (when gold is mixed with mainly copper) to yellow (when gold is mixed with copper and silver) to green-yellow (when gold is mixed with mainly silver).

The United States and Canada both use the karat system to describe gold alloys. Other countries also use the system but with a different spelling, i.e. carat (symbol ct).

Many countries make it a legal requirement that solid gold and gold alloys be identified in an inconspicious area with one or more small stamps (i.e. hallmarked). The practice of hallmarking dates from 1300 when British law required that England's gold (and silver) be assayed at certain "halls" to determine if the gold (or silver) content was equal to or greater than a predetermined standard. The standards for gold between 1300 and 1798 are given in Table 7.1 (information on silver standards can be found in "Chapter 11. Silver"):

TABLE 7.1. GOLD STANDARDS

Date	Gold standard
1300–1477	81.3 wt% gold (19.5 kt)
1477–1575	75.0 wt% gold (18 kt)
1575–1798	91.7 wt% gold (22 kt)*

* In England, 22 kt gold is called crown gold.

As long as the gold (or silver) met its required standard, it was stamped with a "standard mark" as well as other marks, collectively known as the "hallmark." Initially, the same standard mark was used for both silver and gold (the leopard's head from 1300 to 1544, and the lion passant (the one with the lion's head turned sideways) from 1544 to 1798). Separate standard marks for gold and silver were introduced in 1798, after which higher quality gold was marked with a crown followed by a number for karat and lower quality gold was marked with only a number for karat.

Depending on the requirements of the day, other marks were sometimes added to the standard mark. A "maker's mark" containing the name or initials of the maker was required as of 1363. A "town mark" was added as a new location (other than London) opened for assaying the gold and silver. Finally, a "date-letter mark" identifying the year the alloy was assayed was introduced in 1578 (Figure 11.1 on p. 132 contains examples of some of these marks).

In Canada, the quality and marking requirements of precious metal articles are subject to the *Precious Metals Marking Act* and the *Precious Metals Marking Regulations*, administered by Industry Canada. (For more information on the *Act* and *Regulations*, see the Web site for Industry Canada (www.ic.gc.ca); a guide to the *Act* and *Regulations* is also available (strategis.ic.gc.ca/epic/internet/incb-bc.nsf/en/cp01001e.html).) Canada does not require that precious metal articles be marked for quality; however, if a precious metal is marked (e.g. 18 kt), then a trademark registered in Canada must be applied with it (unless the mark is a recognized foreign government mark such as the British hallmark).

Fineness: The amount of gold in gold-containing alloys can also be described in terms of fineness.

In this case the weight fraction of gold is expressed in parts per thousand (ppt). As in the karat system, the fineness describes only the gold content and does not specify the other alloys present. Pure gold (24 kt) has a fineness of 1000 and 18 kt gold has a fineness of 750.

Table 7.2 lists several gold alloys in terms of karats, fineness, and weight percentage.

TABLE 7.2. GOLD ALLOYS

Karats, parts per 24 (kt)	Fineness, parts per 1000 (ppt)	Weight percentage, parts per 100 (wt%)
24	1000	100
22	917	91.7
18	750	75
14	583	58.3
12	500	50
10	417	41.7

GOLD–SILVER ALLOYS

A phase diagram for gold–silver alloys was presented earlier (see Figure 1.2 on p. 7). These two metals are completely miscible and form a single-phase solid solution at all concentrations. Gold or silver atoms randomly fill the atom positions within the solid, thus forming disordered crystal structures.

GOLD–COPPER ALLOYS

A phase diagram for gold–copper alloys was also presented previously (see Figure 1.5 on p. 8). Gold and copper are completely miscible at high temperatures, but certain compositions form ordered structures at low temperatures (the locations are indicated on the phase diagram). These ordered structures can be prevented by rapid cooling (quenching) from above 410°C, but slow cooling or gentle heating after quenching (a process known as aging) allows their formation. In the ordered structures (also known as intermetallic compounds), the copper and gold fill the atom positions in an ordered pattern rather than randomly. For example, the ordered AuCu(I) structure has alternating layers of gold and copper atoms (see Figure 1.6 on p. 9). Certain gold–copper alloys (e.g. 18 kt Au–Cu) are difficult to work if ordered AuCu has formed.

Reference material: Selwyn (2000).

GOLD PLATING ("GILDING")

Gilding is the application of a thin gold layer to the surface of another material, including other metals. The stability of a gilded metal object depends on the thickness, adherence, and porosity of the gold, all of which depend on the technique used to apply it. Several gilding techniques are described below.

Reference material: Lins (2000); Oddy (2000); Scott (2000).

FOIL GILDING

This is an ancient form of gilding in which gold foil that is more than 1 μm thick is attached to a metal surface by a mechanical method such as crimping, riveting, or inserting the foil into grooves. Gold applied in this fashion is not well adhered and the underlying metal can easily suffer damage.

Reference material: Lechtman (1971); Oddy et al. (1990).

LEAF GILDING

In this form of gilding, the layer of gold is applied as thin sheets (typically less than 1 μm) of gold (or gold alloy) leaf. Pure gold leaf is very fragile and cannot support its own weight; modern varieties are available in sheets that measure 80 x 80 mm. Artificial or imitation gold leaf (known as schlag) is made from copper alloys and is thicker than gold leaf; modern varieties are available in sheets that measure 140 x 140 mm or 160 x 160 mm. When examining gilded objects, the presence of overlaps in the foil leaves is a sign that the gold layer was applied by leaf gilding. The distance between the overlaps indicates the approximate size of the individual sheets, and thus provides a clue as to whether the leaf is gold or an imitation.

Gold leaf can be applied directly, glued with water- or oil-based adhesive, or soldered to a prepared surface.

Direct application: Gold leaf can be adhered to a clean copper or silver surface by burnishing (the surface is usually scratched first to increase adhesion of the gold). This method was used to gild the bronze statue of Marcus Aurelius (which dates from the 2nd century) in Rome, and the statue is still intact.

Oil gilding: The gold leaf is glued to a prepared surface (e.g. metal or glass) with an oil-based adhesive such as an oil-based varnish. This method is often used for gilding surfaces in outdoor environments. One example is the gilded flame on the Statue of Liberty in New York City.

Water gilding: In this case, a water-soluble adhesive (called size) is applied onto or incorporated into the substrate to be gilded. One example of the latter is gesso, which is made by mixing rabbit-skin glue with calcium carbonate or calcium sulphate. The surface is then moistened or coated with a layer of adhesive prior to attaching the gold leaf. Water-gilded surfaces are easily damaged by water.

Soldering: Gold leaf (or thicker gold foil) can also be applied by soldering. This method is most commonly used with ferrous substrates. The iron surface is first tinned with soft solder (tin and lead), tin, or lead, and then the gold leaf is attached and heated. In some cases a layer of silver is attached to the tinned surface first, to provide a better surface for gilding.

Reference material: Gohard (1990); Lechtman (1971); Lins (1991, 2000); Oddy (1991); Oddy et al. (1988); Strahan and Maines (2000); Vaccaro (1992).

DIFFUSION GILDING

In diffusion gilding, gold leaf is burnished directly onto an underlying metal (usually copper or silver) to provide good contact between the two metals, and then gently heated. The heat causes the two metals to diffuse into one another (interdiffusion) and form a strong metallurgical bond. The extent of interdiffusion depends on the temperature and length of heating. A variation of this process is rolled gold (plaquage) in which a thin sheet of gold is clamped or pressed onto a thicker sheet of silver or copper, and then heated in a process similar to the manufacture of Sheffield plate (see "Chapter 11. Silver" for more information on Sheffield plate).

Reference material: Lins (2000); Oddy et al. (1981).

MERCURY GILDING (FIRE GILDING)

Mercury gilding (also known as fire gilding or amalgam gilding) is based on the ability of gold to mix readily with liquid mercury to form an amalgam. A gold amalgam is a mixture of mercury and intermetallic gold–mercury compounds (e.g. Au_2Hg, Au_3Hg, Au_5Hg). This process is very evident if a gold ring ever comes into contact with mercury (the ring turns a silver colour because of amalgam formation).

There are two steps in mercury gilding: the first step is the preparation and application of a gold amalgam to the metal surface to be gilded, and the second step is the gentle heating of the surface to drive off a large fraction of the original mercury and leave behind a well-bonded layer of gold.

The gold amalgam is prepared by grinding together gold leaf and mercury to form a silver-coloured paste containing particles (e.g. Au_2Hg) in liquid mercury. This paste is spread on the cleaned metal surface to be gilded and then heated, usually until the surface turns from gray to dull yellow as mercury is removed. In the past, heating was often carried out over the charcoal embers of a fire at a temperature estimated to be 250–350°C. Today, because of the dangers of mercury poisoning, heating is generally carried out in a furnace or with a gas flame equipped with facilities to trap the mercury vapour.

The resulting surface is a matte golden colour, and always contains residual mercury (usually 8–25 wt%) either as intermetallic compounds (with approximate formulas Au_3Hg or Au_5Hg), a solid solution of mercury in gold, or both intermetallic compounds and solid solution. After cooling, the surface is burnished to remove some of the porosity. The thickness of the gold layer ranges from about 2 to 10 μm.

A variation of this technique is to coat a copper or silver surface with mercury, apply gold foil to the mercury to form the amalgam, and then heat the surface to remove the mercury.

Mercury gilding is similar to diffusion gilding because a metallurgical bond is formed between the gold and the underlying metal during the heating step. Mercury gilding works well on fairly pure copper but not on brasses (copper–zinc alloys) or highly leaded bronzes (copper–tin alloys); the problem is thought to be the greater solubility in mercury of lead, tin, and zinc compared to copper. Well-known examples of mercury-gilded sculptures are the horses from the Basilica of St. Mark in Venice.

Silver-gilt: This term refers to silver which has a thin layer of gold on it, usually applied by mercury gilding.

Parcel-gilt: This term refers to partial rather than total gilding of a silver surface. For areas not intended to be gilt, a varnish is applied prior to gilding to prevent adhesion of the gold amalgam.

Ormolu: This term originated as a description of mercury-gilded copper alloys. It comes from the French term "or moulu" which means ground gold. The term is now commonly used to describe decorations on furniture that are made from gilded or gold-coloured copper alloys.

Reference material: Alunno-Rossetti and Marabelli (1976); Lins and Oddy (1975); Murakami (2000); Northover and Anheuser (2000); Oddy (1993, 2000); Oddy et al. (1990); Thornton (2000).

DEPLETION GILDING

Depletion gilding (also known as mise-en-couleur or surface enrichment) is a technique for surface gilding that can be used only for gold-containing alloys (e.g. a gold–copper tumbaga alloy from South America). The gilded surface is produced by removing an alloying element (e.g. copper) with chemicals and then burnishing the remaining gold.

Reference material: Lechtman (1971); Scott (1983, 2000).

ELECTROPLATING

In electroplating, a thin layer of gold is plated onto another metal by passing a current through a solution of gold salt (e.g. potassium gold cyanide) causing the gold ions to be reduced to gold metal on the surface of the metal. This method has been used commercially since around 1840. More recently, solutions have become available for plating gold alloys that typically range from 14 to 24 kt gold. Modern "gold" trinkets are often based on zinc or brass castings which have been nickel-plated and then electroplated with a thin gold layer. During the 19th and 20th centuries, some copper alloys were pretreated with solutions containing mercury salts prior to being electroplated with gold. Such pretreatment (called quicking) can result in residual mercury being present in the electroplated gold layer. On modern pieces, the thickness of the electroplated gold layer can range from thin (~0.2 μm) to thick (1–2 μm or more). When the gold layer is thin, the piece is said to be "gold-washed."

The term "vermeil" is used to describe gold-plated sterling silver. Modern standards require that the gold be at least 2.5 μm thick and have a minimum quality of 10 kt.

Reference material: Child (1993); Lewis (1988); Lins (2000); Lins and Malenka (2000).

GOLD FILLED AND ROLLED GOLD

Gold filled and rolled gold refer to a manufacturing process in which a thin layer of gold alloy is bonded to another metal (often a copper–zinc alloy containing 90 wt% copper and 10 wt% zinc (e.g. UNS C22000)), usually by mechanical means. Modern standards generally require that the quality of the gold alloy is 10 kt or higher. The gold layer in gold filled and rolled gold is generally thicker than a layer of electroplated gold.

In North America, the designation "gold filled" is used for items where the gold layers make up at least 1/20th of the total weight of the item, and the designation "rolled gold" or "rolled gold plate" is used for items where the gold layers make up less than 1/20th of the total weight of the item.

Gold filled items are often marked with a fraction, e.g. "14/20" (where the "14" indicates the gold alloy is 14 kt, and the "20" indicates the gold layer makes up 1/20th the weight of the item) or "1/20 10K G.F." (where the "1/20" indicates the gold layer makes up 1/20th the weight, "10K" indicates the gold alloy is 10 kt, and the letters "G.F." refer to gold filled).

Gold filled and rolled gold items were popular in the early 1900s, and raw material for jewelry manufacturing is still available today (often as sheets with gold on one or both sides of the base metal, or as wire).

More information on gold filled and rolled gold is available in the *Precious Metals Marking Act* which can be found on the Web site for Industry Canada (www.ic.gc.ca).

CORROSION

Pure gold is remarkably resistant to both tarnishing and corrosion. Gold alloys, on the other hand, become increasingly susceptible to tarnishing and corrosion as the content of other elements becomes larger. In general, the lower the gold content of the alloy, the more easily it tarnishes. Several metal sulphides identified on tarnished gold alloys are listed in Table 7.3.

Reference material: Courty et al. (1991); Dick et al. (1993); Frantz and Schorsch (1990); Johnson and Davis (1973); Randin et al. (1992); Wise (1964).

SOLUTION CHEMISTRY

Gold will dissolve if suitable complexing agents (e.g. thiourea, cyanide ions, and chloride ions) are

TABLE 7.3. METAL SULPHIDES ON GOLD ALLOYS

Chemical name	Mineral name	Chemical formula	Colour
silver(I) sulphide	acanthite	α-Ag_2S	black
gold(I) silver(I) sulphide	uytenbogaardtite	Ag_3AuS_2	gray-black
gold(I) silver(I) sulphide	petrovskaite	$AgAuS$	black
copper(I) sulphide	chalcocite	Cu_2S	black

available. The principal oxidation states of gold are +1 (Au^+) and +3 (Au^{3+}). Gold dissolves as gold(I) complexes in acidified thiourea and in alkaline sodium cyanide, and as a gold(III) complex in aqua regia (a mixture of three parts concentrated hydrochloric acid and one part concentrated nitric acid).

The susceptibility of gold alloys to corrosion and attack by acids depends on the alloying elements present and their concentration. The susceptibility of various single-phase alloys of gold, copper, and silver is shown in Figure 7.5. Gold alloys in the region labelled "1" contain more than 50 atomic percent (at%) gold. (An 18 kt gold–copper alloy or a 15.5 kt gold–silver alloy contain 50 at% gold.) These alloys are tarnish- and corrosion-resistant, and are normally attacked only by aqua regia. Alloys in the region labelled "2" contain between 50 at% and 37 at% gold; these alloys are lightly attacked by strong acids, such as nitric acid. In fact, alloys from regions labelled "2", "3", and "4" contain a significant quantity of copper (18 kt and lower) and so they can be patinated brown to black using potassium sulphide. Alloys in the region labelled "3" contain between 37 at% and 25 at% gold; these are attacked by strong acids which leach copper or silver from the surface. The alloys in the region labelled "4" contain less than 25 at% gold; these alloys are the most susceptible to both tarnishing and corrosion because the alloying elements can be selectively attacked.

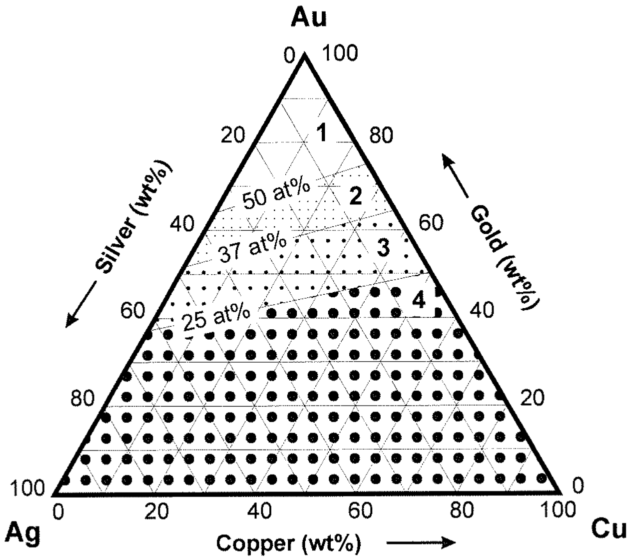

Figure 7.5. Four regions in gold–silver–copper alloys with different susceptibilities to corrosion and attack by acids: (1) attacked only by aqua regia; (2) lightly attacked by strong acids (e.g. nitric acid); (3) attacked by strong acids; and (4) susceptible to tarnishing. Adapted from Drost and Haußelt (1992).

Reference material: Cohn and Stern (1994); Cretu and van der Lingen (1999); Drost and Haußelt (1992); Johnson and Davis (1973); Rapson and Groenewald (1978); Selwyn (2000).

INDOOR EXPOSURE

Gold alloys become tarnished when the alloying elements react with contaminants in the air that contain reduced sulphur (e.g. hydrogen sulphide, carbonyl sulphide). For alloys with the same gold content, those containing silver are more susceptible to tarnishing than those containing copper. Silver and copper sulphides that form can then creep over an adjacent gold surface, partially or totally obscuring the presence of gold. The tarnish layer on the gold may contain silver sulphide, silver–gold sulphides, or copper sulphides (see Table 7.3 for examples of sulphides).

Gold–copper coins (e.g. 90 wt% gold, 10 wt% copper) may develop dark stains (known as copper spots or copper stains) due to tarnishing of an area rich in copper. It is possible that this tarnishing is influenced by local areas of ordered intermetallic compounds that form as a result of aging of the alloy. If two phases are present (unordered and ordered), then galvanic effects between the separated phases will result in the more active phase experiencing accelerated corrosion.

Reference material: Courty et al. (1991); Dick et al. (1993); Egan and Mendizza (1960); Fioravanti and German (1988); Frant (1960); Frantz and Schorsch (1990); German (1981); Halahan (1991); Randin et al. (1992); Selwyn (2000); Tear (2000); Wise (1964).

OUTDOOR EXPOSURE

In general, the gold layer of a gilded metal acts as a barrier that prevents corrosion of the underlying metal as long as the gilding is continuous and non-porous. However, if moisture and oxygen penetrate the gold layer (because it is porous, not well attached, or the adhesive has deteriorated), then the underlying metal will corrode. Expansion of corrosion products beneath the gilding can then lift and detach it. In the past, corrosion of the underlying metal could be minimized by applying red lead primers prior to gilding. Although these primers work well, their use is now banned in many countries. As an alternate measure, zinc chromate primers have recently proved effective but their use is also being restricted.

The mercury-gilded horses of the Basilica of St. Mark in Venice offer a good example of what happens when a gilded metal surface is exposed outdoors. The gilding on these horses became covered with green copper corrosion products from the corrosion of the underlying copper alloy. In this case the underlying copper alloy suffered accelerated corrosion due to the galvanic effect of having gold (the more noble of the two metals) in direct contact with it.

Reference material: Alunno-Rossetti and Marabelli (1976); Kramer (2000); Merk-Gould (2000); Sembrat (1998).

CORROSION DURING BURIAL

During burial, gold alloys can suffer stress corrosion cracking and selective dissolution of their less noble elements — which leaves a gold-rich residue. This can render the object porous and fragile. Susceptibility to this kind of corrosion during burial depends on the gold content of the alloy and on the number of phases it contains. Gold alloys that are homogeneous solid solutions (i.e. ones that have not undergone phase separation) are in general more corrosion-resistant than those that are mixtures of two phases (the presence of two or more phases allows for the possibility of galvanic effects between the separated phases, in which case the more active phase will experience accelerated corrosion).

Reference material: Cohn and Stern (1994); Edwards (2001); Forty (1981); Rapson and Groenewald (1978); Scott (1983); Selwyn (2000); Wise (1964).

DAMAGE BY SOLDERING

Repairing gold objects with lead–tin solder is not recommended. Gold dissolves readily and surprisingly rapidly in molten soft solder (tin–lead alloys), which can lead to holes if soldering is attempted. A contributing factor is the low melting point of solder that has reacted with gold to form intermetallic compounds of tin (e.g. $AuSn$, $AuSn_2$, $AuSn_4$) and lead (e.g. Au_2Pb, $AuPb_2$, $AuPb_3$). The gold–tin phase diagram in Figure 7.6 shows many intermetallic gold–tin compounds and the low melting points of mixtures. The δ phase corresponds to $AuSn$, the ε phase to $AuSn_2$, and the η phase to $AuSn_4$.

The presence of excess intermetallic gold–tin and gold–lead compounds in a gold solder join can cause it to be rough, brittle, and subject to cracking, especially if the gold concentration reaches about 5 wt%. Also, lead is a harmful impurity in gold alloys because it segregates at grain boundaries as the intermetallic Au_2Pb and causes the alloy to be brittle.

Reference material: ASM International (1992).

DELAMINATION OF MERCURY-GILDED SILVER

Mercury-gilded silver may suffer the formation of blisters in the gold and delamination of the underlying silver layer. The cause is thought to be the high temperatures used during the gilding process. The mechanism is attributed to the difference in diffusion rates of gold and silver into one another across an interface (silver atoms are smaller than gold atoms, and diffuse more rapidly). This is known as the Kirkendall effect, and is enhanced at higher temperatures. The result is porosity in the silver layer as silver atoms diffuse out and blisters in the gold layer as silver atoms diffuse in.

Reference material: van Langh (2000).

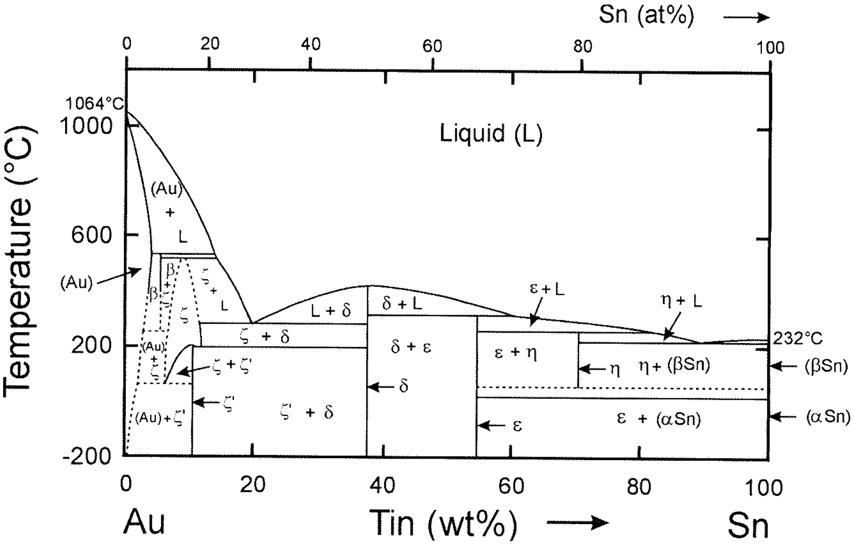

Figure 7.6. Equilibrium phase diagram for gold and tin. The bottom scale is weight percent and the top scale is atomic percent. Adapted from ASM International (1992).

COLOUR PHOTOGRAPHS

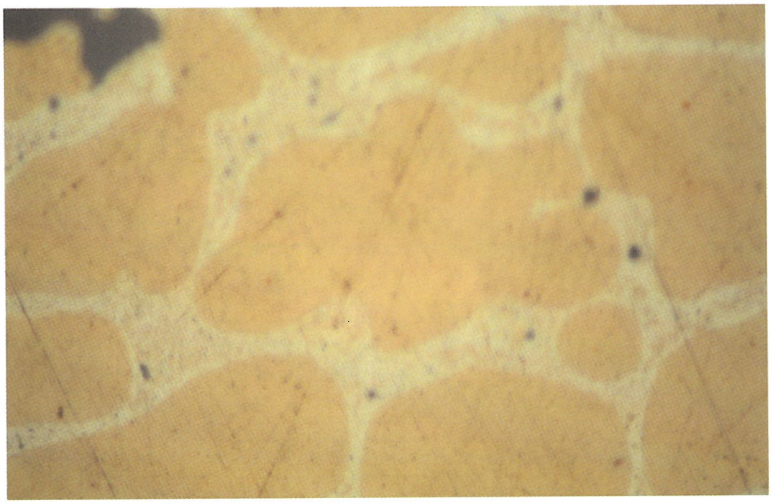

Figure 1.4. A cross section through a silver–copper alloy (~25 wt% silver and ~75 wt% copper) showing two phases; the white areas are rich in silver and the yellow ones are rich in copper. Photograph by Charlie Costain, CCI. Courtesy Laboratoire des Musées d'art et d'histoire de Genève. (See p. 8 for more information.)

Figure 3.1. Green corrosion (described as verdigris) on a pin where it passes through a bee from the National History Museum, London. The copper and zinc in the pin (made of tin-plated brass) have reacted with free fatty acids from the bee and formed the green corrosion products, identified as copper and zinc salts of fatty acids. (See p. 36 for more information.)

Figure 5.4. A photomacrograph of whitish accretions and flaking metal on the surface of aluminum suffering from exfoliation corrosion. The piece of aluminum is from the inside surface of the disconnect section of a Gemini space glove (D1973-0835) belonging to the National Air and Space Museum, Smithsonian Institution. Photo: CCI. (See p. 49 for more information.)

Figure 6.4. Original and recent replacement pieces of copper roofing on the Château Laurier Hotel in Ottawa. The green areas are original (dating to ~1912) and the darker areas are recent replacements (1990 and 1991). This photograph was taken in 1993. (See p. 63 for more information.)

Figure 6.5. A copper alloy Egyptian situla (ROM 976.151.45) covered with a turquoise-blue corrosion product identified as chalconatronite. With permission of the Royal Ontario Museum © ROM. (See p. 65 for more information.)

Figure 6.6. These bright green spots of corrosion (copper chloride hydroxides) on an archaeological copper alloy blade are symptoms of bronze disease. (See p. 66 for more information.)

Figure 6.7. The pale gray area on this elbow fibula (ROM 959.91.22) is nantokite, the main cause of bronze disease on archaeological copper alloys. Surrounding the large gray area are small reddish areas of cuprite and bright green areas typical of copper chloride hydroxides. Photograph by S. Stock. With permission of the Royal Ontario Museum © ROM. (See p. 67 for more information.)

Figure 7.1. A gold ring with red, white, and yellow bands of 18 kt gold. Photo courtesy of Alyea's Jewellers in Ottawa (Canada). (See p. 74 for more information.)

Figure 8.1. A corroded iron chain with the fibrous characteristic of wrought iron. Photograph by H. Unglik, Parks Canada. (See p. 91 for more information.)

Figure 8.2. The iron support in this tintype, dating from about 1900, is rusting and damaging the photograph. (See p. 93 for more information.)

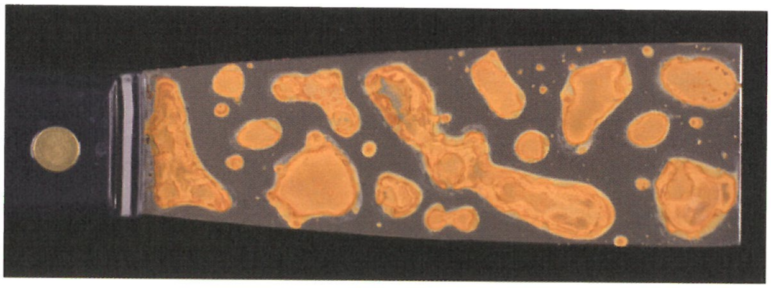

Figure 8.11. This putty knife exhibits the bright orange corrosion (lepidocrocite) that is typical of rapid rusting of iron (known as flash rusting). (See p. 104 for more information.)

Figure 8.13. The bright reddish-brown corrosion forming at the interface between metallic iron and the corrosion layer is evidence that this piece of iron is actively corroding due to chloride ion contamination. (See p. 107 for more information.)

Figure 8.14. A magnified view (about x3) of the elongated particles of akaganéite (β-FeOOH) growing on the surface of a piece of archaeological iron. (See p. 107 for more information.)

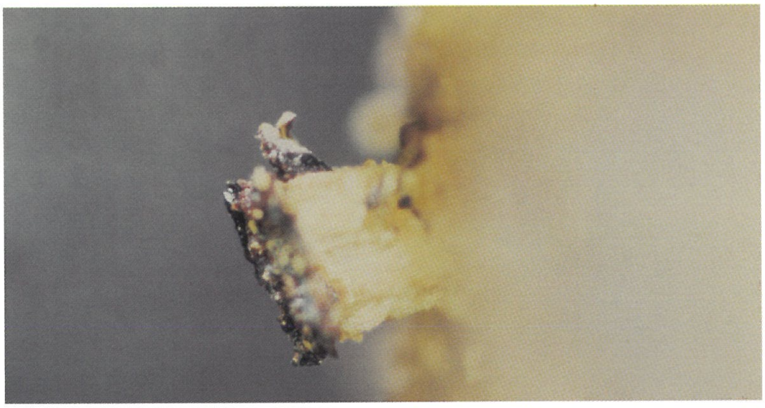

Figure 8.15. Detail of a single particle of akaganéite growing on archaeological iron and pushing off surface material. Magnification x16. *(See p. 107 for more information.)*

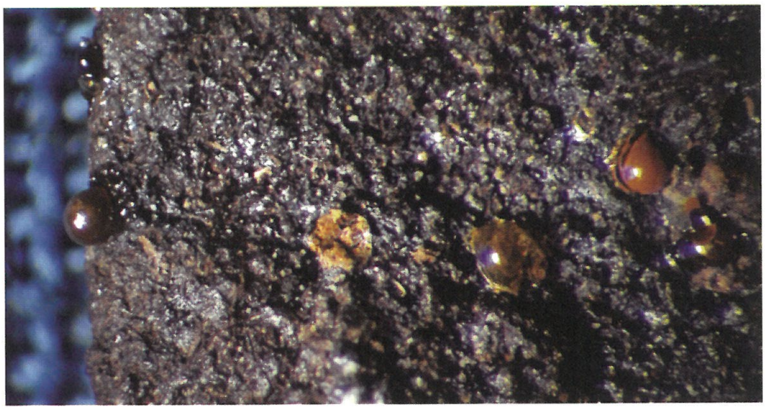

Figure 8.16. Spherical drops of liquid on the surface of archaeological iron are characteristic of weeping iron and active corrosion caused by chloride ion contamination. Magnification approximately x6. *(See p. 108 for more information.)*

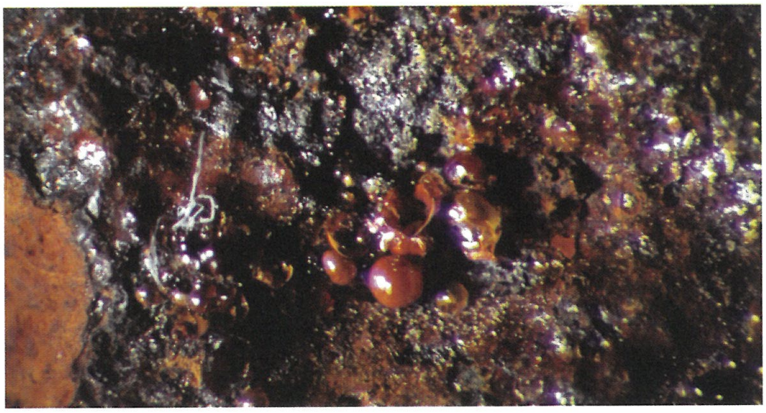

Figure 8.17. Hollow reddish-brown shells on archaeological iron are characteristic of weeping iron after the water has evaporated. Magnification about x9. *(See p. 108 for more information.)*

Figure 8.18. Detail of hollow shells characteristic of weeping iron on archaeological iron. Magnification about x25. *(See p. 108 for more information.)*

Figure 9.3. A close-up of a soft solder join in the stained glass angel pictured in Figure 9.2, which shows that the solder is not corroding. It is probably a lead–tin alloy with sufficient tin to make it more resistant to active corrosion than the adjacent lead cames. (See p. 121 for more information.)

Figure 9.4. Lead formate particles growing on a lead toy soldier (Royal Ontario Museum 991.246.187.13). Photograph by Brian Boyle. With permission of the Royal Ontario Museum © ROM. (See p. 121 for more information.)

Figure 9.5. Detailed photograph of lead formate particles on the toy soldier shown in Figure 9.4 (Royal Ontario Museum 991.246.187.13). Photograph by Susan Stock. With permission of the Royal Ontario Museum © ROM. (See p. 121 for more information.)

Figure 10.2. These Canadian coins illustrate the colours of pure nickel, a nickel–copper alloy, and pure copper (the left-hand 5-cent coin is plated with pure nickel; the middle 5-cent coin is an alloy containing 75 wt% copper and 25 wt% nickel; and the right-hand 1-cent coin is plated with pure copper). (See p. 127 for more information.)

Figure 10.3. Nickel-plated iron was common on automobile trim in the early 1900s, as illustrated on the window trim of this 1926 Series 11-A Sport Touring Franklin, owned by A. Audette, Ottawa. This photograph shows an area where the nickel plating has peeled off, revealing copper (which was used as an intermediate layer between the nickel and the iron to improve adhesion). (See p. 128 for more information.)

Figure 11.5. A freshly cleaned silver-plated bowl (owned by L. Carlyle, CCI). (See p. 138 for more information.)

Figure 11.6. The tarnish film on this silver-plated bowl (owned by L. Carlyle, CCI) has a yellow colour. (See p. 138 for more information.)

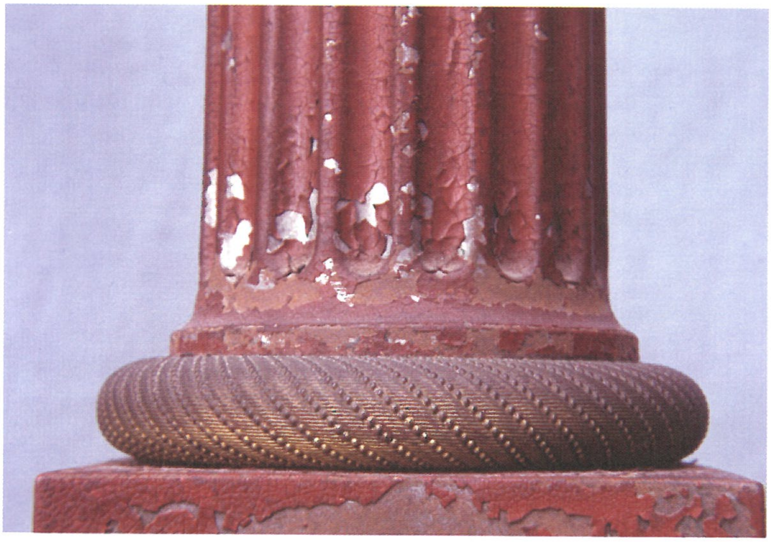

Figure 12.6. Iron corrosion on a painted tinware lamp from a room in a historic house overlooking the sea. Photograph by Lisa Ellis. Courtesy of the Collections Department of the Society for the Preservation of New England Antiquities (SPNEA). (See p. 148 for more information.)

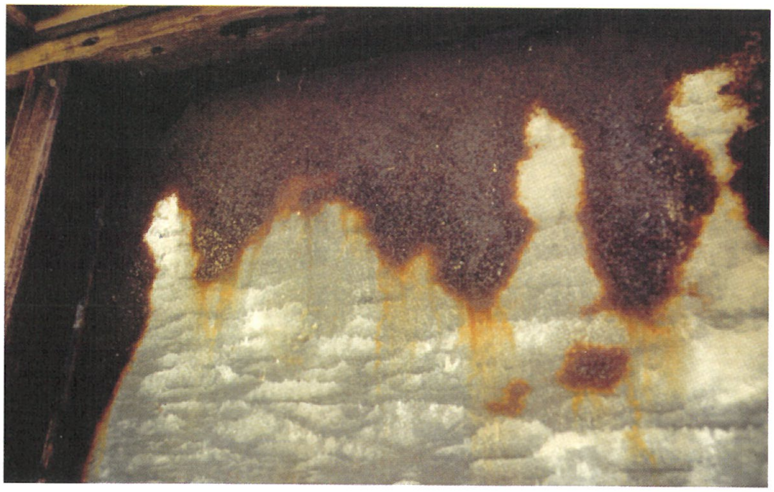

Figure 13.7. This piece of galvanized iron was exposed outdoors. The zinc on the top has corroded away, and the exposed iron is suffering from serious damage, including loss. The zinc on the lower part has corroded and become covered with white zinc corrosion products. Photograph by S. Maltby. (See p. 156 for more information.)

8

IRON (Fe)

Principal oxidation number(s)	Atomic weight (g mol^{-1})	Density at 20°C (g cm^{-3})	Melting point (°C)	Boiling point (°C)	Linear expansivity (°C^{-1})	UNS range for alloys
Fe^{2+} (ferrous) Fe^{3+} (ferric)	55.85	7.87	1538	2861	11.8×10^{-6}	many, e.g. series F, G, J, S, T

GENERAL DESCRIPTION

Pure iron is a silvery-white, relatively soft metal that has high melting and boiling points. It is magnetic at room temperature but becomes non-magnetic if heated above about 900°C. Metallic iron has a strong tendency to rust so it is rarely found in nature or used commercially; for commercial applications it is alloyed with other elements (usually carbon) to make steels, cast irons, stainless steels, and other specialty alloys.

For more information about the iron and steel industry, see the Web sites for the American Iron and Steel Institute (www.steel.org), the International Iron and Steel Institute (www.worldsteel.org), the Nickel Development Institute (www.nidi.org), and the Specialty Steel Industry of North America (www.ssina.com).

Reference material: Lepinski and Myers (1995); Paxton (1997); Street and Alexander (1995).

ORIGIN

Iron may originate from earth or from meteorites that have fallen to earth, but all naturally occurring iron is an alloy of iron and nickel. Natural metallic iron is rarely found because iron is readily oxidized to the familiar red-brown rust; one of the few examples is a large deposit of native nickel-bearing iron (0.05–4 wt% nickel) called "telluric iron" in Western Greenland.

Reference material: Wayman (1987a, 1987b).

METEORITES

Meteoritic iron comes from meteorites that have survived the fall to earth. Meteorites are generally believed to originate from comets or small planets (asteroids) that collide with one another in space. They can be divided into three broad categories (irons, stones, stony-irons) depending on the relative proportions of silicates and metallic iron. Most meteorites contain some metallic iron.

Approximately 4% of all meteorites fall into the category of iron meteorites, also known as siderites. (Note that the term siderite can also be used to refer to the iron carbonate mineral $FeCO_3$.) Iron meteorites are thought to be pieces of asteroids with molten metallic cores that, after slow cooling, were fragmented in space by collisions. They are alloys of iron and nickel (with the nickel content ranging from about 5 to 60 wt%) and generally also contain some phosphorus but less than 0.1 wt% carbon. The outer surface (about 1 mm) is usually covered with a matte or shiny black crust of mainly magnetite, formed by surface heating during rapid passage through the earth's atmosphere.

Iron meteorites can be subdivided into three categories: octahedrites, hexahedrites, and ataxites. Most iron meteorites are octahedrites that contain 7–12 wt% nickel. When a section of an octahedrite is polished and etched, it has a characteristic banded microstructure of interlocking plates known as a Widmanstätten pattern. These etched sections are often the showpieces of meteorite displays in museums. The two main phases present in the microstructure of octahedrites are kamacite (also known as α-ferrite) and taenite (also known as austenite). Kamacite is iron alloyed with less than 7.5 wt% nickel and taenite is iron alloyed with more than 25 wt% nickel. The Widmanstätten structure is formed by the precipitation of kamacite from taenite. This distinct structure is a near-equilibrium microstructure, possible only because of the extraordinarily slow cooling rate of the iron alloy in space (on a time scale of millions of years).

Reference material: Bevan (1992); Buchwald (1977); Budka et al. (1996); Vander Voort (1992); Wayman (1987a, 1987b).

IRON SMELTING

The smelting of iron involves the conversion (reduction) of iron ore to solid metallic iron. This is accomplished by heating iron ore with carbonaceous (carbon-containing) fuel. The combustion of the carbon is accompanied by the formation of carbon monoxide, which reduces the iron oxides and other metal oxides in the ore back to metal.

The chemical reactions involved in the reduction of iron ore are complex. The carbonaceous fuel first burns to produce carbon monoxide:

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

The carbon monoxide then reacts with iron oxides, reducing them to iron, as exemplified by:

$$Fe_2O_3(s) + CO(g) \rightarrow 2FeO(s) + CO_2(g)$$
$$FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$$

Reference material: Barraclough (1991a); Lepinski and Myers (1995); Tylecote (1991).

Ores: Early iron smelting was conducted with iron ore deposits that consisted mainly of goethite (known as bog iron ore), which was recovered from the bottom of marshes and bogs where it had precipitated from water rich in dissolved iron ions. Today, many different iron ores are mined: hematite (the most plentiful), magnetite, goethite, siderite, pyrite, and taconite (a low-grade iron ore that contains about 25 wt% iron in the form of magnetite which is becoming increasingly important as a commercial ore).

In Canada, local bog iron ore was first used as a source of iron in the 13th century Viking settlement at L'Anse aux Meadows in Newfoundland. Canada's first ironworks, Les Forges du Saint-Maurice, was created about 1670 in Trois-Rivières, Quebec. Today, the main iron ore deposits are along the border between Quebec and Labrador, and in an area north of Lake Superior.

Reference material: Lepinski and Myers (1995); Samson (1998).

Fuels: Carbon is the major constituent of charcoal, coal, and coke — making them potential fuels for smelting iron ores.

Charcoal is a good fuel for smelting iron ore. It is made by burning wood chips in the absence of air to drive off water and other volatiles, leaving relatively pure carbon with a low sulphur content. Charcoal was a primary source of all fuel until the beginning of the 17th century, at which time England suffered a growing wood shortage that forced industry to switch to coal.

Coal is a naturally occurring mineral that is usually contaminated with sulphur and phosphorus. It is not suitable as a fuel for smelting iron because the sulphur and phosphorus impurities leave the iron brittle and unsuitable for working into wrought iron. Iron that is contaminated with sulphur is said to be "hot short" and it is brittle when red hot. Iron that is contaminated with phosphorus is said to be "cold short" and it is too brittle for use when cold.

Coke is made by heating coal in coke ovens above 1000°C in the absence of air to drive off volatiles, particularly sulphur. Because the volatiles are removed, coke is a suitable fuel for smelting iron ore. It was first used successfully for this purpose by A. Darby in England in 1709. Coke-smelted iron contains silicon.

Reference material: Hodges (1964); Raymond (1984); Schubert (1958); Tylecote (1991).

Slag: The impurity minerals in metal ores are referred to as gangue, and typically include alumina (aluminum oxide) and silica (silicon dioxide). During smelting, these gangue minerals typically combine with iron oxides to form a molten material known as slag that, on cooling, hardens to a glass-like state. For example, in early wrought iron, the siliceous gangue material combined with iron oxides to form fayalite-type slags (fayalite is iron(II) silicate). Because considerable quantities of iron oxide were needed to react with the silica to form a free running molten slag, a large portion of the iron was removed as slag rather than as iron metal. However, eventually it was recognized that the melting point of the slag could be reduced by adding a flux to the iron ore and fuel mixture. Limestone (calcium carbonate) became a common flux. When added to the iron ore and fuel mixture, limestone formed calcium oxide and carbon dioxide during the smelting process. The calcium oxide then reacted with the silica to form calcium-containing silicates. Because the resulting slag formed at a lower temperature than the earlier fayalite types, it removed the silaceous gangue material before it could combine with the iron oxides. This left more of the iron oxides available to form iron metal.

Reference material: Maddin et al. (1977); Tylecote (1991).

MANUFACTURING TECHNIQUES

The key factors influencing the history of iron technology are the high melting point of pure iron, and the effect of adding only a few weight percent carbon (which lowers iron's melting point by several hundred degrees). Early techniques for manufacturing iron did not melt it or purify it well, and the remaining impurities affected the properties of the iron and how the heated (but still solid) iron could be worked. The beneficial effects of adding carbon eventually led to the development of steel and cast iron. Appendix 4 (on p. 112) contains an overview of the development of iron manufacturing techniques, included here because of its importance in understanding the various forms of iron.

USE

The earliest record of human usage of iron dates to around 2000 B.C. in Iran, Egypt, and Turkey, with the iron coming from meteorites. There is also evidence of Inuit exploitation of iron meteorites for metal (using material found in the vicinity of Cape York, northwest Greenland) long before permanent European settlements were established in Canada. It was in the Mediterranean region sometime around 1300–1200 B.C. that the first iron was recovered from iron ores. Since then, iron has been used in a variety of ways, e.g. as wrought iron, steels, and cast iron.

Reference material: Lepinski and Myers (1995); Paxton (1997); Street and Alexander (1995).

NOMENCLATURE

Iron is referred to in many ways (see Table 8.1): the term "iron" is generally reserved for the relatively pure element; "wrought iron" indicates a special sort of fairly pure iron that contains glassy inclusions of slag and has a characteristic fibrous structure; "steel" refers to iron alloyed with carbon (generally less than 2 wt%); and "cast iron" refers to iron with higher carbon contents (usually about 2–4 wt% carbon).

TABLE 8.1. TYPES OF IRON

Type of material	Carbon content (wt%)
wrought iron	<0.1
steel	0.2–2
cast iron	2–4

Wrought iron is tough, malleable iron that has been used to produce nails, small arms, agricultural implements, horseshoes, wire, locks, bolts, hooks, hinges, chains, and ships' anchors, as well as ornamental pieces such as decorative wrought iron balconies, railings, fences, and gates. As wrought iron remains strong under tension, it has also been used for structural elements such as wrought iron beams. Wrought iron is almost pure iron, with only a small amount of dissolved carbon (usually less than 0.035 wt%). It also contains up to about 2.5 wt% glassy slag inclusions, mainly the iron silicate fayalite, giving it a fibrous structure. An example of a wrought iron chain can be seen in Figure 8.1, and cross sections of wrought iron were shown earlier (p. 15) in Figures 1.10 and 1.11. Wrought iron is not hardened by heat treatments (e.g. sudden cooling by quenching).

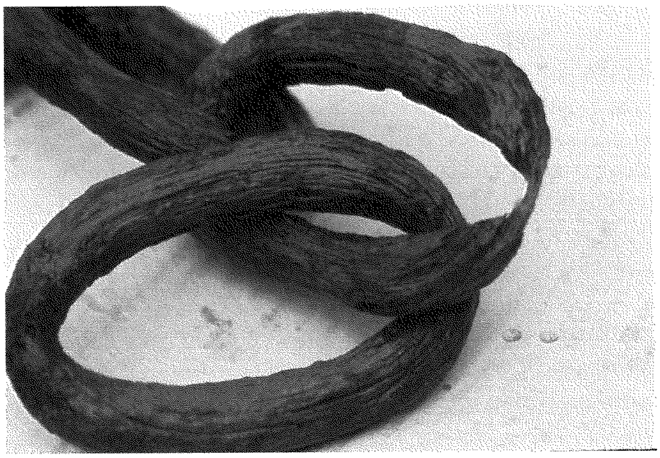

Figure 8.1. A corroded iron chain with the fibrous characteristic of wrought iron. Photograph by H. Unglik, Parks Canada. (A colour version of Figure 8.1 is available on p. 83.)

Steels are iron–carbon alloys with a carbon content (up to 2 wt%) that falls in between wrought iron and cast iron. The addition of these small amounts of carbon increases the hardness and strength of the iron. Other elements that may also be present in steels include manganese, nickel, and chromium. The development of modern steels started in earnest in the 1780s when it became understood that the different characteristics of steel versus iron were due to the presence of carbon. Steels can be hardened by rapid cooling (quenching), an important characteristic for making tools; reheating (tempering) to 200–700°C can lower the hardness and restore ductility. By adjusting the carbon content and the temperatures used for hardening and tempering, steels with a wide range of strength and ductility can be produced. Modern steels have been used for ships' hulls, railroad rails, suspension bridge cables, reinforcing steel in concrete, tools, and guns. Stainless steels are iron–carbon alloys that also contain at least 10.5 wt% chromium and some nickel (they are "stainless" because they are more resistant to rusting than ordinary steels). These are used for cooking utensils, cutlery, decorative architectural hardware, and industrial purposes.

Cast irons are hard, brittle iron–carbon alloys that contain 2–4 wt% carbon. Early cast irons (called pig iron) were produced in blast furnaces and usually contained varying amounts of sulphur, silicon, manganese, and phosphorus; they were used to make pots, pans, fire grates, stoves, cannons, and cannon balls. Cast iron has also been used for building fronts (popular in the mid 1850s in the United States), fountains, lamps, and interior stairs. It was even used for support columns in buildings and bridges (although weak under tension, it is good under compression) until about 1890, when it was replaced by the advent of cheap, mass-produced steels. The first cast iron bridge (the "Iron Bridge") was built in 1781 in Shropshire, England. Early cast iron was also used to produce other forms of iron, including wrought iron and steels. The dome of the United States Capitol Building, completed in 1865, was constructed entirely of cast iron.

Reference material: Barraclough (1991b); Gayle and Look (1992); Goodway (1993); Gordon (1976); Habashi (1999); Lepinski and Myers (1995); Paxton (1997); Raymond (1984); Street and Alexander (1995); Tylecote (1991).

DAMASCUS STEEL BLADES

Damascening (the production of steel blades) was a craft practised in southern India and surrounding regions from about the 7th century onwards. These steel blades were brought to European markets from the city of Damascus and became known as Damascus steel. Damascus steel blades and swords consist of a hard flexible steel with a characteristic wavy pattern. The steel blades were produced by forging steel, and the pattern was generated by etching the steel to reveal a pattern of contrasting silvery-white cementite particles and a dark pearlite matrix. The steel used in the forging step was an early crucible steel, now called Wootz steel, made by mixing iron ore and carbon fuel in tightly sealed crucibles and heating at high temperatures. This type of steel is also known as damask or watered steel.

Reference material: Verhoeven and Pendray (1992).

PIGMENTS

Naturally occurring iron oxides and iron hydroxide oxides are used as yellow, orange, and red pigments (called iron earth pigments). The colour of the pigment is influenced by the size and shape of the iron oxide and iron hydroxide oxide particles as well as the presence of other material. Yellow earth pigments (e.g. yellow ochre, raw sienna) usually contain goethite. Red earth pigments (e.g. red ochre, burnt sienna) usually contain hematite. Heating the yellow earth pigments converts them into the red earth pigments (e.g. goethite is converted to hematite by water loss), hence the terms raw and burnt.

Umbers (raw and burnt) are brown earth pigments that contain manganese compounds in addition to iron oxides. Synthetic iron pigments known as mars colours (mars red, mars yellow) are synthetic analogues to the naturally occurring iron oxides and iron hydroxide oxides. On ancient pottery, contrasting iron oxide colours of red figures (red hematite) on a black background (magnetite) were achieved by firing under alternating oxidizing and reducing conditions.

Reference material: Helwig (1997, forthcoming); Lambert (1997).

MAGNETIC MATERIALS

Magnetic particles are used in toners for photocopying and laser-printing, and in magnetic tapes and disks. Many of these magnetic particles are based on iron-containing material, either particles of iron metal or particles of magnetic iron oxides. Both kinds of particles can contain ferrites. (Note that the term "ferrite" has two meanings: it can be used to define the room-temperature phase of pure iron metal (the α phase); or to describe a group of ferromagnetic compounds with a generalized formula MFe_2O_4 where M is usually a metal.)

Iron particles, various magnetic iron oxides (e.g. maghemite, cobalt-doped maghemite, oxide-type ferrites), and chromium dioxide have all been used to make magnetic tapes. Although the iron oxides are stable, the iron particles and chromium dioxide are subject to degradation (the iron particles can rust and the chromium dioxide particles can convert to non-magnetic oxides over time).

Reference material: Cornell and Schwertmann (1996); Grattan (2000); Wernick (1995).

IRON IN PHOTOGRAPHY

Sheets of iron were used as a support for early photographs known as tintypes, and light-sensitive iron salts were used to make photographic images on paper called platinotypes and cyanotypes.

Tintypes: In 1856, H.L. Smith patented a type of photograph in the United States that eventually became known as the tintype (it was first called melainotype and then ferrotype). A tintype was made from a thin sheet of iron (not tin) that was first painted with black or brown lacquer and then coated with a wet collodion (i.e. cellulose nitrate) emulsion that contained light-sensitive silver salts. After exposure and processing, the tintype image was often lacquered to prevent mechanical damage to the emulsion. However, the iron support could be easily bent and would then rust at any subsequent breaks in the lacquer. If the iron rusted, the iron corrosion products would force the emulsion off the plate, as shown in Figure 8.2. In spite of this problem, tintypes became very popular, especially in the United States. They were small, unbreakable, inexpensive, and easily transportable. They were produced until the 1930s. (The term "tintype" for a photograph on iron may seem puzzling. However, many images could be produced on a single iron sheet, and the use of tin shears to separate individual images could have led to the name.)

Reference material: Hendriks et al. (1991).

Platinotypes: In 1873, W. Willis patented a photographic printing process (known as platinotype) in which the black image in the final print was metallic platinum. This process was popular until 1916 when the cost of platinum increased sharply. The paper was first sensitized with a mixture of iron(III) oxalate and a platinum salt, either potassium hexachloroplatinate or potassium tetrachloroplatinite. When the paper was exposed to light, the Fe^{3+} ions were reduced to Fe^{2+} ions. The exposed paper was then developed by immersing it in a bath of potassium oxalate where the Fe^{2+} ions reacted with platinum ions (in either the +2 or +4 oxidation state). The Fe^{2+} ions were oxidized to Fe^{3+} ions and the platinum ions were reduced to platinum metal. Fine particles of platinum metal imbedded in the paper formed the image. Residual iron salts were then washed out with an acid bath (if the iron salts were not washed out thoroughly, the paper would suffer from iron-catalysed degradation).

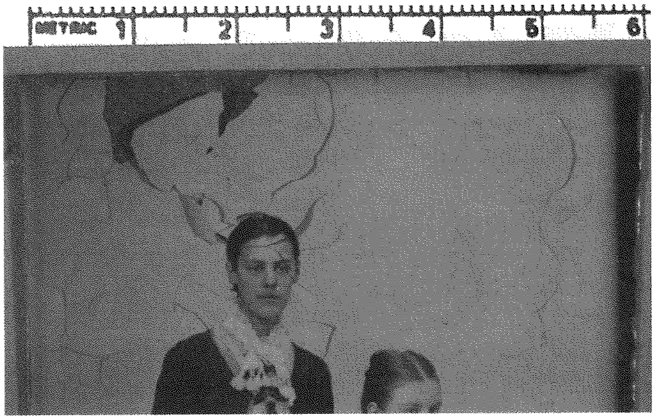

Figure 8.2. The iron support in this tintype, dating from about 1900, is rusting and damaging the photograph. (A colour version of Figure 8.2 is available on p. 84.)

Reference material: Gent and Rees (1994); Gottlieb (1995); Hendriks et al. (1991); Severson (1995).

Cyanotypes: J. Herschel developed this process for photographic printing in 1842. In this case, the blue image in the final print was a complex iron salt called Prussian blue. The paper was first sensitized with a mixture of iron(III) salts: ammonium iron citrate and potassium ferricyanide. On exposure to light, the Fe^{3+} ions in the cyanide complex were reduced to Fe^{2+} ions and the complex then combined with Fe^{3+} ions from the ammonium iron citrate to form Prussian blue, an insoluble mixed Fe(II)–Fe(III) salt with a blue colour (the chemical formula for Prussian blue is $Fe_4[Fe(CN)_6]_3$ and the chemical name is iron(III) ferrocyanide). The exposed paper was then washed with water to remove soluble iron salts, and the fine particles of insoluble Prussian blue imbedded in the paper formed the image. As with platinotypes, the paper would suffer iron-catalysed degradation if the iron salts were not washed out thoroughly.

Reference material: Hendriks et al. (1991); Ware (1998).

ALLOYS AND PLATING

IRON–CARBON PHASE DIAGRAM

Pure iron melts at 1538°C but the addition of a small amount of carbon to iron significantly lowers this melting temperature. A partial phase diagram for iron–carbon alloys (equilibrium conditions with carbon in its most stable phase, graphite) is given in Figure 8.3, and the expanded regions for relatively pure iron at high and low temperatures are in Figures 8.4 and 8.5, respectively.

In most steels, the carbon is present as the metastable iron carbide (cementite) phase rather than as graphite. Iron carbide in steel is quite stable under normal low-temperature conditions even though it can be

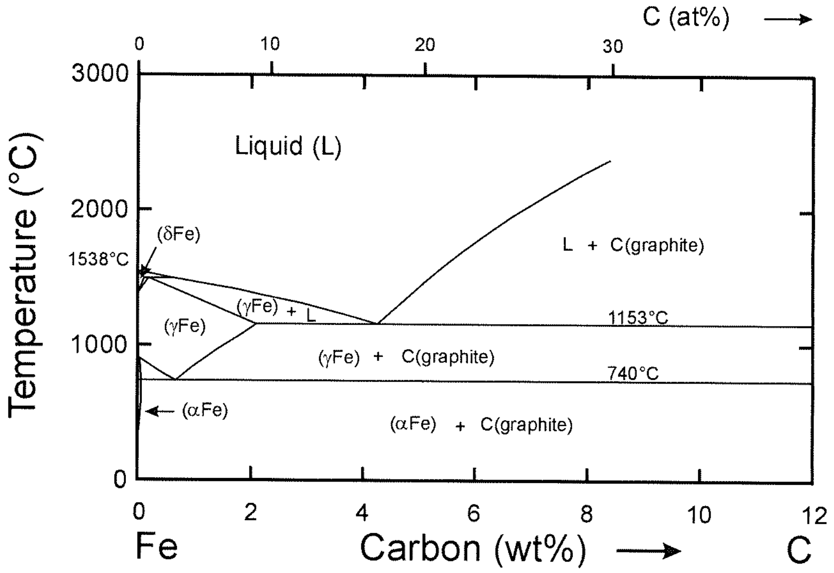

Figure 8.3. Partial equilibrium phase diagram for iron and carbon. The carbon is present as graphite, its most stable phase. The bottom scale is weight percent and the top scale is atomic percent. Adapted from ASM International (1992).

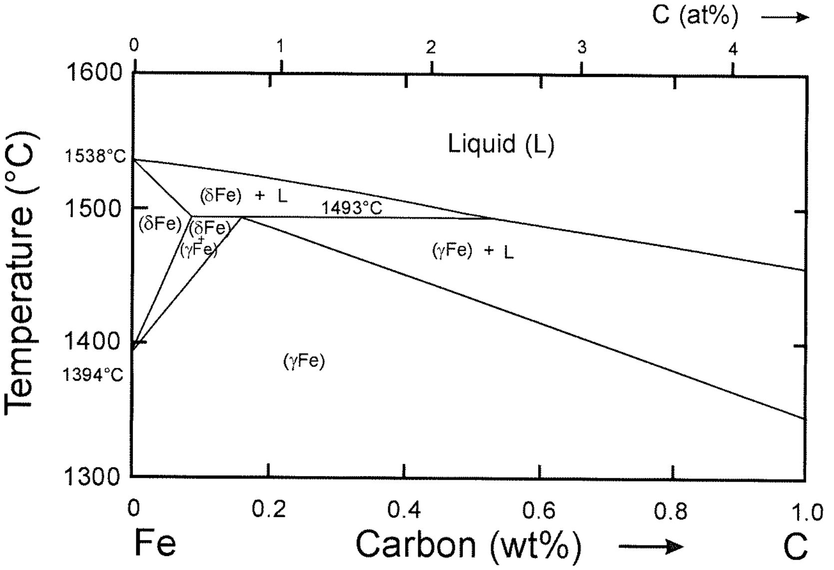

Figure 8.4. Partial equilibrium phase diagram for iron and carbon showing the expanded region around the higher temperature δ phase of iron. The bottom scale is weight percent and the top scale is atomic percent. Adapted from ASM International (1992).

changed to graphite and iron if heated for several days at about 900°C. The partial phase diagram in Figure 8.6 is for iron–carbon alloys with carbon present as the metastable phase cementite rather than graphite.

Reference material: ASM International (1992); Paxton (1997).

CHEMICAL COMPOSITION OF IRON–CARBON PHASES

The chemical compositions of the common phases that can form in iron–carbon alloys are listed in Table 8.2.

TABLE 8.2. COMMON PHASES OF IRON–CARBON ALLOYS

Name of phase	Chemical composition
ferrite (or α-ferrite)	αFe
austenite	γFe
δ-ferrite	δFe
cementite	Fe_3C
graphite	C

Ferrite (also called α-ferrite): This is the low-temperature α phase of iron (details of the α phase region of the phase diagram are shown in Figure 8.5). This phase is stable from room temperature up to 912°C; it dissolves a negligible amount of carbon at room temperature, and a maximum amount (0.02 wt%) at 727°C. Ferrite is magnetic, has a body-centred cubic (bcc) structure, is malleable and ductile, and can be rolled into sheets or drawn out into wire. It also has high tensile strength, so it can withstand high longitudinal stress without breaking.

Austenite: This is the high-temperature γ phase of iron which is stable between 912 and 1394°C. It dissolves up to 2.1 wt% carbon at 1147°C, as shown in Figure 8.6. In contrast to ferrite, austenite is non-magnetic and has a face-centred cubic (fcc) structure. Because the spaces between atoms (interstices) are larger in the fcc structure of γ iron than in the bcc structure of α iron, austenite can accommodate more small interstitial carbon atoms.

δ-*Ferrite :* This is the δ phase of iron. It exists only at high temperatures, between 1394 and 1538°C, and dissolves a maximum of 0.09 wt% carbon at 1493°C. Details of the δ phase region of the phase diagram are shown in Figure 8.4. As with the low-temperature α phase of iron, iron in this phase has a bcc structure and so both are referred to as ferrites.

Cementite: This is the iron carbide phase that forms in certain iron alloys (this phase is located at the

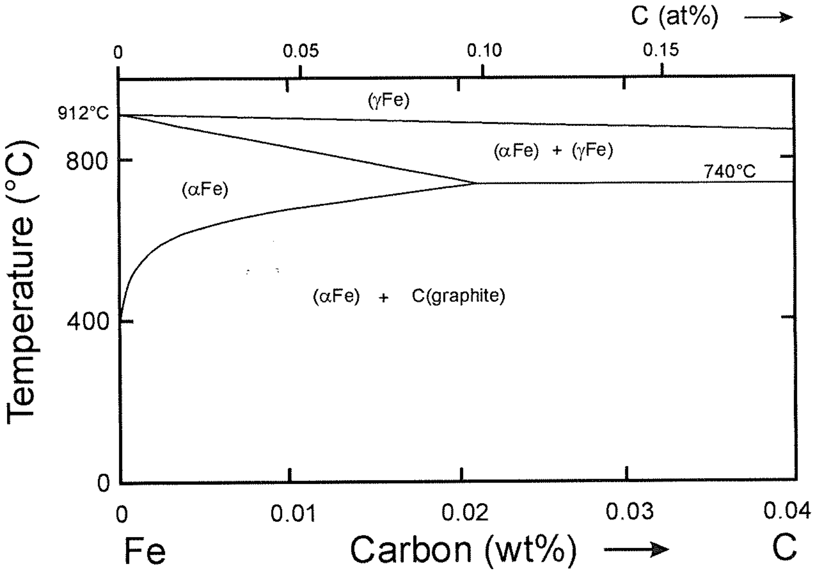

Figure 8.5. Partial equilibrium phase diagram for iron and carbon showing the expanded region around the lower temperature α phase of iron. The bottom scale is weight percent and the top scale is atomic percent. Adapted from ASM International (1992).

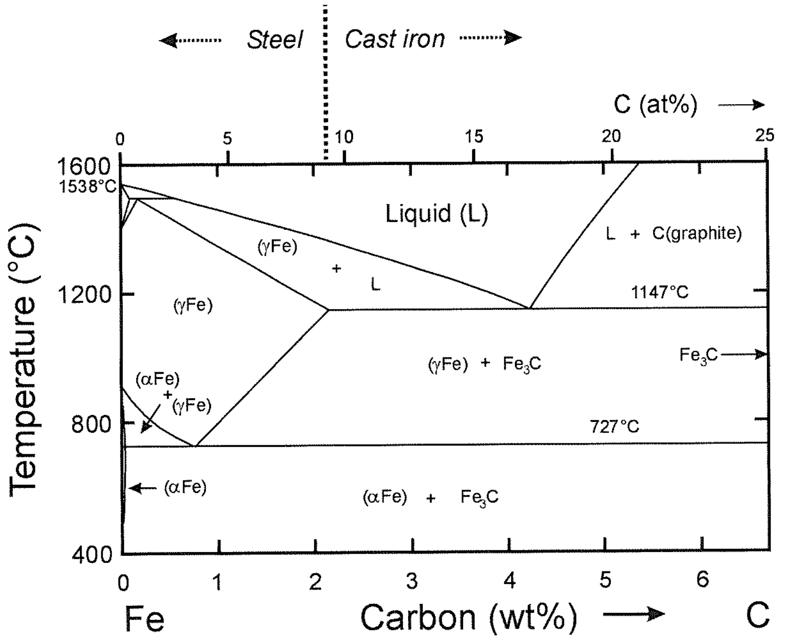

Figure 8.6. Partial equilibrium phase diagram for iron and carbon. Below 1147°C, carbon is present as metastable cementite rather than graphite. The bottom scale is weight percent and the top scale is atomic percent. Adapted from ASM International (1992).

right-hand edge of the partial iron–carbon phase diagram in Figure 8.6. It contains 6.67 wt% carbon, and is hard and brittle.

Graphite: This is elemental carbon with a layered structure. It is soft and can also form in certain iron alloys.

MICROSTRUCTURE OF IRON–CARBON PHASES

The physical and mechanical properties of iron–carbon alloys depend on their microstructure (i.e. the nature, distribution, and amounts of the constituents on a microscopic level) rather than their chemical composition on a macroscopic level. The important microstructures that can form in iron–carbon alloys are listed in Table 8.3.

TABLE 8.3. MICROSTRUCTURES OF IRON–CARBON ALLOYS

Name of microstructure	Chemical composition
pearlite	αFe + Fe_3C
martensite	αFe supersaturated with C
tempered martensite	αFe + Fe_3C

Most of the properties of steels are determined by the amount and distribution of the α phase of iron (α-ferrite) and cementite, although they may also be modified by other alloying elements.

Pearlite: Pearlite has a banded microstructure with alternating layers (of microscopic thickness) of α-ferrite and cementite. Under low magnification, it has an iridescent appearance similar to that of a pearl (hence the name pearlite). When iron containing exactly 0.76 wt% carbon is cooled slowly from slightly above 727°C (where austenite is the stable phase of carbon, see Figure 8.6), austenite transforms into pearlite (i.e. alternating layers of α-ferrite and cementite) as the temperature falls below 727°C. Pearlite always contains 0.76 wt% carbon (at least in iron–carbon alloys without additional alloying elements). When an iron–carbon alloy that contains less than 0.76 wt% carbon is cooled slowly from the austenite phase, the resulting microstructure consists of a mixture of α-ferrite and pearlite; as the carbon content increases, the relative amount of ferrite decreases and the amount of pearlite increases. When an iron–carbon alloy that contains more than 0.76 wt% carbon (up to about 2 wt% carbon) is cooled slowly from the austenite phase, the resulting microstructure is a mixture of pearlite and cementite; in this case, as the carbon content increases, the amount of pearlite decreases and the amount of cementite increases.

Martensite: Martensite is the α phase of iron supersaturated with carbon, and it has a needle-like structure. It forms when an iron–carbon alloy that contains up to about 2 wt% carbon (i.e. steels) is quenched (cooled rapidly) from high temperatures where austenite is stable to below about 150°C. The temperature drops so quickly that the metal does not have time to develop pearlite. Alloys with this microstructure are extremely hard (the higher the carbon content, the higher the hardness after quenching) and brittle, being easily shattered if shocked or hit with a hammer. They are usually too brittle to use without further treatment (i.e. tempering).

Tempered martensite: Tempering is a process in which quenched steels are reheated to reduce the brittleness induced by quenching and make the metal more workable. Martensite is tempered by reheating it to a temperature ranging from 170 to 700°C (the temperature is always kept below about 700°C to avoid transforming the alloy back into austenite), for a period ranging from a few minutes to several hours. Because any excess carbon precipitates as cementite during the reheating process, the resulting structure of the alloy is α-ferrite interspersed with small particles of cementite. Tempering decreases the hardness and increases the ductility of the alloy — the final hardness and ductility depending on the temperature and duration of reheating.

When traditional blacksmiths tempered steel, they judged the reheating temperature by watching for a characteristic colour on the metal surface. (This is possible because, during heating in the fire, the iron reacts with oxygen to form a thin film of iron oxides that produce different colours (i.e. interference colours) depending on the thickness of the film. For example, pale yellow appears at ~230°C (where the steel is suitable for planing tools), purple appears at ~270°C (where the steel is suitable for axes), and blue appears at ~300°C (where the steel is suitable for saws and springs).) Once the desired colour appeared, the piece was quenched to stop further microstructural changes.

Reference material: Barraclough (1991b); Maddin et al. (1977); Paxton (1997).

MODERN IRON ALLOYS

There are thousands of different iron alloys in use around the world today, and many of the major iron-producing countries have developed their own systems for classifying them. A cross-reference between the various systems can be found in ASM International (1990a). Table 8.4 lists the designations used in the UNS system for "ferrous metals and alloys."

TABLE 8.4. UNS DESIGNATIONS FOR "FERROUS METALS AND ALLOYS"

UNS	Description
D00001–D99999	specified mechanical properties steel
F00001–F99999	cast irons and cast steels
G00001–G99999	AISI* and SAE† carbon and alloy steels
H00001–H99999	AISI H-steels (heat-resistant)
J00001–J99999	cast steels (except tool steels)
K00001–K99999	miscellaneous steels and ferrous alloys
S00001–S99999	heat- and corrosion-resistant (stainless) steels
T00001–T99999	tool steels

*AISI stands for the American Iron and Steel Institute.
†SAE stands for the Society of Automotive Engineers.

Reference material: ASM International (1990a); ASTM (2001a); Society of Automotive Engineers (1989).

WROUGHT IRON

True wrought iron is characterized by the presence of slag. It was a readily available commercial product until the end of World War II, but today it is rare (if not impossible) to find. Modern blacksmiths must therefore use low-carbon steels (0.3 wt% carbon) that contain no slag as a substitute for true wrought iron.

STEELS

Steels are generally classified into carbon steels, alloy steels, and stainless steels, based on chemical composition. Within each of these groups there are many subdivisions based on chemical composition, physical or mechanical properties, or uses. Some of the different steels are described below.

Plain carbon steels: Plain carbon steels are iron–carbon alloys that contain few or no additional alloying elements (although they may contain traces of residual manganese, phosphorus, and sulphur). This group of steels is often subdivided into the three categories listed in Table 8.5.

TABLE 8.5. CARBON STEELS

Type of carbon steels	Carbon content (wt%)	UNS	Example of uses
low-carbon steel	0–0.3	G00001–G10290	car body panels, wire
medium-carbon steel	0.3–0.6	G10300–G10550	gears, rails
high-carbon steel	0.6–1	G10590–G10950	springs, strong wire

The low-carbon steels are often referred to as mild steels, and they are some of today's most widely used grades of steel. Steels must contain more than about 0.3 wt% carbon before they can be hardened by quenching.

Reference material: ASM International (1990a); Paxton (1997); Street and Alexander (1995).

Alloy steels: Alloy steels are iron–carbon alloys that contain additional alloying elements such as nickel, chromium, and molybdenum. The alloying content generally ranges from 2 wt% up to about 10 wt%. Alloy steels have better mechanical properties than plain carbon steels. They are usually listed under UNS Gxxxxx.

Reference material: Dulieu (1985); Keown (1985b).

Weathering steels: Weathering steels fall under the category of high-strength low-alloy steels (HSLA). The HSLA steels (also known as microalloyed steels) are low-carbon steels (0.05–0.25 wt% carbon) that contain up to 2 wt% manganese as well as small amounts of other alloying elements (e.g. copper, phosphorus, etc.). They have better mechanical properties and/or greater resistance to atmospheric corrosion than conventional low-carbon steels. Modern HSLA steels are subdivided into six categories, depending on their composition and properties. Weathering steels and other HSLA steels are usually listed under UNS Kxxxxx.

Weathering steels were the earliest of the HSLA steels, and were first developed around 1933 by the United States Steel Corporation. The first weathering steel was introduced as the proprietary steel Cor-Ten A, which is still available as UNS K11510 and is specified under ASTM A242, type 1; it contains a minimum of 0.20 wt% copper, and maximums of 0.15 wt% carbon, 1.00 wt% manganese, and 0.15 wt% phosphorus. Cor-Ten B, which contains less phosphorus (maximum 0.04 wt%) than Cor-Ten A, was introduced soon after; it is still available as UNS K11430 and is specified under ASTM A588, type A. Weathering steels have been used in architecture and for outdoor sculpture since the 1960s (e.g. the *Chicago Picasso,* designed by P. Picasso and made from weathering steel, was unveiled in 1967 in the Daley Plaza, Chicago). With good drainage and alternating periods of wet and dry, weathering steels can be more resistant to atmospheric corrosion than low-carbon steels. When exposed to an outdoor environment, they develop a thin, dark brown patina.

Reference material: ASM International (1990b); ASTM (2001b, 2001c); Dulieu (1985); Murata (2000); Scott (1993); Scott and Searls (1995).

Stainless steels: Stainless steels are iron-based alloys that contain at least 10.5 wt% chromium. The formation of an invisible and adherent surface film of chromium-rich oxide gives these steels their resistance to corrosion and their "stainless" or "rust-resistant" properties. The higher the chromium level, the greater the resistance to corrosion. Carbon is also normally present in stainless steels, in amounts ranging from less than 0.03 wt% to more than 1.0 wt%. Stainless steels were developed in England and Germany, starting around 1910. By the late 1920s, they were used for architectural purposes (e.g. the Chrysler Building and the Empire State Building in New York City) and can also be found in outdoor sculptures (see the example in Figure 8.7).

Figure 8.7. This stainless steel sphere, designed by artist Art Price for the 50th anniversary of the National Research Council of Canada (NRC), has been outdoors at the NRC in Ottawa since 1966. It is made from type 304 stainless steel (UNS S30400), measures 3.65 m (12 feet) in diameter, and weighs almost a tonne. Photograph by NRC (2002).

The phase of iron that is predominant in an iron-based alloy is influenced by the alloying elements that are present. Some elements (e.g. manganese, nickel, cobalt, copper, carbon, and nitrogen) stabilize the austenite phase and enlarge its area of stability in the phase diagram. Other elements (e.g. chromium, silicon, molybdenum, tungsten, vanadium, tin, niobium, phosphorus, aluminum, and titanium) stabilize the α-ferrite phase. In stainless steels, the temperature range over which the austenite phase exists diminishes as the amount of chromium increases, until it disappears at about 12 wt% chromium.

Stainless steels are classified by the phases that are present. Wrought stainless steels are usually listed under UNS Sxxxxx and cast stainless steels under UNS Jxxxxx. The five major families of stainless steels are listed in Table 8.6 along with an example of a UNS alloy and its composition within each family.

Ferritic stainless steels contain 12–30 wt% chromium and a minimum of elements that stabilize the austenite phase. The crystal structure of these steels remains bcc from room temperature through to the melting point. They cannot be hardened by heat treatment. The most common ferritic stainless steel is UNS S43000 (AISI type 430), which has been widely used for automotive and architectural trim.

Austenitic stainless steels contain nickel in addition to iron and chromium. The nickel content can be as high as 35 wt%, and the chromium content is usually in the range of 16–26 wt%. The nickel allows the austenite phase to exist down to ambient temperatures. These steels have a fcc crystal structure and are essentially non-magnetic. (They can develop slight magnetism after cold-working.) One widely used austenitic stainless steel is UNS S30400 (AISI type 304), which contains 18 wt% chromium and 8 wt% nickel and is sometimes referred to as 18-8. Two other important austenitic stainless steels are UNS S31600 (AISI type 316) and UNS S31700 (AISI type 317). These also have the basic 18-8 composition but they have additional molybdenum (2–4 wt%), which makes them more corrosion-resistant than UNS S30400.

Martensitic stainless steels also contain significant amounts of chromium (10.5–18 wt% chromium) and carbon, but are low in nickel. The martensitic structure is ensured by rapid cooling. In industry, the most widely used martensitic stainless steel is UNS S41000 (AISI type 410). Another common alloy, UNS S42000 (AISI type 420), is widely used for stainless steel cutlery.

TABLE 8.6. STAINLESS STEELS

Type of stainless steels	UNS examples	Magnetic	Chromium content (wt%)	Nickel content (wt%)
ferritic	S43000	yes	16.0–18.0	—
austenitic	S30400	no	18.0–20.0	8.0–10.5
martensitic	S41000	yes	11.5–13.5	—
duplex (ferritic–austenitic)	S32900	yes	23.0–28.0	2.5–5.0
precipitation-hardening	S13800	yes	12.25–13.25	7.5–8.5

Duplex stainless steels contain both austenite and ferrite, hence the term duplex. They have lower amounts of nickel than the austenitic stainless steels, so some of the austenite transforms to ferrite as the alloy cools. The alloying elements and heat treatments generally control the relative amounts of the two phases.

Precipitation-hardening stainless steels resemble the austenitic stainless steels in nickel and chromium composition, but they also contain small amounts of precipitation-hardening elements such as copper, aluminum, or titanium. These steels are heat-treated to increase their hardness.

Reference material: Jones et al. (2001); Paxton (1997); Score and Cohen (1995); Truman (1985); Washko and Aggen (1990).

Tool steels: Any steel used to make tools for cutting or forming is considered a tool steel, and most of the modern tool steels were developed during the early 20th century. The formation of carbides in tool steels provides them with hardness and wear-resistance. (These steels generally contain between 0.5 and 2 wt% carbon along with other alloying elements.) High speed tool steels, for example, contain relatively large amounts of carbide-forming elements such as tungsten, molybdenum, cobalt, vanadium, and chromium. A uniform distribution of small, hard, wear-resistant carbides is developed through various heat-treatment techniques, usually involving heating, quenching, and tempering. The carbides in tool steels are often fairly complicated carbides (e.g. chromium iron carbide). Tool steels are usually listed under UNS Txxxxx.

Reference material: Bayer and Walton (1990); Keown (1985a).

CAST IRONS

Cast irons are iron alloyed mainly with about 2–4 wt% carbon and 1–3 wt% silicon. Other elements, such as manganese, sulphur, phosphorus, chromium, nickel, molybdenum, and copper may also be added to alter specific properties (their primary effect is on the form the carbon takes as it precipitates during solidification).

Cast irons were historically classified on the basis of their fracture colour, which was largely determined by the form of the carbon that precipitated. For example, if the carbon precipitated as cementite, then the fractured surface was white and the alloy was classified as white cast iron; if the carbon precipitated as graphite, then the fractured surface was gray and the alloy was classified as gray cast iron. In contrast, modern cast irons are classified according to their microstructural features, and may be either gray, white, malleable, or ductile iron. Cast irons are usually listed under UNS Fxxxxx. A summary of cast irons is given in Table 8.7.

TABLE 8.7. CAST IRONS

Type of cast iron	Carbon content (wt%)	Silicon content (wt%)	Colour of fracture	Processing	UNS
gray	2.5–4.0	1.0–3.0	gray	alloy cooled slowly	F10001–F15501
white	1.8–3.6	0.5–1.9	white	alloy quenched	F45000–F45009
malleable	2.2–2.9	0.9–1.9	silver-gray	alloy quenched, then heat-treated to form graphite	F20000–F26230
ductile	3.0–4.0	1.8–2.8	silver-gray	additives introduced to molten iron before casting	F30000–F43030

Gray cast iron: In gray cast iron, most of the carbon precipitates as graphite in the form of flakes, and the microstructure is usually a mixture of pearlite and graphite. A fracture surface is gray because the break exposes the gray graphite flakes. The precipitation of graphite and the formation of gray cast iron is favoured by slow cooling and by higher concentrations of silicon (e.g. 3 wt%). Gray cast iron is brittle (although not as brittle as white cast irons), is easily machined because the graphite is soft, and is a good lubricant. It is widely used for machine components because it resists wear.

White cast iron: In white cast iron, most of the carbon precipitates as cementite, and the microstructure is usually a mixture of pearlite and cementite. A fracture surface is white because the break exposes cementite and pearlite grains. The precipitation of cementite and the formation of white cast iron is favoured by rapid cooling and by lower concentrations of silicon (e.g. 1 wt%). (Chilled cast iron is produced by the rapid cooling of large castings of gray cast iron; the rapid cooling produces white cast iron on the outside, but the cooling rate is usually not sufficient to alter the interior which forms gray cast iron.) Because cementite is extremely hard, white cast iron is hard and durable, although it is also brittle and difficult to drill or file.

Malleable cast iron: In malleable cast iron, most of the carbon is in the form of irregularly shaped nodules of graphite instead of flakes. Malleable iron is produced by first casting the iron as a white cast iron and then heat-treating it to convert the cementite into irregularly shaped nodules of graphite. Malleable cast irons have properties similar to ductile cast irons. Both are stronger, tougher, and more shock-resistant than ordinary gray cast iron. Modern malleable cast iron is often used for casting thin sections and for parts requiring maximum machinability.

Ductile cast iron: Ductile cast iron is also known as spheroidal graphite cast iron or nodular cast iron. It is produced by adding specific elements (e.g. cerium, magnesium) to the molten iron just prior to casting. The addition of these special agents promotes the formation of spheres of graphite rather than flakes. Modern uses include gears, crankshafts, and universal joints.

Reference material: Lepinski and Myers (1995); Stefanescu (1990).

ALUMINUM-PLATED IRON

The process of hot-dipping iron into molten aluminum to produce aluminized iron (also called aluminized steel) was developed in the 1940s. The resulting aluminum layer is metallurgically bonded to the underlying iron by the formation of intermetallic aluminum–iron compounds (e.g. FeAl). Aluminum and aluminum alloys can also be applied to iron by spraying, with the resulting coated iron being used commercially as a roofing material. The plating of iron with different aluminum–zinc alloys (e.g. trade names Aluzink, Galfan, Galvalume, Zincalume) began during the 1970s.

Reference material: Zahner (1995b).

CADMIUM-PLATED IRON

Cadmium can be electroplated onto iron, often with an electrolyte of cadmium cyanide (although other cadmium salts are being studied as replacements for this dangerous cyanide salt). It used to be common to plate steel fasteners with a thin layer of cadmium to provide corrosion protection, especially in industrial and marine applications. However, because of cadmium's toxicity, its use in plating is diminishing.

Reference material: Child (1993); Lewis (1988).

CHROME-PLATED IRON

Chrome is another name for the element chromium. Plating iron with a durable chromium layer was first carried out in the 1920s, and by the end of that decade the bright, non-tarnishing chrome-plated iron replaced the previously used nickel-plated iron for automobile trim. The electrolyte for chrome plating is usually chromium trioxide (also known as chromic acid), which is dangerous to human health due to the presence of hexavalent chromium. Because it is difficult to plate chromium directly onto iron, it is common for iron to be plated first with nickel (or copper, then nickel). This helps to level the iron surface and provides for better adhesion of the chrome plating. The chromium layer is typically thinner than the nickel layer (e.g. 25 μm nickel covered with 0.3 μm chromium).

Reference material: Child (1993); Lewis (1988).

COPPER-PLATED IRON

Over the years, a variety of methods have been used to plate copper onto iron. Early techniques included melting copper alloys on the surface of iron and dipping the object into molten copper alloys. Both of these methods produced a coherent coating on the iron, with the copper alloy being firmly bonded to the iron by intermetallic compounds. Copper and copper alloys are now usually applied to iron surfaces by electroplating. A brass (i.e. copper plus zinc) coating can be electrodeposited onto iron from an electrolyte containing both copper and zinc salts. Copper-plated iron can be easily patinated to resemble treated bronze objects.

Reference material: Child (1993); Corfield (1993).

NICKEL-PLATED IRON

It can be difficult to electroplate nickel directly onto iron. Sometimes it is necessary to first apply an intermediate layer of copper onto the iron to smooth out any irregularities in the surface, and then electroplate the nickel onto the copper. The copper bonds well with both the underlying steel and the overlying nickel.

Reference material: Child (1993); Lewis (1988).

SILVER-PLATED IRON

Silver can be firmly attached to iron if the iron is first dipped in molten tin, then covered with silver foil and reheated to melt the tin. This process, known as close plating, effectively solders the silver to the iron. Silver can also be electroplated onto iron. In this case the iron is first plated with copper or a copper alloy before the silver is applied. For more information on silver-plated iron, see "Chapter 11. Silver."

Reference material: Child (1993).

TERNE-PLATED IRON

Traditional terneplate is mild steel coated with a lead–tin alloy that contains about 15–20 wt% tin. This alloy contains sufficient tin to form tin–iron intermetallic compounds, thus providing a strong metallurgical bond between the alloy and the underlying steel. Terne-plated iron is often painted when used outdoors. Terne-coated stainless steels were introduced in the 1960s, typically using either UNS S30400 and UNS S31600 stainless steel. The main benefit of the terne coating on stainless steel is the dull silver-gray colour which is long-lasting outdoors. For more information on terneplate, see "Chapter 9. Lead."

Reference material: Zahner (1995b).

TIN-PLATED IRON

Tin-plated iron (also known as tinplate or tinned iron) has been around since about the 14th century. The tin is applied by dipping iron into a molten bath of tin, and the intermetallic compounds that form at the interface provide a strong bond between the iron and the tin. Tin-plated iron was popular as a roofing material in the late 1800s and early 1900s, and is still used today, especially for tin cans. For more information on tin-plated iron, see "Chapter 12. Tin."

ZINC-PLATED IRON

Iron surfaces covered with a zinc layer are known as galvanized iron or galvanized steel. The zinc is applied either by dipping the iron into molten zinc or by electroplating the zinc onto the iron. For more information on zinc-plated iron, see "Chapter 13. Zinc."

CORROSION

Iron and iron alloys become coated with a thin oxide film when exposed to a clean atmosphere at room temperature. Iron compounds normally contain iron in the +2 or +3 oxidation states. Many of the iron minerals and corrosion products discussed in this chapter are listed in Table 8.8.

TABLE 8.8. IRON MINERALS AND CORROSION PRODUCTS

Chemical name	Mineral name	Chemical formula	Colour*
iron(II) oxide	wüstite	FeO	gray-black
iron(II,III) oxide	magnetite	Fe_3O_4	black
iron(III) oxide	maghemite	γ-Fe_2O_3	red-brown
iron(III) oxide	hematite	α-Fe_2O_3	red, black
iron(III) hydroxide oxide†	goethite	α-$FeO(OH)$	yellow-brown
iron(III) hydroxide oxide†	akaganéite	β-$FeO(OH)$	yellow-brown
iron(III) hydroxide oxide†	lepidocrocite	γ-$FeO(OH)$	orange
iron(II) chloride	—	$FeCl_2$	white
iron(III) chloride	—	$FeCl_3$	green
iron(II) silicate	fayalite	Fe_2SiO_4	brown, black
iron(II) carbonate	siderite	$FeCO_3$	yellow-brown
iron(II) phosphate octahydrate	vivianite	$Fe_3(PO_4)_2{\bullet}8H_2O$	dark blue
iron(III) phosphate dihydrate	strengite	$FePO_4{\bullet}2H_2O$	pink
iron(II) sulphide	pyrrhotite	$Fe_{1-x}S$ ($x=0$–0.2)	yellow-brown
iron(II) sulphide	mackinawite	FeS_{1-x} ($x=0.01$–0.08)	yellow-brown
iron(II) sulphide	pyrite	FeS_2	yellow
iron(II,III) sulphide	greigite	Fe_3S_4	blue black
iron(II) sulphate tetrahydrate	rozenite	$FeSO_4{\bullet}4H_2O$	green
iron(II) sulphate pentahydrate	siderotil	$FeSO_4{\bullet}5H_2O$	white
iron(II) sulphate heptahydrate	melanterite	$FeSO_4{\bullet}7H_2O$	blue-green
iron(III) hydroxide sulphate dihydrate	butlerite	$Fe(OH)SO_4{\bullet}2H_2O$	orange
iron(III) potassium hydroxide sulphate	jarosite	$Fe_3K(OH)_6(SO_4)_2$	yellow-brown
iron(III) sodium hydroxide sulphate	natrojarosite	$Fe_3Na(OH)_6(SO_4)_2$	yellow-brown

* The colour of iron compounds varies depending on the size and shape of the particles. For example, small particles of hematite are red but large crystal are black (because they are strongly absorbing); large black hematite crystals (specularite) are often used in jewelry. The colour of iron compounds may also be influenced by the presence of both Fe^{2+} and Fe^{3+} in the compound. For example, pure iron(II) phosphate (vivianite) is white but it turns green and then dark blue on exposure to air as some Fe^{2+} ions are oxidized to Fe^{3+} (the colour change results from a charge transfer between Fe^{2+} and Fe^{3+} ions on adjacent sites).

† Also called iron oxyhydroxides.

Reference material: Cornell and Schwertmann (1996); Fell and Ward (1998); Graedel and Frankenthal (1990); Nassau (1983); Stolzenberg (1995).

SOLUTION CHEMISTRY

The principal oxidation states of iron are +2 (Fe^{2+}) and +3 (Fe^{3+}). When exposed to water, the initial anodic and cathodic half-reactions are usually given by:

Anodic half-reaction: $Fe(s) \rightarrow Fe^{2+} + 2e^-$
Cathodic half-reaction: $\frac{1}{2}O_2(g) + H_2O + 2e^- \rightarrow 2OH^-$
Net reaction: $Fe(s) + \frac{1}{2}O_2(g) + H_2O \rightarrow Fe^{2+} + 2OH^-$

The Fe^{2+} that results from this oxidation can then be further oxidized to Fe^{3+}.

Iron(II) ions undergo a stepwise series of hydrolysis reactions, the extent of which depends on the pH and ion concentration of the environment. Two possible Fe^{2+} hydrolysis reactions are given below:

$$Fe^{2+} + H_2O \rightarrow Fe(OH)^+ + H^+$$
$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2(s) + 2H^+$$

In the absence of dissolved oxygen and the presence of only hydrated iron(II) ions, the solution has a pale green or blue-green colour. Iron(II) ions remain in acidic solutions, but they are hydrolysed and precipitate as relatively unstable iron(II) hydroxide as the pH becomes more alkaline.

In the presence of dissolved oxygen, Fe^{2+} ions can be further oxidized to Fe^{3+} ions. However, because the rate of oxidation of Fe^{2+} ions to Fe^{3+} ions is slow in acidic solutions, the iron(II) ions can remain in solution for a long time even in the presence of dissolved oxygen if the pH is less than about 6. In extremely acidic conditions ($pH < 1$), the hydrated iron(III) ions are the predominant species; such solutions are purple. As the pH rises above 1, Fe^{3+} ions hydrolyse in a stepwise manner to give a series of hydrated species. Three examples are shown below.

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+$$
$$Fe^{3+} + 2H_2O \rightarrow Fe(OH)_2{}^+ + 2H^+$$
$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+$$

Solutions containing mainly $Fe(OH)^{2+}$ ions are yellow. When the pH is higher than about 6, iron(II) hydroxide is easily and rapidly oxidized and hydrolysed to iron(III) hydroxide. With time, this hydroxide transforms to one of several iron hydroxide oxides (e.g. goethite, lepidocrocite), of which goethite is the most stable one. These iron hydroxide oxides are the familiar red-brown rust on iron.

At moderate levels of dissolved oxygen, intermediate iron(II)–iron(III) compounds may precipitate. One example is black magnetite; others include the green rusts, named because of their bluish-green colour. These green rusts incorporate anions (e.g. carbonate ions, chloride ions, or sulphate ions) from the electrolyte into their layered structure.

At a pH higher than about 8, the surface of clean (bare) iron becomes passivated by the precipitation of iron hydroxides. These slowly convert to magnetite and iron hydroxide oxides, the presence of which reduces the corrosion rate of iron. This passivation of iron is more difficult in the presence of chloride ions because these ions interfere with the formation of the passive film; therefore, in the presence of chloride ions, a higher pH is needed for the iron to become passivated.

Solubility: Iron oxides, hydroxides, and hydroxide oxides have minimum solubility around pH 7–8. In general, the iron(II) oxides and hydroxides are more soluble than the iron(III) oxides, hydroxides, and hydroxide oxides. Reducing conditions enhance the solubility of Fe(III) oxides by promoting reduction of Fe^{3+} ions to the more soluble Fe^{2+} ions (i.e. reductive dissolution). Sodium dithionite (also called sodium hydrosulphite), a strong reducing agent, has been used in conjunction with a chelating agent (e.g. ethylenediaminetetraacetic acid, EDTA) to remove iron stains. The solubility of iron oxides is also enhanced by ions (e.g. citrates, oxalates) that form soluble complexes with Fe^{2+} or Fe^{3+} ions.

Reference material: Burgess (1991); Cornell and Schwertmann (1996); Day (1997); Gent and Rees (1994); Hawley et al. (1981); Matero and Tagle (1995); Misawa (1973); Pourbaix (1974); Refait and Génin (1993); Selwyn (1999); Selwyn et al. (2001); Stolzenberg (1995).

PATINATION

Various chemical processes can be used to change the surface colour on iron.

Bluing, browning, blacking: The iron in gun barrels and other firearms is usually darkened to reduce the reflection of light, enhance the appearance, and provide some corrosion resistance. An early approach to producing these dark colours was to heat the steel until a dark iron oxide formed (carbon steel turns brown at 250°C, dark blue at 315°C, and brownish-gray at 360°C). Another approach, employing chemicals to produce a blue, brown, or black coating on iron and steel, is still used today.

Reference material: Dunlap (1963); Fishlock (1962); Young and Fennell (1980); Zahner (1995a).

Bower-Barff process: This process produces an oxide layer of magnetite, and sometimes also black wüstite, on iron. Its development was begun by F.S. Barff, who patented a method for producing a protective, aesthetically pleasing black surface (the colour ranged from brown to black to blue-black) on iron in England in 1876. Barff's method was soon (1877) modified by G. Bower, and eventually became known as the Bower-Barff process. The procedure involves a special furnace in which clean iron or steel is first heated in contact with air. When the iron or steel turns dull or bright red, either superheated steam or a mixture of hydrogen and carbon dioxide gases is admitted into the furnace. The initial heating in air builds up a layer of rust, which is then reduced to magnetite by the superheated steam or gas mixture. The resulting hard magnetite layer is coherent enough to protect the underlying iron from corrosion. The durable, black layer produced by the Bower-Barff process has been used as a decorative finish on wrought iron, cast iron, and steel. On interior ornamental ironwork such as stairs, the black Bower-Barffed areas may be contrasted with other areas finished by electroplating with copper alloys and patinating. Evidence of magnetite, most likely produced by the Bower-Barff process, has recently been identified on exterior metal elements on the Library of Parliament in Ottawa.

Reference material: Cser et al. (2000); Goodway (1993); Matero (1994).

Tannic acid: In museums and conservation laboratories, iron is sometimes coated with tannic acid to give it an aesthetically pleasing blue-black colour. When tannic acid is applied to rusted iron metal, the metal corrodes — forming Fe^{2+} ions in solution. These react with the tannins in solution to form soluble, colourless iron(II) tannate complexes which are easily oxidized to insoluble, blue-black iron(III) tannates. Figure 8.8 contains an example of an iron(III) tannate complex. Because the tannic acid solution is acidic (typically pH 2–2.5), some of the rust dissolves, providing even more iron ions for complexing with the tannins. The overall reaction produces a blue-black iron tannate covering the surface of the rusted iron, changing it from a red-rust colour to a blue-black colour. However, because the iron(III) tannate layer has an open structure, it does not provide a continuous barrier. Therefore, if rusted iron is coated with tannic acid and then exposed to high RH levels or placed outdoors, the blue-black iron tannate will deteriorate quickly and the iron will rust.

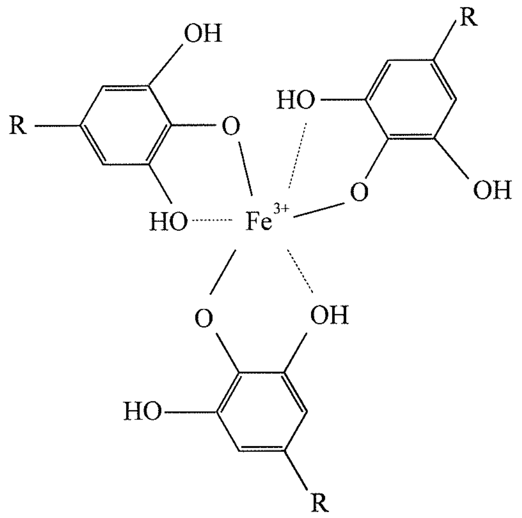

Figure 8.8. Schematic diagram of the blue-black iron(III) tannate structure where R represents the rest of the organic molecule in the tannin component. Adapted from Favre and Landolt (1993).

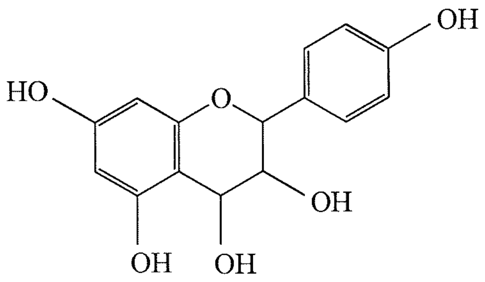

Figure 8.9. Schematic diagram of a building block for condensed tannins (chemical name 3,4 flavanediol). Adapted from Favre and Landolt (1993).

Note: The term "tannic acid" is poorly defined and is often used interchangeably with other terms such as tannins, tannin extracts, gallotannins, and gallotannic acid. Tannins are solids found in the bark, leaves, and fruit of many plants, and they can be extracted with hot water. Their chemistry is complex, but they are generally divided into two groups: condensed tannins and hydrolysable tannins. Hydrolysable tannins can be readily broken down into smaller recognizable groups (e.g. sugar, organic acid) by strong inorganic acids whereas condensed tannins cannot. Figure 8.9 contains an example of 3,4 flavanediol, a building block for condensed tannins. Figure 8.10 contains an example of corilagin, a simple hydrolysable tannin. Both groups have structures containing hydroxyl (i.e. OH groups) on adjacent carbon sites around six-membered aromatic rings (i.e. polyhydric phenols). The more important group is the hydrolysable tannin.

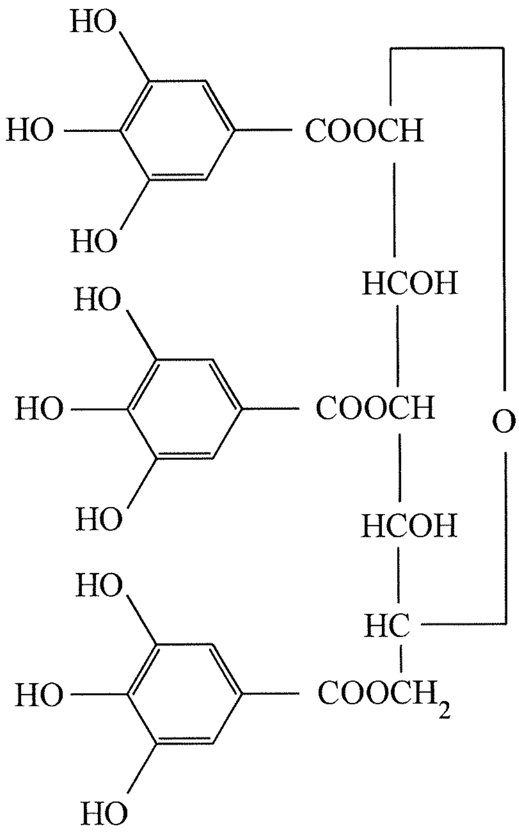

Figure 8.10. Schematic diagram of a simple hydrolysable tannin (chemical name corilagin). Adapted from Budavari (1996).

Commercially available "tannic acid" is a mixture of hydrolysable tannins and is usually listed as having an empirical formula $C_{76}H_{52}O_{46}$.

Reference material: Binnie et al. (1995); Budavari (1996); Canadian Conservation Institute (1997); Favre and Landolt (1993); Favre et al. (1998); Graedel and Frankenthal (1990).

INDOOR EXPOSURE

In a clean indoor environment, iron is generally covered with a thin oxide layer that is stable at RH levels below about 65%. However, if it is suddenly exposed to high moisture levels, it undergoes rapid rusting (i.e. flash rusting) and quickly becomes covered with bright orange rust (typically lepidocrocite) that forms at pH 5–7.5.
An example is shown in Figure 8.11.

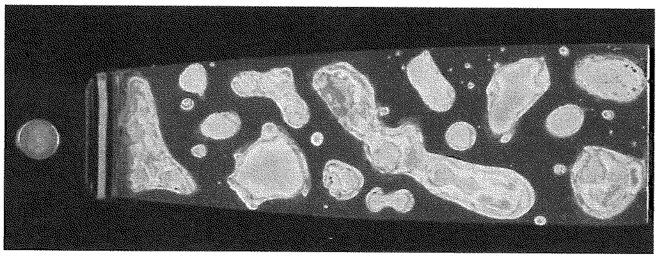

Figure 8.11. This putty knife exhibits the bright orange corrosion (lepidocrocite) that is typical of rapid rusting of iron (known as flash rusting). (A colour version of Figure 8.11 is available on p. 84.)

Rusting of iron may also be promoted if impurities such as dust, salts, and acidic pollutants are present in the indoor environment. All of these impurities can attract and trap moisture next to the metal surface, thereby promoting local corrosion. Salts, especially those containing chloride ions, contribute to corrosion because the chloride ions interfere with the formation of an oxide film. The chloride ions present in perspiration promote the formation of fingerprints on bare iron. Ammonium and sulphate ions, the most abundant ions in fine dust particles found in urban environments, also promote rusting — as do acids. For example, iron that is exposed to nitrogen oxides from degrading cellulose nitrate will corrode. The nitrogen oxides react with water to form nitric acid, which then reacts with iron to form hygroscopic iron(II) nitrates and iron(III) nitrates. Other acids, such as acetic acid (ethanoic acid), formic acid (methanoic acid), or sulphuric acid (from sulphur dioxide in the air) also contribute to iron corrosion.

Reference material: Corbeil and Moffatt (1996); Lee and Thickett (1996); Lobnig et al. (1993); Schwertmann and Cornell (1991); Stolzenberg (1995); Tennent et al. (1993); Williams (1994).

OUTDOOR EXPOSURE

Iron and carbon steels corrode quickly when exposed to humid air in an outdoor environment. The rust layer that develops is porous, poorly adherent, and often cracked. This corrosion will continue unabated unless the iron is protected with paint or plated with another metal. In general, carbon steels corrode faster outdoors than zinc, copper, or aluminum.

Iron develops a layered structure of corrosion products over time. There is an inner layer of magnetite along with other amorphous iron corrosion products, and an outer layer of iron hydroxide oxides, typically goethite and lepidocrocite. The main reduction reaction supporting iron corrosion is oxygen reduction. However, if the oxygen supply to the metal surface is restricted by a build-up of iron hydroxide oxides, other reduction reactions become important. One possibility is the reduction of Fe^{3+} ions in existing iron hydroxide oxides to form an intermediate phase similar to iron(II) hydroxide.

Pitting corrosion is one of the most common types of corrosion on outdoor iron and steels, and may rapidly perforate iron. Pitting involves the formation of small actively corroding pits or crevices; the solution in the pit is acidic which enhances pit growth. Chloride ions (which are present in marine environments, wherever de-icing salts are used on roads, and also in air pollution) play an important role in pitting corrosion.

Acidic air pollutants, especially sulphur dioxide, also accelerate the rusting of iron. Sulphur dioxide is a product of the iron-smelting industry as well as the burning of sulphur-containing fossil fuels, and it is readily adsorbed on metal surfaces and dissolved in water. Once dissolved, it is oxidized to sulphuric acid, which accelerates the corrosion of iron. The sulphate ions react with Fe^{2+} ions to form readily soluble iron(II) sulphate, which is hygroscopic and exists with different waters of hydration. The most common iron(II) sulphate identified on outdoor iron is rozenite. Iron sulphate can be oxidized and hydrolysed according to:

$$FeSO_4(s) + {}^1/_4O_2(g) + 1{}^1/_2H_2O \rightarrow FeO(OH)(s) + 2H^+ + SO_4^{2-}$$

This reaction results in the formation of iron hydroxide oxides and sulphuric acid. Sulphuric acid is hygroscopic and causes further corrosion of the iron. The sulphate ions can precipitate as relatively insoluble iron(III) hydroxide sulphates such as butlerite. If sodium or potassium ions are present in the surface water, natrojarosite or jarosite can precipitate.

Molten sulphur was sometimes used during the 19th and early 20th centuries to grout iron bars, rods, or cramps into masonry. This was not a good idea because elemental sulphur can be oxidized to sulphuric acid.

$$S(s) + 1^1/_2O_2(g) + H_2O \rightarrow 2H^+ + SO_4^{2-}$$

Therefore, mild steel in contact with wet elemental sulphur suffers severe corrosion.

Reference material: Graedel and Frankenthal (1990); MacDonald et al. (1978); Prytulak (1999); Stolzenberg (1995); Stratmann (1990); Stratmann and Müller (1994); Tullmin and Roberge (2000); Weaver (1993); Zahner (1995a).

Paint: One of the most practical ways to protect iron outdoors is to cover it with a continuous layer of paint or some other coating. These offer some protection, but are not true barriers to the penetration of moisture and oxygen. Over time, water and other ionic species gradually permeate the coating and the iron starts to rust. Another reason for paint failure is a failure of the bond between the primer and the metal caused by residual dirt, grease, and pollutants (especially chloride ions) that were not removed prior to painting. Also, two coats of paint are better than one (with a single coat of paint it is difficult to avoid small holes which allow localized corrosion of the underlying metal).

Reference material: Weaver (1993).

Phosphate coatings: The commercial use of phosphate coatings to protect iron and steel was developed in the early 1900s. Phosphate coatings are composed of crystalline metal phosphates that are formed intentionally on iron by treating it with a dilute solution containing phosphoric acid, soluble metal phosphate salts, and other chemicals. They are typically light to dark gray, and range in thickness from less than 3 μm up to about 50 μm. Their greatest use is as a base for painting; they promote good paint adhesion and help slow the spread of any corrosion that may occur. Phosphate coatings also provide temporary resistance to mild corrosion.

There are three principal kinds of phosphate coatings (zinc, iron, and manganese phosphates), all of which are produced by the same type of chemical reaction. The solutions used for phosphating contain phosphoric acid (typically 0.6–1.0% w/v) and one or more soluble metal phosphate salts. The acid in the solution reacts with the iron surface, causing a slight increase in the pH of the solution adjacent to the metal surface as the metal corrodes. As the pH increases, insoluble metal phosphates precipitate on the iron surface.

Phosphoric acid cleaners (as opposed to phosphating solutions discussed above) consist mainly of phosphoric acid (15–20% w/v). These cleaners are used to remove oil, grease, and rust, and provide a slight etch of the metal. The high concentration of phosphoric acid prevents the formation of any substantial phosphate coating.

Reference material: ASM International (1994); Narayanan (1994).

CORROSION DURING BURIAL

When iron corrodes during burial underground, its surface gradually becomes covered with insoluble iron corrosion products cemented with soil particles, dirt, clay, and sand. When it corrodes during burial in a marine environment, the surface gradually becomes covered with an insoluble concretion (primarily calcium carbonate) mixed with iron corrosion products. In both cases, the structure of the corroded archaeological iron is usually layered (shown schematically in Figure 8.12). The outer layer is a mixture of iron corrosion products (typically iron(III) hydroxide oxides) and extraneous material such as a concretion or small rocks, sand, clay, and soil minerals. The second layer contains iron corrosion products in a lower oxidation state, usually magnetite. Finally, the core is iron metal (unless the object is completely mineralized).

As the iron corrodes during burial, the anodic half-reaction takes place at the interface between the metal and its corrosion products (or beneath concretion in a marine environment). At this interface, iron(II) ions dissolve, accumulate, and undergo hydrolysis. These hydrolysis reactions cause local acidification (i.e. production of hydrogen ions) within the electrolyte filling the pores and cavities in the corrosion products. To maintain electrical neutrality, the charge of the Fe^{2+} cations is balanced by anions diffusing in from the surrounding environment. Chloride ions, in particular, tend to concentrate at the interface (partly because of their

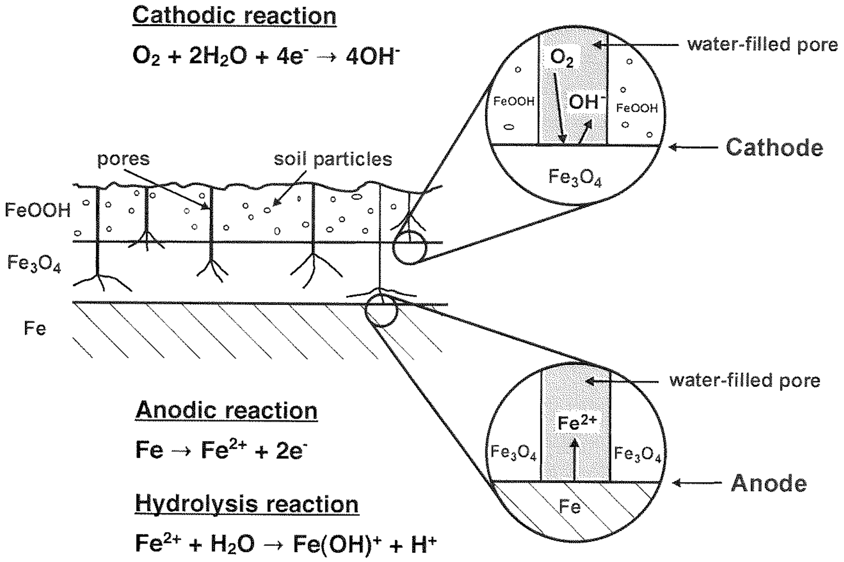

Figure 8.12. Schematic diagram showing the corrosion layers on buried iron as well as the separation of anodic and cathodic regions. Adapted from McNeil and Selwyn (2001).

high mobility and partly because they are often the predominant environmental anions, especially in a marine environment). The net result is that the cracks, pores, and open spaces within the corrosion layer on archaeological iron are filled with an acidic iron(II) chloride solution. The presence of this solution can have important consequences, especially after the object has been excavated.

Freshly excavated iron objects can be covered with a wide range of corrosion products that were thermodynamically stable under the conditions of burial but will not necessarily remain stable under the surface conditions.

Goethite and magnetite are two common iron oxides that form during burial, with the latter forming when the level of dissolved oxygen is low. (Hematite, which forms when goethite is heated, is sometimes identified on archaeological iron. However, it does not normally form as a corrosion product under burial conditions; its presence is usually attributed to an object being exposed to a fire before it was buried.)

The iron carbonate siderite and the iron phosphate vivianite are two more compounds that are commonly found on excavated iron. Both of these form under relatively reducing conditions: the carbonate forms when there are high levels of dissolved carbonate ions, and the phosphate forms when the iron is located near a source of phosphate ions such as bones in cemeteries, fish waste, or garbage dumps.

Other compounds that have been identified on excavated iron objects include the iron sulphides mackinawite, pyrite, and greigite, which form under anaerobic conditions in the presence of sulphate-reducing bacteria. Iron sulphides have also been identified on other archaeological materials (e.g. pyrite on waterlogged wood and pyrrhotite on a copper alloy), and elemental sulphur has been identified on waterlogged wood. Many of the iron sulphides, with their metallic lustre and yellow-brown colour, resemble gold. Pyrite and chalcopyrite, for example, are called "fool's gold" because of their gold-like appearance. A gold-like layer of pyrite or chalcopyrite on an object is often referred to as pseudogilding. It is sometimes difficult to tell if these sulphides have been intentionally applied (deliberate pseudogilding) or deposited during burial (microbiological pseudogilding). For more information on chalcopyrite and pseudogilding, see "Chapter 6. Copper."

Reference material: Duncan and Ganiaris (1987); Fell and Ward (1998); Matthiesen et al. (2003); McNeil and Little (1999); McNeil and Mohr (1993); McNeil and Selwyn (2001); Sandström et al. (2002); Selwyn (1999); Turgoose (1982a, 1985, 1993).

CORROSION AFTER EXCAVATION

When iron is excavated, its new surface environment usually has lower RH and more available oxygen than the burial environment. If the iron is allowed to dry, the acidic iron(II) chloride solution concentrates and the corrosion layers crack, making it easy for oxygen to reach the metal surface. Solids or ions in solution that were stable in the burial environment may no longer be stable after excavation, and may oxidize to new corrosion products or to new ions in solution. For example, the Fe^{2+} ions in solution may now be oxidized to Fe^{3+} ions and form new compounds. These transformations can cause chemical and/or physical damage to the object.

If an acidic solution of iron(II) chloride is exposed to air, the iron(II) ions in solution undergo oxidation to iron hydroxide oxides. Askey et al. (1993) proposed the following corrosion cycle for iron contaminated with an acidic chloride solution:

$$2Fe(s) + 4H^+ + 4Cl^- + O_2(g) \rightarrow 2Fe^{2+} + 4Cl^- + 2H_2O$$
$$2Fe^{2+} + 4Cl^- + 3H_2O + {}^1\!/_2O_2(g) \rightarrow 2FeO(OH)(s) + 4H^+ + 4Cl^-$$

The key factor in this cycle is that the salt that forms with chloride ions and iron(II) ions is soluble. It is this solubility that allows the cycle to continue; if the iron chloride salt was insoluble, it would precipitate and the cycle would be broken. The hydrogen ions formed by this oxidation reaction subsequently react with the iron causing chemical damage (they consume any remaining iron and can totally destroy an object).

Refait and Génin (1997) studied the oxidation of Fe^{2+} ions in the presence of chloride ions. They found that goethite and/or lepidocrocite precipitated at low chloride ion concentrations whereas akaganéite precipitated at high chloride ion concentrations. The structure of akaganéite is stabilized by chloride ions within tunnels, although this is not reflected in the chemical formula (usually written simply as β-FeO(OH)).

Along with the chemical damage caused by this corrosion cycle, there may also be physical damage. This occurs because the new solids (iron hydroxide oxides) that form within the surface corrosion layers have molar volumes that are about three times greater than the molar volume of iron metal. The objective of archaeological iron treatments is therefore to remove the acidic iron(II) chloride ion contamination, thus preventing the corrosion cycle and the formation of iron hydroxide oxides.

Archaeological iron that is suffering from chloride ion contamination exhibits various signs. Pieces of the corrosion crust may be pushed away from the surface by elongated corrosion particles close to the metal surface (an example of this is shown in Figure 8.13). These elongated particles of iron corrosion are usually akaganéite (see Figures 8.14 and 8.15), although, as demonstrated by Refait and Génin (1997), the newly formed iron corrosion products could also be goethite or lepidocrocite. The particles give the iron surface a "fuzzy" or "velvety" appearance. Their presence on archaeological iron indicates a high chloride ion level within the object, and is usually considered a symptom of active corrosion. Akaganéite has also been identified on corroding iron meteorites, indicating chloride ion contamination (which is usually attributed to exposure to chloride ions on earth).

Other symptoms of active corrosion on iron include wet areas of acidic liquid (i.e. weeping or sweating) or characteristic hollow red bubbles on the surface. Weeping is attributed to the hygroscopic nature of iron chloride salts. Iron(II) chloride and iron(III) chloride are both hygroscopic and form a series

Figure 8.13. The bright reddish-brown corrosion forming at the interface between metallic iron and the corrosion layer is evidence that this piece of iron is actively corroding due to chloride ion contamination. (A colour version of Figure 8.13 is available on p. 84.)

Figure 8.14. A magnified view (about x3) of the elongated particles of akaganéite (β-FeOOH) growing on the surface of a piece of archaeological iron. (A colour version of Figure 8.14 is available on p. 84.)

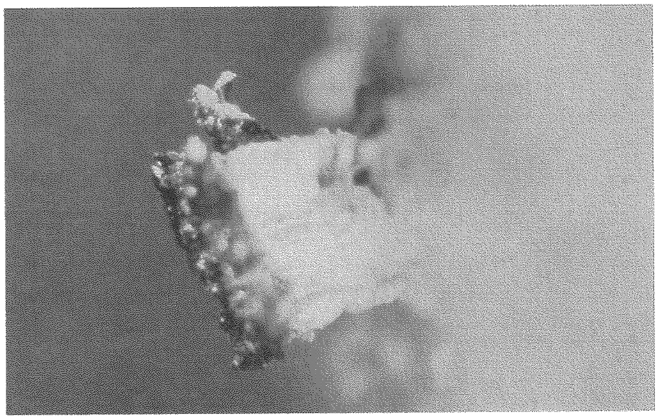

Figure 8.15. Detail of a single particle of akaganéite growing on archaeological iron and pushing off surface material. Magnification x16. (A colour version of Figure 8.15 is available on p. 85.)

of salts with different waters of hydration depending on the RH. Iron(II) chloride, for example, deliquesces above a RH of 56%. When the RH is high, these salts absorb water, dissolve, and form droplets of orange liquid. A skin forms on this liquid as iron(II) ions are oxidized to iron(III) ions which then precipitate as iron hydroxide oxides. As the RH decreases, the drops dry out and leave behind a shiny crust, or orange-brown blisters (bubbles). An example of droplets of moisture on archaeological iron is shown in Figure 8.16, and two examples of the hollow shells of weeping iron after the water has evaporated are shown in Figures 8.17 and 8.18.

In some cases, additional iron compounds form after archaeological objects are exposed to air. Strengite (an iron(III) phosphate) may form from the oxidation of vivianite (an iron(II) phosphate). Iron sulphates may also form from the oxidation of iron sulphides such as pyrite. The oxidation of pyrite has been referred to as "pyrite disease" when observed in geological and fossil collections. Above about 60% RH, pyrite is initially oxidized to iron sulphate. The following is a simplified description of the initial reaction of pyrite exposed to moist air:

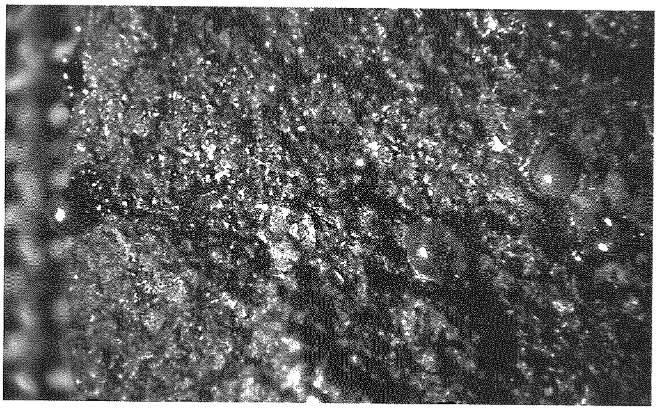

Figure 8.16. Spherical drops of liquid on the surface of archaeological iron are characteristic of weeping iron and active corrosion caused by chloride ion contamination. Magnification approximately x6. (A colour version of Figure 8.16 is available on p. 85.)

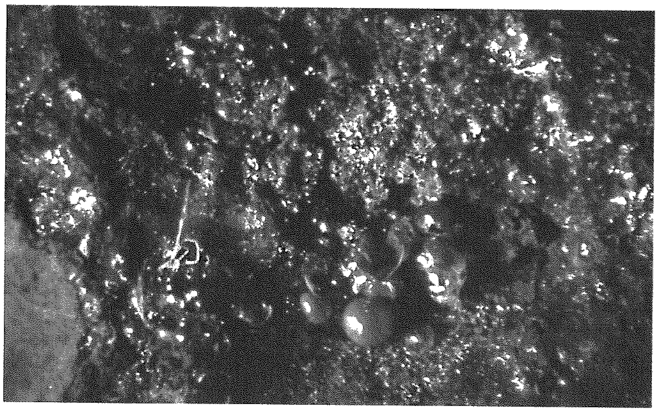

Figure 8.17. Hollow reddish-brown shells on archaeological iron are characteristic of weeping iron after the water has evaporated. Magnification about x9. (A colour version of Figure 8.17 is available on p. 85.)

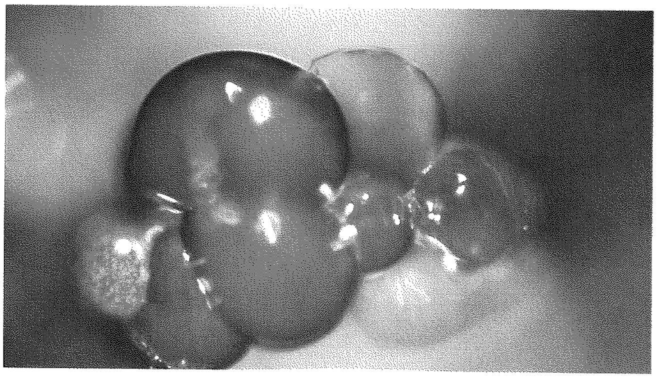

Figure 8.18. Detail of hollow shells characteristic of weeping iron on archaeological iron. Magnification about x25. (A colour version of Figure 8.18 is available on p. 85.)

$$2FeS_2(s) + 7O_2(g) + 2H_2O \rightarrow 2FeSO_4(s) + 4H^+ + 2SO_4^{2-}$$

This reaction produces an iron(II) sulphate (e.g. rozenite, siderotil, melanterite) and sulphuric acid. The iron(II) sulphates can be further oxidized to iron(III) hydroxide sulphates (e.g. butlerite, jarosite, natrojarosite). Sulphuric acid is damaging to the underlying iron (or other associated material) because, besides being an acid, it is also hygroscopic, picking up moisture even at low RH levels.

Reference material: Askey et al. (1993); Bevan (1992); Buchwald (1977); Buchwald and Clarke (1989); Fellowes and Hagan (2003); Howie (1992); Jespersen (1989); Knight (1990); Lowson (1982); MacLeod and Kenna (1991); McNeil and Selwyn (2001); Post and Buchwald (1991); Post et al. (2003); Refait and Génin (1997); Selwyn (1999); Selwyn et al. (1999); Ståhl et al. (2003); Stolzenberg (1995); Turgoose (1982b); Walker (2001).

GALVANIC CORROSION

Iron alloys can suffer galvanic (accelerated) corrosion if they are in direct contact with more noble metals such as copper alloys, stainless steels, lead alloys, or nickel. Galvanic corrosion can also occur if iron is exposed to water that is contaminated with ions of these more noble metals and becomes plated with them.

The wrought iron armatures inside the Statue of Liberty in New York City suffered galvanic corrosion because of direct contact between the iron and the more noble copper outer skin. The iron was attached to these external copper sheets with small copper pieces and copper rivets, and was surrounded by copper at the points of attachment. As iron corrosion products formed, they exerted pressure on the attachment points and pulled some of the copper rivets through the copper sheets, leaving holes. During a recent restoration, the iron armatures were replaced with stainless steel type 316L (UNS S31603) because of the similarity in electrochemical potential between the stainless steel and the copper.

Modern zinc-rich primers that are applied to iron contain fine metallic zinc particles that offer galvanic protection to the iron. These zinc-rich primers typically contain 85 wt% metallic zinc or more. When the primer is applied, the zinc particles and iron are in direct contact and act in a manner similar to the zinc layer on galvanized iron (i.e. the anodic zinc corrodes and protects the cathodic iron). Paint that is applied on top of a zinc-rich primer should not be oil- or alkyd-based, because these types of paints are prone to soap formation (between zinc and free fatty acids) which results in poor adhesion between the primer and the paint.

Reference material: Baboian (1990).

Plating: Iron is often plated with another metal to prevent, or at least slow, rusting. As long as the plating is continuous and adherent, it acts as a physical barrier that prevents water and oxygen from reaching the iron. However, if the plating is damaged or there are holes in it, galvanic corrosion can occur. Whether it is the iron or the plating that suffers the galvanic corrosion depends on whether the plating material is more active or less active than the underlying iron.

Plating metals that are more active than iron (e.g. aluminum, cadmium, zinc, tin) provide additional corrosion protection to iron. At any breaks in the coating, these active metals become anodic (corroding preferentially) while the underlying iron becomes cathodic (supporting reduction reactions). In other words, the more active metal coating serves as a sacrificial coating and provides cathodic protection to the underlying iron. For more information on the galvanic series and galvanic protection, see "Chapter 2. Corrosion."

However, metals plated onto iron and steels to provide a decorative surface (e.g. chromium, copper alloys, lead, nickel, silver, tin) are usually more noble than iron. These coatings provide a good barrier as long as they are continuous and adherent, but at any breaks they act as a cathode (supporting reduction reactions) while the underlying iron acts as an anode (and corrodes preferentially). In other words, the noble metals can accelerate the corrosion of iron and cause pitting, especially if there are only a few breaks in the plating layer. On steel coated with a lead–tin alloy (terne-coated steel), for example, corrosion of the underlying steel at small breaks in the coating results in red rust staining the dull gray terne coating. (However, under certain conditions, tin is more noble than iron; for more information, see "Chapter 12. Tin.")

Conducting iron oxides such as magnetite and wüstite can also act as cathodic (noble) materials on the surface of iron. Wüstite is the main iron oxide in mill scale, an adherent iron oxide layer formed on the outer surface of iron at high temperatures (e.g. during hot-rolling or forging). Magnetite was sometimes applied intentionally as a protective layer using the Bower-Barff process. Because iron is anodic (active) relative to these cathodic (noble) oxide coatings, any breaks in a layer of mill scale or magnetite on iron result in accelerated corrosion of the underlying iron.

Reference material: Ashurst and Ashurst (1988); Zahner (1995a).

FILIFORM CORROSION

Iron coated with a varnish or paint can suffer from filiform corrosion underneath the coating. This type of corrosion starts at a break in the coating and proceeds under it in relatively straight lines that have a hair-like or filamentary appearance. Under transparent varnishes on iron, the active heads of the filaments are filled with green-blue solutions and the tails are filled with red-brown corrosion products. The blue-green colour is characteristic of Fe^{2+} ions, which dissolve in the solution in the head as the iron corrodes. As the Fe^{2+} ions diffuse toward the back and encounter oxygen-rich areas, they are oxidized to Fe^{3+} ions and precipitate as the red-brown corrosion products (e.g. iron hydroxide oxides). Filiform corrosion is sometimes found on tintypes (photographs on lacquered iron).

Reference material: Fontana (1986); Ruggeri and Beck (1983).

CORROSION OF WEATHERING STEEL

Weathering steels are low-carbon steels with minor additions of other alloying elements (e.g. copper, phosphorus, manganese). When exposed outdoors, they develop a dense adherent oxide film that helps slow their rate of corrosion relative to plain carbon steels. The additional minor alloying elements have a beneficial effect in forming a rust layer that is a good barrier to both oxygen and water. However, the formation of this stable rust layer depends on alternating wet and dry cycles. If the weathering steel is submerged or buried, it will corrode at a rate similar to that for plain carbon steel. Outdoor sculptures made of weathering steel may suffer severe corrosion if the design includes areas where water is allowed to pool. Furthermore, water that runs over the weathering steel's surface can leave rust stains on adjacent materials such as stone bases or sidewalks.

Reference material: ASM International (1990b); Graedel and Frankenthal (1990); Scott (1993); Scott and Searls (1995); Zahner (1995a).

CORROSION OF IRON IN CONCRETE

Reinforced concrete was first developed in Europe in the late 19th century when steel wire was embedded in wet concrete to compensate for concrete's poor performance under tension. The alkaline (pH 12–13) conditions that normally exist within the concrete (concrete is alkaline because its pores are filled with a solution containing calcium, sodium, and potassium hydroxides) promote the formation of a passive layer on the reinforcing steel, making it quite resistant to corrosion. However, if this alkaline environment becomes contaminated with ions or acid that disturb the passivating layer, the iron will corrode. And because the corrosion products occupy a larger volume than the original iron, their formation causes the concrete to crack and spall.

When steel bars in concrete do corrode, the usual culprit is chloride ions. These may originate from de-icing salts or be a natural consequence of a marine environment, and they reach the embedded steel bars by diffusing through pores in the concrete. Because pore size plays an important role in determining how easily chloride ions and other dissolved gases can diffuse through concrete, it is an important determinant in how quickly embedded steel will corrode.

The normally passivating alkaline environment in concrete can also be changed to a corrosive environment by a process known as carbonation. Carbonation happens when carbon dioxide in the atmosphere reacts with water in concrete pores to form carbonic acid, which then neutralizes the alkaline hydroxides in the pore water. When enough carbon dioxide has dissolved and diffused inward, the pH at the iron surface falls to a level (below about pH 8) that allows corrosion to proceed. Carbonation becomes a significant problem when the concrete layer is thin or defective.

Reference material: American Concrete Institute (1997); Broomfield (1997, 2000); Craig (2001); Gayle and Look (1992).

CORROSION OF CAST IRON

Many cast iron architectural elements are hollow, and these can suffer serious damage if they are filled with concrete in an attempt to stabilize them. Such damage occurs because the concrete shrinks during curing and leaves a crevice that can trap water between it and the cast iron. The trapped water can then cause the iron to rust or, if it freezes (and expands), cause brittle cast iron to crack.

Some cast irons, especially gray cast iron, are susceptible to dealloying. This process is known as graphitic corrosion (replacing the older term graphitization) because the corroded surface has the appearance of graphite and can be easily cut with a knife. Graphitic corrosion occurs because the graphite flakes in gray cast iron are cathodic relative to the surrounding matrix of anodic iron (α-ferrite), so the iron corrodes selectively from the surface of the metal. Some of it is dissolved and diffuses away, and some of it precipitates as insoluble oxides and hydroxide oxides. The resulting graphitized layer is a mixture of porous iron corrosion products interlaced with flakes of graphite. Although it retains the shape of the object, it is soft and relatively easily damaged compared to the uncorroded hard core. Graphitic corrosion is common on gray cast iron recovered from seawater, and is occasionally found on outdoor unpainted cast iron pieces (especially on concealed surfaces where the iron stays wet).

Reference material: Craig (2001); Fontana (1986); Waite (1992).

CORROSION OF STAINLESS STEEL

Stainless steels are generally corrosion-resistant due to the passivating effects of a 2-nm-thick film of chromium-rich oxide. The presence of chromium in iron alloys is essential in the formation of this continuous, insoluble, and non-porous film, as is the presence of oxygen.

Although this passivating oxide film generally forms spontaneously on stainless steels in the presence of oxygen, industry uses a "passivation process" to ensure the formation of a good film. This process involves soaking the stainless steel in a warm nitric acid bath to remove dirt, iron particles, and other surface impurities left after processing (i.e. the main purpose of this passivation process is to clean the steel rather than to actually create the passive film). For example, when new stainless steel (UNS S31603, also known as type 316L) was being prepared for use during the restoration of the Statue of Liberty in New York City, it was passivated in a bath of about 20 wt% nitric acid for 30 minutes at about 35°C.

Stainless steels generally maintain their corrosion resistance in the presence of oxygen (e.g. air) because, if the film is scratched or damaged, the oxidizing conditions promote its re-formation. However, if the passivating film is restricted or prevented from re-forming, stainless steels can corrode — usually in localized areas beginning at non-metallic inclusions such as manganese sulphide (and sulphides are unavoidable contaminants in the steel-making process). Several forms of localized corrosion that may occur on stainless steels are discussed below.

Reference material: Einbinder (1990); Graedel and Frankenthal (1990); Score and Cohen (1995); Washko and Aggen (1990).

Pitting: Pitting corrosion is commonly initiated by chloride ions, which interfere with the formation of passive oxide films. It results from the combined action of aqueous chloride ions in the environment and manganese sulphide inclusions in the steel. Recent analytical studies have demonstrated that, during the processing of stainless steel, manganese sulphide inclusions become enriched in chromium and the areas surrounding the inclusions become depleted in it. It is in these chromium-depleted regions next to the manganese sulphide inclusions that pitting usually occurs. One sign of pitting is the formation of small rust spots on the surface of stainless steel.

Take, for example, outdoor stainless steel that is exposed to windblown material. As dirt builds up, it traps moisture and contaminants next to the metal surface, and also restricts oxygen. With limited oxygen, the stainless steel is unable to re-form its passivating oxide film if it becomes damaged by chloride ions (and the areas most affected are those in which chromium is limited to begin with). Without the passivating layer, pitting corrosion can proceed.

To maintain the original finish of stainless steel (especially if highly polished) and prevent localized corrosion, the steel must be kept clean. A common recommendation for maintaining stainless steel is routine cleaning with a mild detergent and warm water. This is especially important on outdoor stainless steel that is sheltered from regular washing by rain.

Some stainless steels are more resistant to pitting corrosion than others. For example, two popular stainless steels for architectural use outdoors are types 304 (UNS S30400) and 316 (UNS S31600). But type 316 is more corrosion-resistant (and more expensive) than type 304 in environments contaminated by chloride ions and industrial pollutants.

Reference material: Ryan et al. (2002); Waite (1992); Washko and Aggen (1990); Zahner (1995a).

Crevice corrosion: Stainless steel surfaces that are only partially covered (e.g. by dirt, a gasket, biofouling, or paint) may form an oxygen-depleted region under the covering if water penetrates the restricted area. If the passive film on the stainless steel surface is damaged (e.g. by chloride ions), the reduced-oxygen conditions in the restricted area will prevent it from re-forming in that region. When this happens, the well-aerated exposed area acts as a cathode (supporting oxygen reduction) while the oxygen-depleted region acts as an anode, leading to preferential corrosion within the crevice. Rust leaching out from a seam is visual evidence of crevice corrosion.

Reference material: Washko and Aggen (1990); Zahner (1995a).

Intergranular corrosion: Stainless steel that is welded is often susceptible to intergranular corrosion (i.e. preferential corrosion at grain boundaries). This happens because the heat used to weld stainless steel promotes the precipitation of carbon as chromium carbides, often at grain boundaries. As these chromium carbides form they deplete the chromium in adjacent areas, thereby reducing the ability of these areas to form a protective film. Local galvanic cells are then established between the cathodic (noble) carbides and the surrounding anodic (active) chromium-depleted iron. In stainless steel welds suffering from this type of corrosion, the grains have a sugary appearance as they are about to fall off. To counter this problem, low-carbon versions of stainless steel types 304 (UNS S30400) and 316 (UNS S31600) have been developed specifically for use where welding is required (the low carbon content minimizes chromium carbide formation). These have a maximum carbon content of 0.03 wt% and are designated type 304L (UNS S30403) and type 316L (UNS S31603).

Reference material: Fontana (1986); Jones et al. (2001); Zahner (1995a).

Stress corrosion cracking: The combination of stress and corrosion can cause cracking in susceptible stainless steels exposed to environments containing chloride ions. This type of corrosion usually results from precipitation of chromium-rich carbides at grain boundaries and, as in intergranular corrosion, the grain-boundary composition plays a dominant role in its formation. Austenitic stainless steels are susceptible to stress corrosion cracking, but most ferritic and duplex stainless steels are not.

Reference material: Jones et al. (2001); Washko and Aggen (1990).

Galvanic corrosion: Stainless steel is generally corrosion-resistant due to its chromium-rich oxide film. As long as the film is present, stainless steel remains noble relative to most common metals. For more information, see the discussion on the galvanic series of metals in seawater in "Chapter 2. Corrosion."

In most cases, contact between passivated stainless steel and other metals results in accelerated corrosion of the other metal. For example, if small iron particles become imbedded in stainless steel (e.g. by cleaning with steel wool or a steel brush), it is the more active (anodic) iron pieces that rust and stain the stainless steel surface.

However, the situation is different if the stainless steel is damaged (i.e. has lost its passivating layer). In this case, when it comes in contact with common metals such as lead, nickel, or copper alloys, it acquires its "active" potential and becomes susceptible to galvanic (accelerated) corrosion.

Reference material: Score and Cohen (1995); Waite (1992); Zahner (1995a, 1995b).

APPENDIX 4: IRON

MANUFACTURING TECHNIQUES

WROUGHT IRON

Wrought iron can be made directly or indirectly. It was first produced in Europe about 1000 B.C. using a direct bloomery process, i.e. iron ore was reduced directly to iron (called bloomery iron) in a furnace and then converted to wrought iron by forging. This process was used until sometime around the 15th century, when an indirect process that involved burning off the carbon in cast iron was developed. Both processes were used from the 15th century until the early 18th century, when the direct process was more or less abandoned.

Direct bloomery process: The bloomery process involved only one step — crushed iron ore was mixed with charcoal and heated in a furnace. The carbon then reacted with the iron oxides in the ore, reducing them to iron metal:

$$FeO(s) + C(s) \rightarrow Fe(s) + CO(g)$$

Bloomery furnaces could be either simple (700–1000°C) or more complicated (1100–1200°C), but in neither case was the resulting iron melted (the melting point of iron is 1538°C). Instead, the iron ores were reduced to a spongy mass of iron (called a bloom) mixed with iron oxide and iron silicate slag. Blacksmiths used this iron bloom as their raw material. They reheated it in a forge, repeatedly hammering it and heating it to drive off excess iron oxide and slag. The hammering also turned the porous iron bloom into wrought iron, a continuous network of iron interspersed with stringers of residual glass-like slag. This residual slag gave wrought iron its characteristic fibrous or wood-like structure.

Indirect process (finery): In contrast to the direct bloomery process, the indirect finery process involved two steps. First, the iron ore was smelted in a blast furnace where newly formed iron particles absorbed enough carbon (around 4 wt%) from the fuel to melt and form pig iron (cast iron). Next, the pig iron was refined in a finery (a hearth for converting cast iron into wrought iron); small pieces of the pig iron were then remelted and exposed to air for about 2 days to remove as much carbon as possible. High temperatures, typically 1300–1350°C, were needed to melt the iron and these temperatures could be reached in a charcoal-fired hearth, with air blown in from bellows.

The carbon was gradually removed from the pig iron (i.e. the pig iron was decarburized) as it reacted with the oxygen in air to form carbon monoxide, which escaped from the molten metal as a gas. The carbon monoxide then burnt in air with a blue flame as it was further oxidized to carbon dioxide. As the carbon content decreased, the metal's melting point increased. Eventually, almost carbon-free iron separated out as a solid conglomerate of metal plus slag, similar to that produced by the direct bloomery process. This pasty mass was then removed from the furnace and forged to expel most of the slag and consolidate the metal into wrought iron.

Initially, some of the iron was oxidized to iron(II) oxide:

$$2Fe(s) + O_2(g) \rightarrow 2FeO(s)$$

The iron oxide then reacted with the impurity elements in the alloy, such as carbon, manganese, silicon, and phosphorus, to form various oxides:

$$\begin{gathered} FeO(s) + Mn(s) \rightarrow Fe(s) + MnO(s) \\ 2FeO(s) + Si(s) \rightarrow 2Fe(s) + SiO_2(s) \\ FeO(s) + C(s) \rightarrow Fe(s) + CO(g) \\ 5FeO(s) + 2P(s) \rightarrow 5Fe(s) + P_2O_5(s) \end{gathered}$$

The silica then reacted with the other oxides to form various silicates:

$$\begin{gathered} 2MnO(s) + SiO_2(s) \rightarrow Mn_2SiO_4(s) \\ 2FeO(s) + SiO_2(s) \rightarrow Fe_2SiO_4(s) \\ 3FeO(s) + P_2O_5(s) \rightarrow Fe_3P_2O_8(s) \end{gathered}$$

These silicates were removed in the slag.

Indirect process (puddling): The production of wrought iron increased following the development of the puddling process by H. Cort in 1784. At this time, the use of charcoal for fuel had diminished and pig iron was being produced by smelting iron ore with coke. But pig iron produced by smelting with coke contained more impurities (e.g. phosphorus) than pig iron produced by smelting with charcoal. The high levels of impurities made any resulting wrought iron so brittle that it crumbled under the hammer. The puddling process solved this problem by providing a new and efficient method for converting the contaminated pig iron to wrought iron. Fuel was burned on a separate hearth in a reverberatory furnace to provide the heat necessary for the melting of the pig iron. (A reverberatory furnace has a curved room that deflects heat so that the fuel is not in direct contact with the ore; the first reverberatory furnaces were developed in 1612.) The puddler used a long iron bar with an oar-shaped end to turn and stir the molten mass, exposing the metal to air that slowly removed the carbon. The molten metal turned into a white hot spongy lump which was then dragged from the furnace and rolled or hammered to squeeze out most of the slag. Wrought iron made by this indirect process was used to construct the internal armature in the Statue of Liberty in New York City, unveiled in 1886.

Reference material: Barraclough (1991a, 1991b); Goodway (1990); Habashi (1999); Raymond (1984); Schubert (1958); Tylecote (1991).

STEELS

Steels are iron–carbon alloys that contain 1–3 wt% carbon. The earliest versions were hard and tough, and were used to make articles such as knives, swords, tools, and springs. Steel remained expensive and was produced only on a small scale up until the Industrial Revolution. The early methods for making steels (in which the alloy was not melted) produced products that contained a non-uniform distribution of carbon in the iron. The earliest of the alloy steels (a high-carbon manganese steel) was prepared by R.F. Mushet in 1830. L. Guillet introduced stainless steels in the early 1900s after studying iron alloyed with chromium, nickel, and other elements.

Early methods: Iron has been intentionally "steeled" or "carburized" to make it stronger since about 1200 B.C. Early methods involved reheating wrought iron in white-hot charcoal, which allowed the carbon from the charcoal to diffuse into the surface layer of the iron and turn it into steel. The resulting metal retained a sharper cutting edge than wrought iron. Edges on tools could be further hardened by quenching after heating in hot charcoal — a process that produced a thin hard skin of steel around the softer iron inside, and became known as case-hardening.

Cementation process (blister steel): The cementation process for making small quantities of steel from wrought iron was patented in England in 1614. This procedure was carried out by placing a mixture of wrought iron pieces and finely divided charcoal into closed pots and heating them to high temperature for several days, allowing the carbon to diffuse into the iron and form a hard surface layer of steel. However, as the carbon diffused in, it reacted with residual iron oxide in the slag to form carbon monoxide gas, which bubbled to the surface. This created blisters on the surface, and the product became known as blister steel.

Crucible process (crucible or cast steel): The crucible process for making steel was invented by B. Huntsman in 1740. This procedure produced a more homogeneous steel than had previously been possible. In this case, clay crucibles were charged with a mixture of blister steel and a flux, then covered and placed into a coke-fired furnace (~1550°C). Because this temperature was high enough to melt the mixture, it produced a steel with an even, homogeneous distribution of carbon in the iron. The molten metal was then poured into narrow moulds and the resulting product was called crucible or cast steel.

Bessemer process: This procedure was introduced by H. Bessemer in 1856. By using high temperatures and a controlled introduction of air at the bottom of molten iron in a converter, Bessemer was able to rapidly remove the carbon from pig iron. Bessemer converters resembled huge concrete mixers; they could be tilted to receive molten pig iron and then brought upright so that air could be blown through holes in the base. After the carbon was removed, the still molten metal was transferred to another container and additions (e.g. carbon, manganese) were made to remove residual oxides and bring the steel to the desired composition. The introduction of the Bessemer process marked the first time that steel could be produced cheaply and in large quantity.

Open-hearth process: In this steel-making process, introduced in 1861, pig iron was heated in an open-hearth furnace using fuel, and carbon was removed with iron oxides.

Oxygen process: The oxygen steel-making process uses pure oxygen to refine molten pig iron. Modern steel has been made in this manner since about 1970.

Reference material: Barraclough (1991b); Habashi (1999); Lambert (1997); Maddin et al. (1977); Paxton (1997); Raymond (1984); Schubert (1958); Street and Alexander (1995); Tylecote (1991).

CAST IRON

Archaeological evidence shows that the technology to produce cast iron existed in China by the 3rd century B.C. However, it wasn't until the development of blast furnaces (the earliest known water-powered blast furnace began operating in Italy in 1463) that cast iron was mass-produced in Europe. Rapid developments in furnace technology and iron production followed during the Industrial Revolution (~1750 to ~1850).

Blast furnace: In a blast furnace, a blast of air is forced through the bottom of a charge (a mixture of iron ore, fuel, flux) through nozzles called tuyeres. This blast of air enables the burning fuel to reach a higher temperature. The combustion of carbon is accompanied by the formation of carbon monoxide, which reduces the iron oxide and other metal oxides in the ore back to metal. For example,

$$FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$$

Because the newly formed iron particles are in contact with excess carbon, the hot iron absorbs some of it. Eventually, when enough carbon is absorbed to form molten metal, it collects at the base of the furnace. (Iron containing 4.27 wt% carbon melts at 1153°C, which is significantly lower than the temperature at which pure iron melts (1538°C).) The molten metal is poured into blocks or small bars connected by runners (called pig iron) or into desired shapes (called cast iron).

The early production of cast iron in blast furnaces was wasteful because many of the iron compounds in the ore combined with silica in the gangue material instead of being converted to metal. Eventually, however, it was found that if limestone was added to the contents of the furnace, it would combine with the gangue minerals to form a molten slag — thus leaving the iron compounds free to be converted to metal. The newly created molten slag, being lighter than the molten iron, could then be run off separately.

When England experienced a wood shortage early in the 17th century, it became necessary to smelt iron ore with coal instead of charcoal. But early attempts were unsuccessful because sulphur in the coal contaminated the iron. This problem was overcome in 1709 by A. Darby. By converting coal to coke before mixing it with iron ore in a blast furnace, Darby became the first man to make good quality pig iron with fuel made from coal rather than wood. However, coke-smelted pig iron contained higher impurity levels than charcoal-smelted pig iron, making it more difficult to refine.

Reference material: Barraclough (1991a); Raymond (1984); Schubert (1958); Tylecote (1991).

9

LEAD (Pb)

Principal oxidation number(s)	Atomic weight (g mol^{-1})	Density at 20°C (g cm^{-3})	Melting point (°C)	Boiling point (°C)	Linear expansivity (°C^{-1})	UNS range for alloys
Pb^{2+} (plumbous) Pb^{4+} (plumbic)	207.19	11.35	327	1749	28.9×10^{-6}	L50001– L59999

GENERAL DESCRIPTION

Lead is the heaviest common metal. Bluish-gray in colour, it is non-magnetic, very soft (it can be easily scratched with a fingernail — making it difficult to clean the surface of lead mechanically without damaging it), and quite resistant to corrosion. It has a low melting point, a high boiling point, and is flexible enough to withstand small movements. One of its distinguishing features is the ability of a freshly exposed lead surface to leave a black mark when rubbed onto white paper. (Early pencils were made with "black lead" or "plumbago," a mineral thought to be a form of lead but later identified as graphite, a form of carbon.) Lead is easily alloyed with many other metals to make low-melting lead alloys which are easy to cast.

For more information about lead, see the Web sites of the Lead Development Association International (www.ldaint.org) and the Lead Industries Association (www.leadinfo.com).

Reference material: Gayle and Look (1992); Goodwin (2000); Prengaman (1995).

ORIGIN

Lead is rarely found in the metallic (native) state, but is easily extracted from minerals such as galena, cerussite, and anglesite. In ancient times, the principal sources of lead were mines in Greece, Spain, and Britain. Today, lead comes mainly from Australia, the United States, Canada, and China. In Canada, lead–zinc ores were first discovered (in British Columbia) in the 1820s, and by 1900 the production of lead had begun with ore from the Sullivan mine near Kimberley, BC.

Reference material: Lambert (1997); Street and Alexander (1995); Willies (1991).

USE

Lead is one of the oldest known metals, and has been used in a variety of ways since well before 3000 B.C. The Romans employed it for water pipes. It has appeared as a roofing material — although it is so heavy that steep roofs are subject to creep (slow flow by gravity) and lead sheets are subject to tearing when exposed to extreme temperature fluctuations. Cast lead was popular for garden ornaments in England during the late 17th and 18th centuries; some of it was even gilded. Lead can also be found in statues, fountains, decorative and utilitarian items (e.g. toy soldiers, coins, tokens, seals, medals, toys, ship model accessories, jewelry), printing type, textiles weighted or coloured with lead-based compounds, stained glass windows (with lead cames), weights (used in conservation and containing lead shot), and pewter. Lead, lead–tin alloys, or tin-coated lead were also used in many early collapsible metal tubes (e.g. toothpaste, paint). Today, because of environmental hazards, lead is sometimes replaced with other metals. The current principal uses of lead alloys include lead–acid batteries, ammunition, and building construction materials (e.g. roofing, solders).

Reference material: Ashurst and Ashurst (1988a, 1988b); Gayle and Look (1992); Naylor (1983); Vogel and Achilles (1993); Zahner (1995a).

PIGMENTS

Many lead compounds are intensely coloured (e.g. white lead (hydrocerussite), red lead (minium), yellow lead (massicot), and blue lead (galena)), and have been used as pigments in paint. Historic buildings and industrial equipment are often covered with paints containing lead pigments (e.g. red, blue, white, or yellow lead), and many older paintings contain a white lead ground layer.

White lead: White lead (cerussa) is considered the most important of all the lead pigments. In use since late classical times, it has until recently been one of the main white pigments used on easel paintings. (Between 1950 and the late 1970s, the use of lead-containing pigments in paints decreased significantly. Canada introduced legislation in 1976 that limited the amount of lead in consumer paints to 0.5 wt% of the dried paint film.) Pure white lead pigment is lead carbonate hydroxide (also called basic lead carbonate), which occurs in nature as the mineral hydrocerussite. Over the years, a range of processes have been used to make white lead. Until the 19th century, classic white lead was produced mainly by the stack (or Dutch) process where pots containing lead metal and acetic acid were stacked in a warm atmosphere containing carbon dioxide generated from the fermentation of bark. More recently, other processes have been developed to speed up the reactions producing white lead. When made by these various (relatively uncontrolled) processes, white lead may also contain other lead carbonates (because the carbonate that precipitates depends on the local pH).

Reference material: Dunn (1975); Fitzhugh (1986); Gettens and Stout (1966); Gettens et al. (1967); Greninger et al. (197-); Keisch (1971); Kühn (1968); Olby (1966); Shoesmith et al. (1988); Wainwright et al. (1986).

DRIERS

Lead soaps (i.e. lead salts of fatty acids) such as lead stearate and lead oleate are often used as driers in paint (they have good solubility in oil, thus creating an abundance of lead ions that catalyse the drying process). Lead compounds such as lead monoxides have also been used as driers; these react with traces of free fatty acids (e.g. linoleic acid) in an oil to form oil-soluble soaps (e.g. lead linoleate).

Reference material: Carr et al. (1995); Gettens and Stout (1966); Greninger et al. (197-); Landau (1993); Wicks (1993).

ALLOYS AND PLATING

LEAD–ANTIMONY ALLOYS

Lead–antimony alloys, typically containing up to 11 wt% antimony, are the most widely used of modern lead alloys. The lowest-melting-point (eutectic) mixture of lead and antimony contains 11 wt% antimony and melts at 252°C. Such alloys are used in lead–acid batteries, lead shot, and cable sheathing.

Type metal: The printing process using metal type was perfected in Germany in the mid 1450s by J. Gutenberg, who printed the first major European book — the Gutenberg Bible. Since that time, print makers have used low-melting lead alloys (known as type metal) to cast letters. Casting of printing type is done by pouring a molten metal into a permanent mould (die casting) to form the letters, numbers, and symbols used in the printing process. Modern type is lead alloyed with 10–25 wt% antimony and 3–14 wt% tin. By varying the tin and antimony content, type can be obtained that is particularly suited for the desired printing process. Linotype metal, for example, contains 86 wt% lead, 11 wt% antimony, and 3 wt% tin, and melts around 247°C.

Reference material: Gaver (1997); Prengaman (1995).

LEAD–TIN ALLOYS

Lead and tin are not readily soluble in one another at room temperature, as can be seen in the phase diagram for lead–tin alloys that is shown in Figure 9.1. When the two metals are melted together and then cooled, the solid consists of two phases — one that is rich in tin and one that is rich in lead. The eutectic lead–tin mixture contains 61.9 wt% tin and 38.1 wt% lead, and melts at 183°C. Lead–tin alloys have traditionally been used as solders and as a plating material called terne. The alloys that are rich in lead are generally more susceptible to corrosion than the tin-rich ones.

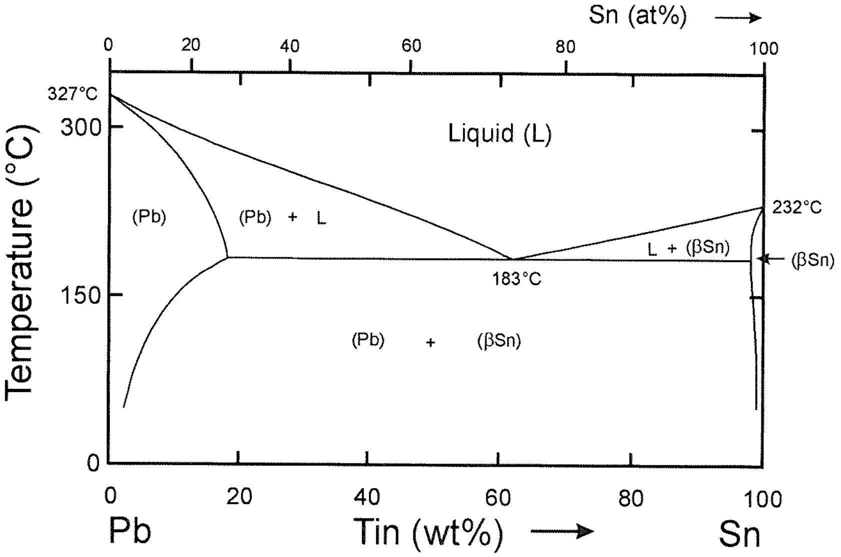

Figure 9.1. Equilibrium phase diagram for lead and tin. The bottom scale is weight percent and the top scale is atomic percent. Adapted from ASM International (1992).

Reference material: ASM International (1992).

Pewter: One common use for tin–lead alloys is the production of pewter. More information about pewter can be found in "Chapter 12. Tin."

Solder: Metal pieces can be joined together by soldering them with an alloy that has a lower melting temperature than they do. Most alloys used as low-melting solders (i.e. alloys melting below 450°C) are mixtures of lead and tin, although small amounts of other elements (e.g. bismuth, cadmium, silver, and antimony) may also be present. The tin component in the alloy reacts with the metals to be joined to form a metallurgical bond. Solder joins are relatively weak because the solder and the base metal do not diffuse significantly into one another. To a certain extent, the thinner the solder deposit, the stronger the join. The low surface tension of the tin in solder helps to wet the metals being joined. Some examples of lead–tin solders are given in Table 9.1.

Plumbing systems are often soldered with lead–tin alloys such as L54915 and L55030. These solders have wide melting ranges which enable joins to be worked or positioned as the solder solidifies. For plumbing systems that involve drinking water, lead-free solders are now recommended; examples include tin–antimony solder (UNS number L13950: 95 wt% tin, 5 wt% antimony, melts at 233–240°C) and tin–silver solder (UNS number L13960: 95 wt% tin, 5 wt% silver, melts at 221–245°C).

During soldering, a flux is used to remove residual surface oxides, prevent oxidation of the metal during heating, and reduce the surface tension of molten solder. Most inorganic fluxes are a combination of a salt (e.g. zinc chloride, stannous chloride, or ammonium chloride) and an acid (e.g. hydrochloric acid) and must be removed after soldering to prevent subsequent metal corrosion.

TABLE 9.1. LEAD-TIN SOLDERS

Lead (wt%)	Tin (wt%)	Melting range (°C)	UNS number	Uses
95	5	270–312	L54320	coating and joining metals
80	20	183–277	L54710	filling seams in car bodies
65	35	183–247	L54850	general purpose
60	40	183–238	L54915	wiping solder for joining lead
50	50	183–216	L55030	general plumbing

Pieces of lead can also be joined by lead burning. This process does not require solder or a flux; it is accomplished by heating the edges of the lead pieces until local melting allows the formation of a continuous join.

Reference material: Avery (1988); Maryon (1971); Prengaman (1995); Rabinkin (1997); Waite (1992).

LOW-MELTING ALLOYS

Alloys with relatively low melting temperatures (47–174°C) are known as low-melting or fusible alloys. These alloys usually contain large amounts of bismuth with lesser amounts of lead, tin, cadmium, and/or indium. For example, an alloy containing 50 wt% bismuth, 27 wt% lead, 13 wt% tin, and 10 wt% cadmium melts at 70°C. Low-melting alloys have a wide variety of uses, e.g. fuses, sprinkler systems, and in pipe-bending applications.

Reference material: ASTM (2001).

LEAD-COATED COPPER

Lead-coated copper was developed and gained widespread use between 1900 and World War I. It was developed to provide a metal for roofing and flashing that had the appearance and corrosion resistance of lead but weighed significantly less. The lead coating is usually applied to the copper by hot-dipping, although it can also be applied by spraying or electroplating. The alloy used in hot-dipping is a lead–tin alloy containing about 4 wt% tin. The tin helps in achieving a good bond between the coating and the copper.

Reference material: Gayle and Look (1992); Prengaman (1995); Zahner (1995b).

TERNE-COATED METALS

Metals are sometimes coated with lead–tin alloys to produce a dull gray appearance. Such coatings are referred to as "terne" (which means dull).

Terne-coated iron (terneplate): Terneplate is sheet iron coated with a lead–tin alloy containing at least 5 wt% tin. It was first manufactured around 1720 in Wales, and early varieties consisted of tin-plated iron dipped in molten lead. Such terneplate was typically used for roofing, usually being painted for additional corrosion protection.

The usual composition of the lead–tin alloy in terneplate is 80–85 wt% lead and 15–20 wt% tin (although the tin content can range from 5 to 50 wt%), and it is traditionally applied by hot-dipping. The tin in the alloy reacts with the iron to form intermetallic compounds, which provide good adhesion between the coating and the iron. Modern terneplate may also be produced by electroplating.

Reference material: Gayle and Look (1992); Prengaman (1995); Zahner (1995b).

Terne-coated stainless steel: Terne-coated stainless steel was introduced in the 1960s as a roofing material. It is dull silver-gray in colour and no painting is required for corrosion protection. The stainless steel is usually type S30400 or S31600.

Reference material: Zahner (1995b).

Terne-coated copper: Copper can also be coated with a dull terne by hot-dipping. Terne-coated copper was recently identified on the roof of the Library of Parliament in Ottawa.

Reference material: Cser et al. (2000).

GILDED LEAD

Outdoor lead has occasionally been gilded, usually by the oil-gilding technique. Many of the lead garden sculptures at Versailles (built in the 1680s) in France were originally gilded, although the gilding has now worn off. There was also a gilded lead equestrian statue of King George III in New York City (unveiled 1770) which, in 1776, was pulled down, broken up, and the lead turned into bullets. During the 1990s, the gilded lead statue of King George II in Jersey, UK (unveiled 1751) and the gilded lead associated with the Albert Memorial in London (unveiled 1876) both underwent restoration.

Reference material: Glass (2001); Wilson (2001).

SILVER-PLATED LEAD

Silver can be electroplated onto lead. Such pieces are usually stamped with the letters EP lead (electroplated lead). For more information on silver plating, see "Chapter 11. Silver."

CORROSION

Lead is generally resistant to corrosion. When corrosion does occur, the products usually contain lead as Pb^{2+} although it is present in some lead oxides as Pb^{4+}. Some of the lead minerals and lead compounds mentioned in this chapter are listed in Table 9.2.

Reference material: Carr et al. (1995); Greninger et al. (197-).

TABLE 9.2. LEAD MINERALS AND LEAD COMPOUNDS

Chemical name	Mineral name	Chemical formula	Colour
lead(II) oxide	litharge	α-PbO	red
lead(II) oxide	massicot	β-PbO	yellow
lead(II,IV) oxide	minium	Pb_3O_4	bright red
lead(IV) oxide	plattnerite	PbO_2	dark gray
lead(II) sulphide	galena	PbS	black
lead(II) sulphite	scotlandite	$PbSO_3$	white
lead(II) sulphate	anglesite	$PbSO_4$	white
lead(II) carbonate	cerussite	$PbCO_3$	white
lead(II) carbonate hydroxide*	hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	white
lead(II) carbonate hydroxide oxide	plumbonacrite	$Pb_{10}(CO_3)_6O(OH)_6$	white
lead(II) chloride	cotunnite	$PbCl_2$	white
lead(II) chloride hydroxide	laurionite	PbClOH	white
lead(II) carbonate chloride	phosgenite	$Pb_3CO_3Cl_2$	white
lead(II) chloride phosphate	pyromorphite	$Pb_5Cl(PO_4)_3$	yellow
lead(II) acetate	—	$Pb(CH_3CO_2)_2$	white
lead(II) formate	—	$Pb(HCO_2)_2$	white

* Lead carbonate hydroxides are also called basic lead carbonates.

SOLUTION CHEMISTRY

The principal oxidation states of lead are +2 (Pb^{2+}) and +4 (Pb^{4+}). When lead corrodes, which can happen when it is exposed to moist air or to an aqueous solution, the initial anodic and cathodic half-reactions are usually given by:

Anodic half-reaction: $Pb(s) \rightarrow Pb^{2+} + 2e^-$
Cathodic half-reaction: $^1/_2O_2(g) + H_2O + 2e^- \rightarrow 2OH^-$
Net reaction: $Pb(s) + {}^1/_2O_2(g) + H_2O \rightarrow Pb^{2+} + 2OH^-$

Lead does not corrode when exposed to pure water (i.e. water that contains no dissolved salts) provided the water does not contain gases. Conservators can therefore minimize the risk of corrosion by using distilled water that has been boiled (which removes any gases) for rinsing lead artifacts following chemical treatments. In contrast, lead corrosion does occur in pure water whenever oxygen gas is present.

The rate of lead corrosion in an aqueous solution depends on the solution composition (i.e. dissolved gases, salts, pH) and the solubility and adhesion of the resulting corrosion products. Lead's generally good resistance to corrosion stems from the fact that most of its corrosion products are sparingly soluble or insoluble, and usually form adherent protective layers. However, when exposed to clean water (e.g. distilled water, soft waters) that contains dissolved gases, there are not enough dissolved salts present to allow the lead to form a protective corrosion layer. Hence lead is prone to corrosion in clean water.

The presence of a variety of dissolved gases and salts can lead to the formation of a range of insoluble corrosion products. For example, in the presence of dissolved oxygen and carbon dioxide, carbonate-containing lead corrosion products form according to the pH of the solution: cerussite forms at $pH < 11$; hydrocerussite forms at pH 11–13; and plumbonacrite forms at $pH > 13$. When lead corrodes in solutions that contain sulphate ions (e.g. seawater, sodium sulphate), lead sulphate precipitates and forms a protective layer on the lead. This reaction provides conservators with another opportunity to reduce the rate of corrosion of lead objects undergoing treatment; by adding sodium sulphate or dilute sulphuric acid to rinse water they can induce the formation of a protective layer of insoluble lead sulphate.

Lead is an amphoteric metal, and can suffer accelerated corrosion in both acidic and alkaline media. For example, the monoxides that form when lead is exposed to clean water are slightly soluble in pure water but have increasing solubility in acids and alkalies — which leads to an increased rate of corrosion in both cases. Significant corrosion of lead can occur if it is exposed to aqueous solutions with a pH <5 (acidic) or >10 (alkaline). Furthermore, lead is readily soluble in nitric acid and acetic acid (ethanoic acid) because of the high solubilities of lead nitrate and lead acetate (lead ethanoate).

Reference material: Carr et al. (1995); Graedel (1994); Greninger et al. (197-); North (1987); Shoesmith et al. (1988).

INDOOR EXPOSURE

When lead is exposed to clean indoor air, a thin film of lead monoxides (e.g. litharge, massicot) forms on its surface. (Note that the term "litharge" can have two meanings: it can refer specifically to the red lead monoxide (α-PbO) or collectively to lead monoxides that can exist in two polymorphs (α-PbO and β-PbO).) The red tetragonal form (α-PbO) is stable up to 489°C and the yellow orthorhombic form (β-PbO) is stable above 489°C (when studied as pure compounds). However, the high-temperature yellow form can exist at room temperature as a corrosion product if impurities have stabilized its structure.

Over time, the composition of the natural oxide layer gradually changes as some or all of the lead oxides react with moisture and adsorbed atmospheric carbon dioxide gas to form insoluble, well-adhered lead compounds such as lead carbonate and lead carbonate hydroxide (hydrocerussite). The development of this patina causes historic lead pieces to darken over time.

Lead corrosion products are generally insoluble — so lead alloys and their corrosion crusts are usually chemically stable in an indoor environment. However, any lead object can suffer active corrosion if the indoor environment has high levels of volatile organic acids.

Reference material: Abel (1973); Graedel (1994); Green (1989); Greninger et al. (197-); Tétreault et al. (1998).

Active corrosion: Lead objects can suffer serious (active) corrosion if they are exposed to an environment contaminated with volatile organic acids such as acetic acid (vinegar) and formic (methanoic) acid. This corrosion is due to the formation of soluble lead salts (e.g. lead acetate, lead formate), and the lead objects will continue to corrode as long as they remain in an environment with sufficient levels of volatile organic acids and moisture to stimulate the formation of these salts. The sources of these contaminants in the indoor environment are usually wood (with oak and cedar being the worst), wood products, oil-based paints, some emulsion paints, and certain adhesives — all of which emit volatile organic acids as they dry or age. When display cases and storage cabinets are constructed with materials that emit these volatile acids, the enclosed space may accumulate high levels of acids which can corrode metals, especially lead, contained in the space.

Active corrosion on lead is generally characterized by surface areas of white powder (see Figure 9.2). The white corrosion is often loosely adherent and can be voluminous. Collectors of toy and miniature soldiers describe this corrosion as "lead disease" or "lead rot."

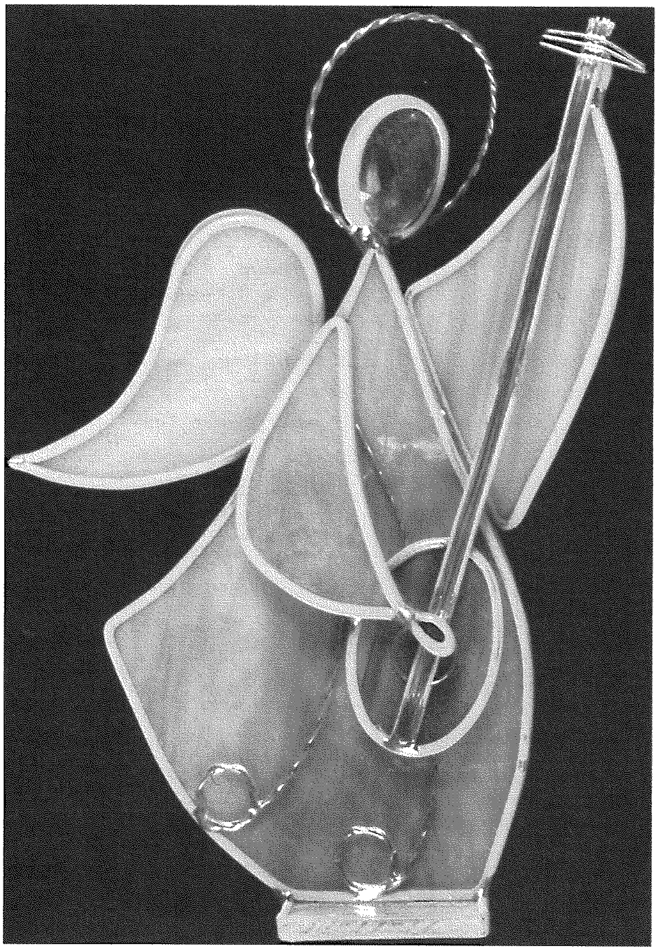

Figure 9.2. This stained glass angel was stored in a closed wooden cabinet; the lead cames surrounding the glass are suffering from active corrosion, and have turned white.

The white corrosion may cover the entire surface or be localized in small spots. As corrosion proceeds, the object can turn into a white mass. If the surface is painted (e.g. toy soldiers), the corrosion can expand and push the paint off.

Analysis of the corrosion products on actively corroding lead has identified mainly hydrocerussite and occasionally plumbonacrite, although lead formate (lead methanoate) has also been identified on some lead objects as well as on leaded copper alloys. (The solubility of lead in copper alloys is negligibly small so lead in copper alloys is normally present as separate globules.)

If the objects are removed to a "clean" environment, it is probable that any residual organic acid on the lead surface will evaporate. Active corrosion should then cease, as long as there is sufficient air movement to dilute these evaporating organic acids to a level below that needed to stimulate corrosion.

Reference material: Bradley and Thickett (1999); Goodwin (2000); Green (1989); Tétreault (1999, 2003); Tétreault et al. (1998); Thickett et al. (1998).

Acetic acid: The following corrosion cycle is thought to occur on lead, given sufficient moisture and acetic (CH_3CO_2H) acid:

$$3Pb(s) + 6H^+ + 6CH_3CO_2^- + 1\tfrac{1}{2}O_2(g) \rightarrow 3Pb^{2+} + 6CH_3CO_2^- + 3H_2O$$

$$3Pb^{2+} + 6CH_3CO_2^- + 4H_2O + 2CO_2(g) \rightarrow Pb_3(CO_3)_2(OH)_2(s) + 6H^+ + 6CH_3CO_2^-$$

As the lead corrodes, it forms soluble lead acetate. The lead ions diffuse away from the surface and react with dissolved carbon dioxide gas, precipitating as insoluble lead carbonate hydroxide. The lead carbonate hydroxide forms as a loose white powder away from the metal surface, and is not protective. The acetate ions ($CH_3CO_2^-$) remain in the corrosion layer and continue to cause the metal to corrode. Lead that contains more than about 1 wt% tin is more resistant to this type of corrosion than high-purity lead (>99 wt%). An example of the resistance of lead–tin solder to this type of corrosion is shown in Figure 9.3.

Evidence provided by Thickett et al. (1998), Tétreault et al. (1998), and Bradley and Thickett (1999) suggests that lead does not suffer from active corrosion as long as the acetic acid level is below about 0.16 parts per million (ppm) (i.e. 0.400 mg m^{-3}, 400 $\mu g\ m^{-3}$). However, Thickett et al. (1998) observed active

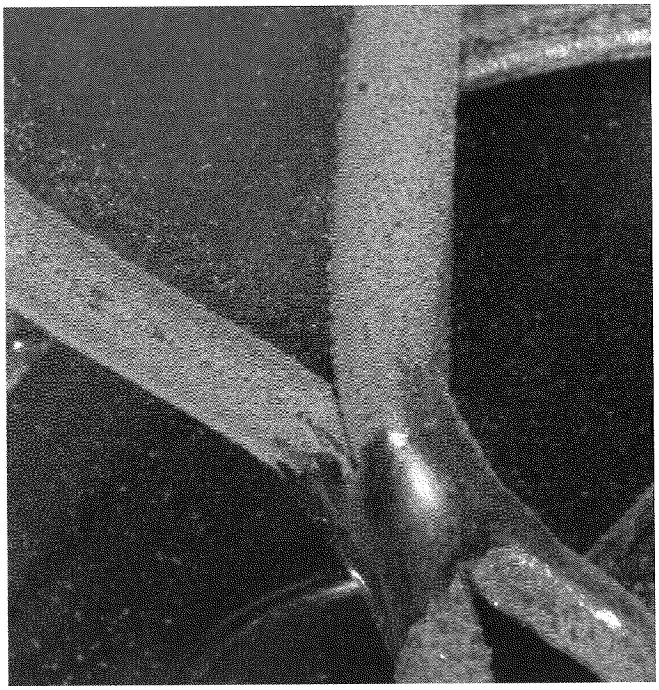

Figure 9.3. A close-up of a soft solder join in the stained glass angel pictured in Figure 9.2, which shows that the solder is not corroding. It is probably a lead–tin alloy with sufficient tin to make it more resistant to active corrosion than the adjacent lead cames. (A colour version of Figure 9.3 is available on p. 86.)

corrosion on lead at 0.5 ppm acetic acid and 50% RH. Given that people cannot usually smell acetic acid until the levels reach about 1 ppm, the presence of a detectable "vinegar" odour indicates that the level of acetic acid is high enough to put lead objects at risk of corrosion.

Reference material: Bradley and Thickett (1999); Gottlieb et al. (1993); Green (1989); Heath and Martin (1988); Ruth (1986); Tennent et al. (1993); Tétreault et al. (1998); Thickett et al. (1998).

Formic acid: Lead reacts with formic (HCO_2H) acid to form lead formate (lead methanoate), which has been identified in the corrosion products on some lead objects (see, for example, the lead formate growing on the lead toy soldier shown in Figures 9.4 and 9.5). Formaldehyde is thought to play a role in this process (possibly by being oxidized to formic acid), but the exact mechanism is not understood.

Reference material: Gottlieb et al. (1993); Greninger et al. (197-); Grzywacz and Tennent (1994); Heath and Martin (1988); Leveque (1986); Oddy and Bradley (1993); Tennent et al. (1993); Thickett et al. (1998).

Figure 9.4. Lead formate particles growing on a lead toy soldier (Royal Ontario Museum 991.246.187.13). Photograph by Brian Boyle. With permission of the Royal Ontario Museum © ROM. (A colour version of Figure 9.4 is available on p. 86.)

Figure 9.5. Detailed photograph of lead formate particles on the toy soldier shown in Figure 9.4 (Royal Ontario Museum 991.246.187.13). Photograph by Susan Stock. With permission of the Royal Ontario Museum © ROM. (A colour version of Figure 9.5 is available on p. 86.)

OUTDOOR EXPOSURE

Lead has been used outdoors for roofing, sculptures, lettering in stone, spacers between stone, and grout to set iron bars in masonry. When exposed outdoors, lead usually corrodes until it develops an adherent film of insoluble lead compounds that protect the surface from further attack.

When lead is first placed outdoors, it forms a thin layer of lead oxides (predominantly the yellow massicot but also some litharge). Over time, carbon dioxide that dissolves in any surface water on the lead reacts with the lead oxides to form carbonate compounds (mainly hydrocerussite but sometimes also cerussite). These carbonate compounds eventually form an adherent, relatively insoluble layer that decreases the corrosion rate of the lead. If sulphur dioxide dissolves in the surface water, it reacts with hydrocerussite to form lead sulphite and lead sulphate. It takes about 1 year for newly exposed lead to develop a layer of lead sulphate that provides good corrosion resistance outdoors. If outdoor lead undergoes creep, its corrosion rate will increase because of the continued exposure of a fresh lead surface.

Reference material: Allen et al. (2003); Black and Allen (1999); Goodwin (2000); Graedel (1994); Tranter (1976); Zahner (1995a).

Underside corrosion: Repeated condensation of a thin film of water on the surface of lead can cause corrosion. Such corrosion (also known as condensation corrosion) has been observed on the underside of lead roofing that is subject to cycles of condensation and evaporation due to temperature changes. Because carbon dioxide gas is readily absorbed into the thin water film, the corrosion products that form are initially lead oxide and then hydrocerussite. Depending on the exact conditions, the corrosion layer can be either adherent and protective or friable and non-protective. In the presence of weak organic acids such as acetic acid, the hydrocerussite that forms tends to be of the friable form — thus allowing corrosion to continue. Friable corrosion products can be found on the underside of lead roofs supported by wooden beams which release organic acids.

Reference material: Allen et al. (2003).

CORROSION DURING BURIAL

Many different lead corrosion products have been identified on lead recovered from burial environments — a result of the wide variety of dissolved anions (e.g. carbonates, sulphates) that can react with lead ions and precipitate as insoluble lead compounds. Under most circumstances, these corrosion products lower the corrosion rate of lead.

In natural waters, the corrosion of lead depends on the hardness of the water, its pH, and the presence of other dissolved material. When lead is exposed to hard waters that contain dissolved minerals such as carbonates, sulphates, or silicates, the formation of insoluble lead salts (or calcium carbonate) provides for good corrosion resistance. In contrast, soft waters do not usually contain enough dissolved material to allow the formation of a protective layer of corrosion products on the lead surface. As a result, the corrosion rate of lead in soft water can be significant — enough to contaminate drinking water. In addition, soft waters that contain organic acids from plants (e.g. peat bogs) promote lead corrosion due to the formation of soluble lead salts.

Lead that is exposed to seawater has a low rate of corrosion because it becomes covered with a protective layer of insoluble lead salts. Under aerobic conditions, this protective layer is lead sulphate along with lesser amounts of lead carbonate chloride, lead chloride hydroxide, hydrocerussite, and lead chloride. The exact composition is influenced by the pH level. When MacLeod and Wozniak (1996) studied the corrosion of lead in seawater at various pH levels, they identified lead chloride at pH 6–7 and lead carbonate at pH 8–9.

When lead is buried in soil, it usually builds up a fairly dense insoluble film of lead monoxides covered with a thin loose film of cerussite or hydrocerussite. Under certain soil conditions, lead compounds that contain chlorides (e.g. cotunnite, laurionite, phosgenite, pyromorphite) may form.

Under anaerobic conditions, the presence of sulphate-reducing bacteria may lead to the formation of lead sulphide rather than lead sulphate. In this circumstance the lead sulphide, with its good electrical conductivity, can act as a cathode and promote pitting on lead.

Reference material: Davis et al. (1995); Hofmann and Maatsch (1970); MacLeod (1991); MacLeod and Wozniak (1996); North (1987); Turgoose (1985); Tylecote (1983); Wesson and Littauer (1976); Zhang (2002).

ALKALINE CONDITIONS

As an amphoteric metal, lead is susceptible to corrosion not only under acidic conditions but also under alkaline conditions, e.g. when it is buried in alkaline soil or associated with alkaline building materials such as cement, lime-based mortar, and concrete. When lead is exposed to an alkaline solution, it dissolves as the $HPbO_2^-$ ion which then decomposes into lead monoxides (e.g. red litharge, yellow massicot, or alternating layers of red and yellow). In concrete, the pores are filled with an alkaline solution (pH 12–13) that contains calcium hydroxide. This solution absorbs carbon dioxide from the atmosphere, which then precipitates as calcium carbonate. The formation of the calcium carbonate prevents the carbonate ions from reaching the lead and therefore prevents the formation of a protective layer of lead carbonate hydroxide on the lead surface.

Reference material: Allen et al. (2003); Hofmann and Maatsch (1970); Wesson and Littauer (1976).

LEAD SOAPS

Lead objects that come in contact with material containing fatty acids (e.g. leather, wax, fat, oil) may react to form a waxy corrosion product consisting of lead soap. In lead-based oil paintings, the formation of lead soaps can result in paint loss. For more information on metal soaps, see "Chapter 3. Specific Corrosion Problems."

Reference material: Boon et al. (2002); Robinet and Corbeil (2003).

GALVANIC CORROSION

Aluminum and zinc are anodic relative to lead in almost all environments, and will suffer accelerated corrosion (particularly aluminum) if in direct contact with lead. However, for other metals it is difficult to predict the galvanic behaviour of lead because the relative potentials may depend on the pH of the environment. For example, iron is anodic to lead in acids and cathodic to it in alkalies.

In certain environments, even though the lead is anodic to other metals, the acceleration of its corrosion rate is negligible due to the formation of a protective surface film. For example, when lead is connected to a copper alloy in sulphuric acid, the lead is anodic relative to the copper but the formation of a protective film of lead sulphate suppresses further corrosion.

Reference material: Goodwin (2000); Smith (1987); Zahner (1995a).

TOXICITY

Lead and its compounds are toxic to humans and, because the poisons can be stored in the body, the effects of exposure to lead are cumulative. Lead and its compounds are also probable human carcinogens, based on animal studies where they are confirmed carcinogens. Lead can enter the body by absorption, ingestion, or inhalation. Small lead dust particles and lead fumes are especially dangerous because they are easily inhaled. Lead fumes are created when lead is heated enough to vaporize the metal, such as occurs during soldering. Lead dust is often created when working with lead-containing objects and materials. Lead-containing dust can also be generated when lead and lead alloys suffer from active corrosion, or when paints containing lead pigments are removed by abrasive methods.

Anyone in Canada who is occupationally exposed to lead is subject to Occupational Health and Safety legislation. More health and safety information about lead exposure can be found on Canada's National Occupational Health and Safety Web site (www.canoshweb.org) or the Web site of the Canadian Centre for Occupational Health and Safety (www.ccohs.ca).

Reference material: Fischbein (1981); Fischbein et al. (1992); Graham et al. (1981); Nriagu (1983); Pant et al. (1994); Parks and Hicks (1995); Rossol (2002).

10

NICKEL (Ni)

Principal oxidation number(s)	Atomic weight (g mol^{-1})	Density at 20°C (g cm^{-3})	Melting point (°C)	Boiling point (°C)	Linear expansivity (°C^{-1})	UNS range for alloys
Ni^{2+} (nickelous)	58.69	8.90	1455	2913	13.4 x 10^{-6}	N00001–N99999

GENERAL DESCRIPTION

Nickel is a hard, corrosion-resistant, silvery-white metal. It is magnetic at room temperature, can be polished to a bright finish, and is often alloyed with other metals to make specialty alloys such as Monel, Inconel, and Hastelloy. These alloys are generally strong and corrosion-resistant, but tend to be heavy and expensive.

For more information on nickel, see the Web site for the Nickel Development Institute (www.nidi.org).

Reference material: Agarwal (2000); Gayle and Look (1992); Tundermann et al. (1996).

ORIGIN

The element nickel was discovered in 1751 by Swedish chemist A.F. Cronstedt. It is usually recovered from nickel sulphide ores which are yellow and have a metallic lustre. The most common nickel sulphide is the mineral pentlandite; other rarer nickel sulphides include millerite and heazlewoodite. Nickel is a constituent of most meteorites (a property that is used to help distinguish meteorites from other minerals). In Canada (one of the largest producers of nickel in the world), nickel is mined in Thompson (Manitoba) and in the Sudbury Basin (Ontario).

Reference material: Tundermann et al. (1996).

USE

Nickel is often combined with other metals to produce a wide range of corrosion-resistant alloys that are used in various industrial applications (e.g. chemical, petrochemical, marine, pulp-and-paper, agrichemical, oil and gas, heat treatment). Some nickel alloys (e.g. Monel) are used in building components and to make magnets, and nickel is an important alloying element in stainless steels (for more information on stainless steels, see "Chapter 8. Iron"). It is also widely used in the plating of iron and copper.

Reference material: Agarwal (2000); Antonsen (1996); Gayle and Look (1992); Tundermann et al. (1996).

COINS

Because it is so resistant to corrosion, nickel has often been used for coins. Over the years, many of Canada's coins have been made with pure nickel or nickel alloys. The various uses of nickel in the 5-cent piece offer a good example. When the first large 5-cent piece was introduced in 1922, it was made from pure nickel (and was the first use of nickel in a Canadian coin). The 5-cent piece continued to be made of pure nickel until 1981, except during World War II and again in the early 1950s when other materials (e.g. a copper–zinc alloy or chromium-plated steel) were used. From 1982 to 2000, it was made from an alloy of 75 wt% copper and 25 wt% nickel. As of 2001, the 5-cent piece is made from nickel-plated steel.

Canada has paid tribute to the use of nickel in various ways. In 1951, a 5-cent nickel coin commemorating the 200th anniversary of the isolation and naming of the element nickel was issued. This coin incorporated a nickel refinery in the design on the reverse side. The design of this commemorative coin was also used for a 9-m-tall stainless steel monument (the "Big Nickel") unveiled in Sudbury in 1964.

More information on Canadian coins can be found on the Web site for the Royal Canadian Mint (www.rcmint.ca).

Reference material: Gayle and Look (1992); Krause and Mishler (1991).

ALLOYS AND PLATING

Nickel can be alloyed with various other metals to create products with properties (e.g. strength, corrosion resistance) tailored to specific uses. These alloys are referred to as specialty or superalloys. Some examples of nickel alloys are listed in Table 10.1.

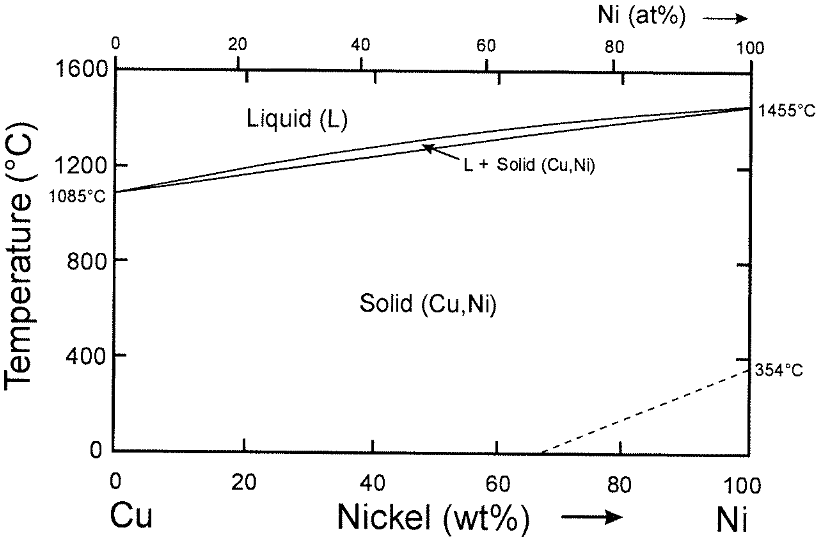

Figure 10.1. Equilibrium phase diagram for copper and nickel. The bottom scale is weight percent and the top scale is atomic percent. The diagonal broken line indicates a magnetic transition: the alloys below the broken line are magnetic and those above it are non-magnetic. Adapted from ASM International (1992).

TABLE 10.1. NICKEL ALLOYS

Nickel alloys	Example (older name)	Example (UNS number)	Approximate composition of example
nickel	Nickel 200	N02200	≥99.0 wt%
nickel + copper	Monel 400	N04400	66 wt% nickel, 34 wt% copper
nickel + iron	Alloy 52	N14052	50 wt% nickel, 50 wt% iron
nickel + chromium	Chromel	N06010	90 wt% nickel, 10 wt% chromium
nickel + molybdenum	Hastelloy B	N10001	60 wt% nickel, 30 wt% molybdenum
nickel + chromium + iron	Inconel 600	N06600	76 wt% nickel, 16 wt% chromium, 8 wt% iron
nickel + chromium + molybdenum	Hastelloy C	N10002	58 wt% nickel, 16 wt% chromium, 16 wt% molybdenum, 6 wt% iron, 4 wt% tungsten

Although pure nickel is magnetic at room temperature, the alloys may or may not be (magnetism depends on temperature and alloy composition).

NICKEL–COPPER ALLOYS

Nickel and copper are completely miscible in one another, and in the solid state they form a continuous single-phase solid solution (see the nickel–copper phase diagram in Figure 10.1). The broken line in the phase diagram represents a magnetic transition, with alloys below the line being magnetic and alloys above it being non-magnetic. Near where the broken line reaches room temperature, small changes in composition or temperature can change the alloy from magnetic to non-magnetic. This behaviour makes certain alloys, such as Monel (see below), difficult to identify based on their magnetic properties. Nickel–copper alloys with more than 12 wt% nickel are white. The silvery-white colour of pure nickel and a nickel–copper alloy containing 25 wt% nickel are shown next to the reddish colour of pure copper in Figure 10.2.

Reference material: ASM International (1992).

Nickel silvers (German silver): Nickel silvers are copper-rich alloys that contain nickel and zinc, and are usually white in colour. The name nickel silver is misleading because these alloys contain no silver and only 30 wt% nickel at most. For more information on nickel silvers, see "Chapter 6. Copper."

Monel: The white-coloured Monel alloys (e.g. Monel 400, Monel K500) are nickel–copper alloys with a nickel content of about 66 wt%. The magnetic properties of these alloys change with temperature (which makes magnetism a poor criterion for identification).

Monel 400 was developed in 1905 by R.C. Stanley who produced the first nickel–copper alloy from ore deposits near Sudbury, Ontario. He originally named it "Monell Metal" (in honour of A. Monell, the then-president of the

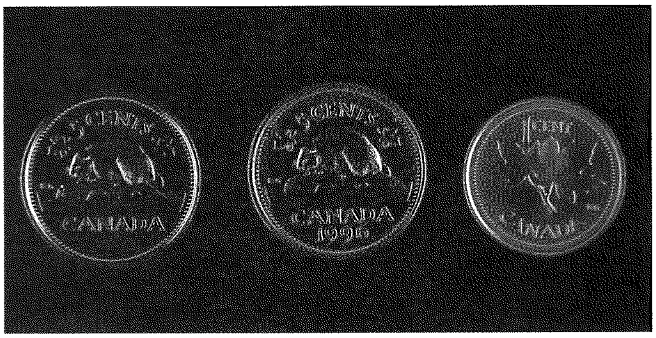

Figure 10.2. These Canadian coins illustrate the colours of pure nickel, a nickel–copper alloy, and pure copper (the left-hand 5-cent coin is plated with pure nickel; the middle 5-cent coin is an alloy containing 75 wt% copper and 25 wt% nickel; and the right-hand 1-cent coin is plated with pure copper). (A colour version of Figure 10.2 is available on p. 87.)

International Nickel Company), but one "l" had to be dropped when the alloy was registered as a trademark because the law prohibited the use of a family name. Monel K500 is similar in composition to Monel 400 (except for small additions of aluminum and titanium), but unlike Monel 400 it can be age-hardened. When Monel K500 is age-hardened by heating at low temperatures, fine particles of the intermetallic compound $Ni_3(Al,Ti)$ precipitate and increase the alloy's strength and hardness.

Between about 1909 and the mid 1950s, Monel alloys were often used as an architectural material in Art Deco designs on both exterior and interior decorative metalwork. They were sometimes given a two-tone finish by heating the surface and then selectively polishing it to form a thin black oxide layer. In 1953, Canada donated seven nickel silver doors decorated with 28 Monel alloy cast sculptural panels to the United Nations General Assembly building in New York City. Monel alloys were also a popular corrosion-resistant industrial material until after World War II, when stainless steel became cheaper. They are still used today as a specialty metal for industrial plumbing, marine equipment, and other industrial applications. Because of their corrosion resistance, Monel staples are favoured by conservators.

Reference material: Agarwal (2000); Gayle and Look (1992); Trelstad (1995); Tundermann et al. (1996); Zahner (1995).

NICKEL–IRON ALLOYS

Stainless steels: These are iron-based alloys to which various amounts of nickel and chromium have been added. For more information on these alloys, see "Chapter 8. Iron."

Meteorites: Nickel is found as a constituent in most iron meteorites, which are alloys of iron and nickel in which the nickel content ranges from about 5 to 60 wt%. For more information on meteorites, see "Chapter 8. Iron."

Soft magnetic materials: Nickel–iron alloys are defined as soft magnetic materials when they have high magnetization in a magnetic field (i.e. they are attracted to a permanent magnet) but the magnetism is not retained when the applied field is removed. One example (Alloy 52) contains roughly equal amounts of nickel and iron, but most other examples contain more nickel and less iron. These alloys are used in electric motors, and other applications where a rapidly fluctuating magnetic field is required.

Hard magnetic materials: These nickel–iron alloys are permanent magnets (i.e. materials that retain their magnetism after an applied field is removed). Some trade name examples of these alloys include Alnico, Cunico, and Cunife. The Alnico alloys are iron-based, and contain 6–12 wt% aluminum, 14–28 wt% nickel, and 5–35 wt% cobalt along with small amounts of copper or titanium.

Reference material: Agarwal (2000); Bradbury (1985); Tundermann et al. (1996).

OTHER NICKEL ALLOYS

Nickel–molybdenum (B-family): The original alloy of nickel and molybdenum (Hastelloy alloy B) was developed in the 1920s. To correct for certain corrosion problems in the original, other alloys in the series (e.g. B-2, B-3, B-4, and B-10) were soon developed. These alloys are resistant to corrosion by hydrochloric acid and other non-oxidizing acids, even at high temperatures.

Nickel–chromium: The addition of some chromium to nickel produces an alloy that is stronger and more corrosion-resistant than pure nickel. These alloys are referred to as nichrome-type alloys and are used as heating elements.

Nickel–chromium–iron: These alloys are strong and resistant to corrosion and oxidation even at high temperatures, and have a large number of industrially important applications. One major example is Inconel alloy 600 and its related modifications.

Nickel–chromium–molybdenum (C-family): The original alloy of nickel, chromium, and molybdenum (Hastelloy alloy C) was developed in the 1930s. During the latter part of the 20th century, many related alloys with improved corrosion resistance were developed for use in marine environments.

Reference material: Agarwal (2000); Tundermann et al. (1996).

PLATING

The electroplating of nickel onto other metals such as iron or copper-based alloys (e.g. brass, nickel silver) has been carried out since the 1870s. The electrolyte is based on nickel salts such as nickel sulphate or nickel chloride. The nickel layer is hard enough to resist scratches and is relatively corrosion-resistant. Under certain plating conditions, a matte black finish can be obtained.

Steel is difficult to electroplate directly with nickel, so in this case an intermediate plating of copper is used to smooth out any irregularities in the steel surface and to bond with both the steel substrate and the final nickel coating. Figure 10.3 shows an example where a small amount of nickel plating has peeled off, revealing the intermediate copper layer.

Nickel plating is initially shiny but tends to tarnish when exposed outdoors. Chromium, on the other hand, remains shiny. Thus, in the 1920s, when durable chromium (i.e. chrome) platings were developed, the use of nickel plating diminished. To minimize cost, intermediate layers of copper and nickel are often plated onto steel before the final chromium layer.

Nickel electroforming is the basis for a modern processing technique that was developed to make complex shapes (the nickel is electrodeposited onto a mould which is subsequently removed). For more information on electroforming, see "Chapter 1. Metals."

Nickel can also be plated using an electroless process. Electroless nickel solutions for coating metals with nickel first became commercially available in the mid 1940s. These solutions, used at 90–100°C, contain a reducing agent (e.g. hypophosphite $H_2PO_2^-$ ion) and a nickel salt (e.g. nickel sulphate, nickel chloride). An electroless nickel solution capable of plating nickel onto plastics at room temperature became available in the mid 1960s.

Reference material: Child (1988, 1993); Krulik (1994); Tundermann et al. (1996).

Figure 10.3. Nickel-plated iron was common on automobile trim in the early 1900s, as illustrated on the window trim of this 1926 Series 11-A Sport Touring Franklin, owned by A. Audette, Ottawa. This photograph shows an area where the nickel plating has peeled off, revealing copper (which was used as an intermediate layer between the nickel and the iron to improve adhesion). (A colour version of Figure 10.3 is available on p. 87.)

CORROSION

Various nickel minerals and corrosion products discussed in this chapter are listed in Table 10.2.

Reference material: Antonsen (1996); Graedel and Leygraf (2000); Persson and Leygraff (1992).

SOLUTION CHEMISTRY

The principal oxidation state of nickel is +2 (Ni^{2+}) although it can range from -1 to +4. Most known nickel compounds and corrosion products contain nickel as Ni^{2+}. The common initial anodic and cathodic half-reactions of corroding nickel are given by:

Anodic half-reaction:	$Ni(s) \rightarrow Ni^{2+} + 2e^-$
Cathodic half-reaction:	$^1/_2O_2(g) + H_2O + 2e^- \rightarrow 2OH^-$
Net reaction:	$Ni(s) + {}^1/_2O_2(g) + H_2O \rightarrow Ni^{2+} + 2OH^-$

When nickel is first exposed to air, it forms a thin inner layer of nickel(II) oxide and an outer layer of nickel(II) hydroxide. Although it is a corrosion-resistant metal even in its pure form, many of its alloys have been tailored to develop even higher corrosion resistance for specific environments (e.g. high temperatures or concentrated chemicals). In general, pure nickel resists corrosion in salt water, strong alkalis, and most acids, although it is readily dissolved in nitric acid and can be attacked by other oxidizing acids. Nickel-based alloys are more

TABLE 10.2. NICKEL MINERALS AND CORROSION PRODUCTS

Chemical name	Mineral name	Chemical formula	Colour
nickel(II) oxide	bunsenite	NiO	green
nickel(II) hydroxide	theophrastite	$Ni(OH)_2$	green
nickel(II) chloride hydroxide	—	$NiCl(OH)$	—
nickel(II) chloride hexahydrate	nickelbischofite	$NiCl_2 \cdot 6H_2O$	green
nickel(II) sulphate hexahydrate	retgersite	$NiSO_4 \cdot 6H_2O$	green
nickel(II) nitrate hexahydrate	—	$Ni(NO_3)_2 \cdot 6H_2O$	green
nickel(II) sulphide	millerite	NiS	yellow
nickel sulphide	heazlewoodite	Ni_3S_2	yellow
iron nickel sulphide	pentlandite	$(Fe,Ni)_9S_8$	yellow
nickel(II) hydroxide sulphate hydrate	—	possibly $Ni_4(OH)_2(SO_4)_3 \cdot xH_2O$*	—
nickel(II) formate dihydrate	—	$Ni(HCO_2)_2 \cdot 2H_2O$	green
nickel(II) acetate tetrahydrate	—	$Ni(CH_3CO_2)_2 \cdot 4H_2O$	green

*x can vary, depending on the number of waters of hydration.

corrosion-resistant than stainless steels, and can be used in more severe environments.

Reference material: Agarwal (2000); Antonsen (1996); Graedel and Leygraf (2000).

INDOOR EXPOSURE

Because nickel and its alloys form a stable oxide film when exposed to air, polished nickel remains bright for long periods in air that is free of moisture and pollutants. However, if the air is moist, this stable oxide film layer will thicken and the surface will dull. The presence of pollutants (e.g. acetic (ethanoic) acid, formic (methanoic) acid, sulphur dioxide) in the indoor air may stimulate nickel corrosion. Persson and Leygraff (see references below) have detected carboxylates in corrosion films on nickel exposed indoors; they suggest that these carboxylates are nickel acetate (nickel ethanoate) and nickel formate (nickel methanoate).

Reference material: Persson and Leygraff (1992, 1996); Waite (1992).

OUTDOOR EXPOSURE

Although nickel and nickel alloys are considered corrosion-resistant and are usually placed outdoors without a protective coating, they do corrode. They gradually develop a patina in response to moisture and pollutants. Depending on the alloy, this can result in varying degrees of surface discoloration. Bright nickel becomes dull (a process referred to as "fogging") and acquires a thin, adherent corrosion film (usually some form of nickel sulphate because of exposure to sulphur dioxide). The patina on Monel 400 can range from light gray-green to a thin brown film. Factors that contribute to and increase the rate of corrosion include the presence of nitrogen oxides, sulphur-containing gases, and chloride ions. These can react with nickel to form several different relatively soluble nickel compounds, including nickel nitrates, nickel sulphates, and nickel chlorides. Sulphur compounds are the most common corrosion products identified on outdoor nickel. Pitting may occur if water is allowed to pool, especially if salts and other dissolved pollutants are present. Over time, less soluble salts (e.g. nickel hydroxide sulphates, also known as basic nickel sulphates) form and contribute to the overall patina.

Reference material: Evans (1994); Graedel and Leygraf (2000); Trelstad (1995); Waite (1992).

CORROSION DURING BURIAL

As yet, nickel objects have only rarely been recovered from archaeological sites. However, nickel(II) chloride hydroxide was identified on a nickel silver object recovered from a shipwreck.

Reference material: MacLeod (1991).

GALVANIC CORROSION

Nickel and its alloys are more noble (less active) than many other common metals (e.g. copper, iron, aluminum, and zinc). When any of these more active metals are in direct contact with nickel, they may experience more rapid deterioration due to galvanic corrosion. Copper alloys usually do not suffer too much because they are relatively close to nickel in the galvanic series, but metals such as iron, aluminum, and zinc may corrode more severely than normal. Such metals are never used as fasteners for nickel alloys (e.g. Monel 400).

Reference material: Trelstad (1995).

TOXICITY

Some individuals develop an allergic response (contact dermatitis) following prolonged contact with metallic objects containing nickel. About one in ten people is allergic to nickel. Metallic nickel has been classified as a human carcinogen.

Reference material: Antonsen (1996); Rossol (2001).

11

SILVER (Ag)

Principal oxidation number(s)	Atomic weight (g mol^{-1})	Density at 20°C (g cm^{-3})	Melting point (°C)	Boiling point (°C)	Linear expansivity (°C^{-1})	UNS range for alloys
Ag^{1+} (argentous)	107.87	10.5	962	2162	18.9×10^{-6}	P07001–P07999

GENERAL DESCRIPTION

Silver is one of eight precious metals, and in its pure form has a lustrous white colour that is sensitive to tarnishing by sulphur-containing gases. It is soft, ductile, malleable, and easily scratched. It is often alloyed with copper to make it harder and more useful. In Canada, collections of silver objects can be found at the National Gallery of Canada in Ottawa, the Royal Ontario Museum in Toronto, and the Soo Line Historical Museum in Weyburn (Saskatchewan).

More information about silver can be found on the Web site of the Silver Institute (www.silverinstitute.org).

Reference material: Etris (1997); Fox (1985).

ORIGIN

Silver occurs in nature in the metallic state (native silver), as the mineral silver chloride (horn silver), and associated with lead ores such as galena (lead sulphide). Today, the major producers of silver are Mexico, the United States, and Peru. Veins of silver were first reported in Canada near Thunder Bay (Ontario) in 1846, and the most famous of the early silver producers was the Silver Islet mine, Lake Superior, discovered in 1868.

Reference material: Etris (1997).

USE

Silver is one of the earliest metals used by humans (early civilizations associated the brilliant white colour of silver with the moon), and can be found in coins, jewelry, flatware, hollowware, etc. Europeans coming to North America during the 18th and early 19th centuries used silver in the form of small trinkets and ornaments (i.e. trade silver) to trade with Aboriginal people for goods and services. Silver is also widely used by the plating industry and in photography.

Reference material: Blair (2000); Fredrickson and Gibb (1980); Glanville and Goldsborough (1990); Hamilton (1995).

SILVER IN PHOTOGRAPHY

Because silver salts are light-sensitive, they are widely used in photography — especially the silver halides (e.g. silver iodide, silver bromide, silver chloride). Silver chloride, for example, darkens when exposed to light because silver metal precipitates and chlorine gas is released, as described by the following reaction:

$$2AgCl(s) + \text{light} \rightarrow 2Ag(s) + Cl_2(g)$$

The precipitated silver has a dark colour because it is finely divided.

In photographic processes based on silver halides, the support (e.g. paper, flexible film, glass, metal) is coated with a silver halide and then exposed to light. The image begins to form as light interacts with the silver halide particles and silver precipitates. This image is then "developed" by exposure to a reducing agent (e.g. hydroquinone). During this exposure, the silver halide particles covered with precipitated silver are more easily reduced than unexposed silver halide particles. Finally, the image is "fixed" by dissolving unexposed and unwanted silver halide, usually with sodium thiosulphate or ammonium thiosulphate, leaving behind the intact image made of precipitated silver particles.

Reference material: Hendriks et al. (1991).

Daguerreotypes: Daguerreotypes are one of the earliest types of photographs (this process was used between 1839 and the mid 1860s). They were made by cold-rolling a silver layer to a copper base, and then polishing the silver layer to a mirror finish and exposing it to iodine and bromine vapours to form a light-sensitive surface (i.e. silver bromide, silver iodide). The plate was then placed in a camera and an image captured. The image was developed by exposing the plate to mercury vapours; the mercury reacted with silver particles to form a silver amalgam and the resulting image occurred because of light scattering diffusely off of the small silver amalgam particles. The final image was fixed by washing in a solution of sodium thiosulphate to remove any remaining unreacted silver halides.

Reference material: Barger and White (1991); Hendriks et al. (1991); Pobboravsky (1978).

ALLOYS AND PLATING

Silver is too soft for most uses so it is alloyed with copper to make it harder. The composition of several common silver alloys are listed in Table 11.1.

TABLE 11.1. SILVER ALLOYS

Common name	Silver content (wt%)	Copper content (wt%)
sterling silver	92.5	7.5
Britannia silver	95.8	4.2
coin silver (USA)	90	10
coin silver (Canada)	80	20

AMOUNT OF SILVER IN AN ALLOY

Many countries make it a legal requirement that silver alloys be identified in an inconspicuous area with one or more small stamps (i.e. hallmarked). The practice of hallmarking dates from 1300 when British law required that England's silver (and gold) be assayed at certain "halls" to determine if the silver (or gold) content was equal to or greater than a predetermined standard. The standards for silver between 1300 and 1798 are given in Table 11.2 (information on gold standards can be found in "Chapter 7. Gold").

TABLE 11.2. SILVER STANDARDS

Date	Silver standard
1300–1697	92.5 wt% silver (sterling)
1697–1720	95.8 wt% silver (Britannia)
1720–1798	92.5 wt% silver or 95.8 wt% silver

As long as the silver (or gold) met its required standard, it was stamped with a "standard mark" as well as other marks, collectively known as the "hallmark." Initially, the same standard mark was used for both silver and gold (the leopard's head from 1300 to 1544, and the lion passant (the one with the lion's head turned sideways) from 1544 to 1798). Separate standard marks for gold and silver were introduced in 1798, after which higher quality silver was marked with a lion passant.

Figure 11.1 presents a selection of British hallmarks identifying sterling silver, towns, London date-letter styles, and makers: the "standard mark" indicates that the object meets the required standard (e.g. sterling silver); the "town mark" shows the location where the object was assayed (e.g. London); the "date-letter mark" identifies the year the object was assayed (the letter in the punch mark for the date-letter changes every year and the style of the punch mark changes after each cycle through the alphabet); and the "maker's mark" identifies the smith who made the object. Figure 11.2 shows an example of a hallmark for a sterling silver object assayed in Birmingham in 1911. This Birmingham example illustrates more clearly the real punch marks shown in the photograph in Figure 11.3. Many other

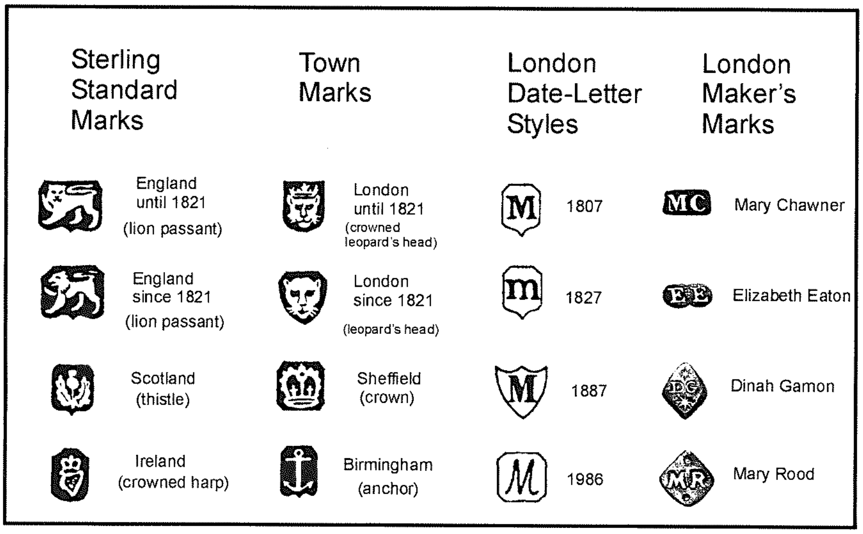

Figure 11.1. A selection of British hallmarks. Adapted from Bly (2000), Forbes (1998), and Glanville and Goldsborough (1990).

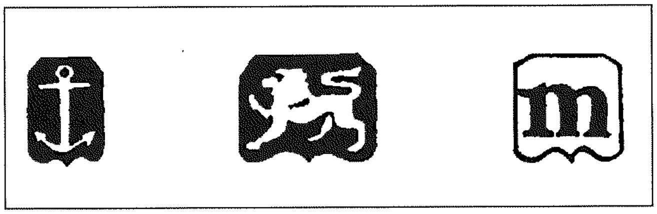

Figure 11.2. A schematic diagram of the hallmarks used on sterling silver assayed in Birmingham (England) in 1911.

Figure 11.3. A photograph of the hallmarks on a sterling silver picture frame, assayed in Birmingham (England) in 1911 and sold by Birks in Canada.

countries around the world also have official hallmarks that show the standard of the silver and usually a maker's mark. The reference material below includes several general reference books that can be consulted for assistance in identifying hallmarks.

In Canada, the quality and marking requirements of precious metal articles are subject to the *Precious Metals Marking Act* and the *Precious Metals Marking Regulations*, administered by Industry Canada. (For more information on the *Act* and *Regulations*, see the Web site for Industry Canada (www.ic.gc.ca); a guide to the *Act* and *Regulations* is also available (strategis.ic.gc.ca/epic/internet/incb-bc.nsf/en/cp01001e.html).) There is no hallmarking system in Canada, and it is not mandatory to mark precious metal articles such as sterling silver for quality. However, if a precious metal is marked with a quality mark (e.g. sterling), then a trademark registered in Canada must be applied with it (unless the mark is a recognized government mark such as the British hallmark).

Reference material: Blair (2000); Bly (2000); Forbes (1998); Glanville and Goldsborough (1990); Kaellgren (2000); Wyler (1937).

SILVER–COPPER ALLOYS

The phase diagram for silver–copper alloys was presented earlier (see Figure 1.3 on p. 8). Because silver and copper are almost insoluble in one another at 25°C, two phases separate out when the mixture is cooled — one that is copper-rich and one that is silver-rich. Sterling silver consists mainly of a silver-rich phase, with a smaller amount of a copper-rich phase. If sterling silver is quenched (i.e. cooled) rapidly, the copper remains in solution, and the alloy is soft and ductile. Working the alloy causes it to become harder (i.e. work-hardening); therefore, to continue working the metal it must be reannealed at frequent intervals.

Sterling silver: This alloy was first introduced in Britain in 1238 with a specification that it should contain not less than 92.5 wt% silver. It is still used around the world as a silver standard.

Sovereign sterling silver: This is a new (patented in 1993 by P. Johns) type of sterling silver alloy in which some of the copper is replaced with about 1.1 wt% germanium (Ge). The presence of germanium is reported to help slow tarnishing and prevent firestain (the formation during the annealing process of copper oxides that discolour the silver).

Britannia silver: This alloy standard was used in England from 1697 to 1720; it has a higher purity (95.8 wt% silver) than sterling (92.5 wt% silver). The silver content was increased in an attempt to deter silversmiths from melting sterling silver coins and using the metal for making objects.

Coin silver: This silver alloy, containing 90 wt% silver and 10 wt% copper, was adopted in the United States in 1837 for coinage (e.g. dimes, quarters, half dollars) and used until 1965. Canada used sterling silver for quarters and half dollars, and an alloy with 80 wt% silver and 20 wt% copper for dimes and dollar coins, until 1967. For more information on Canadian coins, see the Web site of the Royal Canadian Mint (www.rcmint.ca).

Reference material: ASM International (1992); Blair (2000); Butts and Coxe (1975); Johns (1997).

NICKEL SILVER

Nickel silver (also known as German silver) is a generic name for bright silvery-gray metal alloys composed of copper, nickel, and zinc (e.g. UNS C75200 contains 65 wt% copper, 18 wt% nickel, 17 wt% zinc). It is something of a misnomer in that these alloys contain no silver at all. For more information on nickel silvers, see "Chapter 6. Copper."

SILVER PLATING

Several silvering techniques are described below. For more information, refer to "Chapter 7. Gold" in which analogous techniques for the application of a gold layer to another surface were described in greater detail.

FOIL AND LEAF SILVERING

This approach to covering an object with silver is one of the earliest methods employed. In ancient times, thick silver foil was wrapped around a base metal and secured with an adhesive, hammered into grooves, or joined using solder. Modern silver leaf can be applied to wood, metal, gesso, and other materials with the same processes used to apply gold leaf. Sometimes the silver leaf is coloured with varnishes to resemble gold. Modern silver leaf comes in small sheets (e.g. 95 x 95 mm) and imitation silver leaf, made from aluminum, is available in larger sheets (e.g. 130 x 130 mm).

Reference material: La Niece (1990, 1993).

MERCURY SILVERING (FIRE SILVERING)

The process of mercury silvering is similar to that of mercury gilding and has been used in the past mainly to coat copper and copper alloys with silver. The earliest use of mercury for silvering is thought to have been in China. Silver readily reacts with mercury to form an amalgam because of the formation of intermetallic compounds (e.g. Ag_4Hg_5, Ag_5Hg_8, Ag_2Hg_3).

The first step in mercury silvering is the preparation of a silver amalgam, made by grinding together silver powder and mercury. Next, the surface to be silvered is cleaned with a few drops of mercuric nitrate, followed by application of the amalgam. The surface is then heated until the colour changes from bright silver to dull gray as much of the mercury is removed. The final step is burnishing the surface to obtain a bright finish. Mercury silvering can be found on early scientific instruments, decorative metal objects, and coin forgeries.

Reference material: La Niece (1990, 1993).

FRENCH PLATING

This method of plating was used in France in the early 1700s to attach leaves of pure silver to brass and copper. The metal object was first degreased by heating it until it turned red. It was then plunged into a bath of nitric acid, following which the silver leaves were attached by burnishing (using steel burnishing tools).

Reference material: Turner (1993).

CLOSE PLATING

This technique originated with the Romans who used soft solders (tin–lead alloys) to attach silver foil to base metals. Many centuries later (in 1779) the technique was patented in England by R. Ellis and became known as close plating. The process involved a number of steps. An object made from iron, copper, or a copper alloy was first heated to red hot, then plunged into a solution of sal ammoniac (ammonium chloride), and then dipped into molten tin. After being removed from the molten tin, the excess tin was wiped off and the object's surface was covered with silver foil. A soldering iron was then passed over the surface to remelt the tin, effectively soldering the silver to the base metal. Finally, the surface was finished by burnishing.

Reference material: La Niece (1993); Turner (1993).

SHEFFIELD PLATE (FUSED PLATE)

This technique was developed by T. Boulsover in England in the 1740s, and formed the basis of the plating industry of Sheffield (the heyday of which was from 1790 to 1830). The process was carried out by covering a copper slab with a thinner sterling silver slab on one or both sides. This sandwich was then hammered together and heated to form a low-melting alloy at the interface (e.g. a eutectic silver–copper alloy melts at 779°C) which bonded the two metals together by interdiffusion. After cooling, the slab was rolled to the required thickness, and then worked like sterling silver. The edges of the plate were silvered or tinned to disguise the copper. The popularity of this technique declined with the advent of electroplating.

Reference material: Turner (1993).

DEPLETION SILVERING

In depletion silvering, a bright silver surface is formed on the surface of a copper–silver alloy by a process of surface enrichment. This technique was used by the pre-Hispanic cultures of the New World and by the Romans. Chemicals were used to dissolve copper (the more active metal) from the surface of the alloy, leaving the silver content enriched. The surface was then finished by burnishing. This technique was effective for copper–silver alloys with as little as 12 wt% silver.

Reference material: Cope (1972); La Niece (1990, 1993).

ELECTROPLATING

Electroplating was patented in 1840 by Elkington and Co. of Birmingham, England, and its development quickly superseded other methods of silver plating. It provided an economical use of silver that produced a thin, durable, and even deposit of pure silver on almost any clean base metal surface (copper alloys are frequently electroplated with silver; iron and steel can also be electroplated, but they are often plated with a copper alloy first). A common electrolyte was potassium silver cyanide.

Metal objects electroplated with a thin layer of silver are called "silver plate." They are usually marked with EP or a variant such as EPBN (electroplated Britannia metal — an alloy of mainly tin with some copper and antimony), EPNS (electroplated nickel silver — an alloy of mainly copper with some nickel and zinc), EP lead (electroplated lead), and EP copper (electroplated copper). (For more information on Britannia metal, see "Chapter 12. Tin"; for more information on nickel silver, see "Chapter 6. Copper.") An example of the mark EPNS is shown in Figure 11.4.

Figure 11.4. The mark EPNS is used on silver-plated objects to indicate "electroplated nickel silver" — meaning the silver has been electroplated onto a nickel–silver alloy (a copper-rich alloy containing nickel and zinc, but no silver).

During the 19th and 20th centuries, solutions containing mercury salts were sometimes used as a pretreatment (called quicking) prior to electroplating copper alloys with silver. Thus, residual mercury may be present in an electroplated silver layer. Modern silver, especially jewelry, is sometimes electroplated with a thin layer of rhodium to protect the underlying silver from tarnishing.

Reference material: Child (1993); La Niece (1990); Lins and Malenka (2000).

ELECTROFORMING

Reproductions of metal objects can be done with a version of the electroplating process known as electroforming. Reproductions of silver objects are often made by electroforming with copper and then finished by electroplating with silver. For more information on electroforming, see "Chapter 1. Metals."

Reference material: Blair (2000); Child (1993); Lewis (1988).

ELECTROLESS SILVERING

An electroless silvering process for depositing metallic silver onto glass was introduced in the 1830s, and eventually (by the 1850s) led to the production of silver-backed mirrors. This plating process, which produces a continuous silver film on a glass surface, is based on the use of chemicals rather than an electric current. To carry out the process, two solutions are prepared: one containing silver (usually a mixture of silver nitrate and ammonium hydroxide) and the other a reducing agent (e.g. formaldehyde, sugar, hydrazine). These solutions are mixed together and poured over the glass; the silver ions are reduced to silver metal and the mirrored surface forms. Before silvering, the glass surface is sometimes immersed in an acidic stannous chloride solution which allows Sn^{2+} ions to adsorb on the glass. The presence of these tin ions helps to initiate the reduction of silver at the glass surface, and provides for better coverage and adhesion.

Reference material: Krulik (1994).

ELECTROCHEMICAL REPLACEMENT PLATING

In electrochemical replacement plating, a silvering paste is used to plate silver onto copper and brass surfaces for use in scientific instruments and clocks. This silver paste typically contains equal parts of fine ground silver chloride, sodium chloride, and cream of tartar (potassium hydrogen tartrate), and is applied with a damp cotton wool. During this plating procedure, a small amount of copper corrodes as the silver ions are reduced to silver metal. The potassium hydrogen tartrate acts as a complexing agent, keeping the copper ions in solution.

Reference material: Birnie (1993).

CORROSION

Various silver compounds and minerals mentioned in this chapter are listed in Table 11.3.

Reference material: Graedel (1992); Thompson (1973).

SOLUTION CHEMISTRY

The principal oxidation state of silver is +1 (Ag^+). Although it is generally corrosion-resistant, when it does corrode the initial anodic and cathodic half-reactions are given by:

Anodic half-reaction: $Ag(s) \rightarrow Ag^+ + e^-$
Cathodic half-reaction: $^1/_4O_2(g) + {}^1/_2H_2O + e^- \rightarrow OH^-$
Net reaction: $Ag(s) + {}^1/_4O_2(g) + {}^1/_2H_2O \rightarrow Ag^+ + OH^-$

Silver is not affected by most acids or bases, but it is soluble in nitric acid and in hot concentrated sulphuric acid.

PATINATION

When corrosion products adhere to the surface of a metal, the resulting appearance is often called a patina. It is important to identify the presence of an intentional patina to prevent its accidental removal by any of the various silver-cleaning procedures.

Toning: The term "toning" is used by coin collectors to describe a thin layer of silver sulphide (i.e. tarnish) on silver coins. Although tarnish on silver is generally not desired or appreciated, toning on coins is an exception. Silver coins covered with beautiful rainbow colours are considered particularly valuable.

Reference material: Canadian Conservation Institute (1997); White (1993).

Oxidized silver: The term "oxidized silver" refers to the intentional patination (i.e. intentional tarnishing) of silver using sulphur compounds to produce a darkened silver surface, coloured in shades of dark-gray or blue-black. Chemicals used to produce these dark colours include potassium sulphide, ammonium sulphide, and barium sulphide. Although traditionally called "oxidization," a more accurate description of this process would be "coloured" (because the surface is darkened ("coloured") by the formation of silver sulphide). Oxidized silver became fashionable in France in the 1840s and its use continued in Europe up to the time of World War I. Some of these finishes have been referred to as French gray and argent noir.

Reference material: Hughes and Rowe (1982); Rudoe (1993); Shearman (1976); Young and Fennell (1980).

Niello: Niello is a lustrous black or blue-black material that is used to decorate silver surfaces (it is inlaid or melted into the recesses of designs engraved in the surface). It is composed of one or more metal sulphides, and can be prepared by burning a metal or mixture of metals with excess sulphur. Table 11.4 lists various metal sulphides, all of which (except mckinstryite) have been detected in niello.

The metals used to make niello include silver, copper, lead, and/or gold. Silver sulphide or copper sulphide, used alone, can be softened by gentle heating, but they cannot be melted in air because they decompose before they reach melting temperature. Sulphides made from mixtures of metals can usually be melted. The lowest melting point for mixtures of silver and copper sulphides is about 650°C, and for mixtures of silver, copper, and lead sulphides is about 440°C. It is important to identify the presence of niello on silver objects, especially those from a burial environment, because the cleaning procedures used to remove tarnish will also remove the niello.

TABLE 11.3. SILVER MINERALS AND CORROSION PRODUCTS

Chemical name	Mineral name	Chemical formula	Colour
silver(I) sulphide	acanthite	α-Ag_2S	black
silver(I) sulphide	argentite	β-Ag_2S	black
silver(I) chloride	chlorargyrite	$AgCl$	white
silver(I) bromide	bromargyrite	$AgBr$	yellow

TABLE 11.4. METAL SULPHIDES DETECTED IN NIELLO

Chemical name	Mineral name	Chemical formula	Colour
silver(I) sulphide	acanthite	α-Ag_2S	black
copper(I) silver(I) sulphide	jalpaite	Ag_3CuS_2	black
copper(I) silver(I) sulphide	mckinstryite	$(Ag,Cu)_2S$	black
copper(I) silver(I) sulphide	stromeyerite	$AgCuS$	black
gold(I) silver(I) sulphide	uytenbogaardtite	Ag_3AuS_2	gray-black
copper(I) sulphide	chalcocite	Cu_2S	black
copper(I,II) sulphide	djurleite	$Cu_{1.9}S$	black
copper(I,II) sulphide	digenite	$Cu_{1.8}S$	black
lead(II) sulphide	galena	PbS	black

Reference material: La Niece (1983); Moss (1953); Newman et al. (1982); Oddy et al. (1983).

INDOOR EXPOSURE

Silver is susceptible to tarnishing when exposed to gases that contain sulphur in a reduced oxidation state (e.g. hydrogen sulphide, carbonyl sulphide) or elemental sulphur. Other naturally occurring volatile organic sulphides (e.g. carbon disulphide, methanethiol, dimethyl sulphide, dimethyl disulphide) may also contribute to the formation of tarnish. These tarnishing gases can originate from food (eggs, onions, mayonnaise), rubber vulcanized with sulphur (latex gloves, ebonite, o-rings, elastic bands), protein-based glues and wool, some materials (paints, modelling clays), and other sources (some natural waters, pulp-and-paper industry, heating fuels based on coal). Objects (e.g. wood) that have been recovered from anaerobic environments and are contaminated with reduced-sulphur compounds produced by sulphate-reducing bacteria can also be a source of tarnishing gases, especially if they are displayed in the same case as silver objects. (For more information on tests to detect sulphur-containing material, see Appendix 3 on p. 39.)

Tarnishing can be minimized by coating silver objects with a wax or lacquer, or else placing them in an enclosed space with a substance (e.g. activated charcoal) that removes the sulphur-containing gases.

The major component in black tarnish is silver sulphide, which occurs in nature as the mineral acanthite (α-Ag_2S). Acanthite is stable up to about 175°C but above that point it converts to the mineral argentite (β-Ag_2S). Argentite is stable at high temperatures (it does not decompose until it is heated above 565°C), but it is found at room temperature only if some copper is present in its structure. It has been identified on archaeological silver corroding along with copper objects in an anaerobic environment. One of the most insoluble salts known ($K_{sp} = 6 \times 10^{-50}$), silver sulphide can be dissolved only with complexing agents (e.g. acidified thiourea, acidified thiosulphate, ammonium thiosulphate).

The reaction of silver and sulphur to form tarnish is based on an electrochemical process. The proposed anodic half-reaction is:

$$2Ag(s) + OH^- + HS^- \rightarrow Ag_2S(s) + H_2O + 2e^-$$

This reaction can occur (and a thin film of silver sulphide form) in the presence of hydrogen sulphide concentrations as low as parts per trillion (ppt). Typical indoor levels for hydrogen sulphide (50–100 ppt) and carbonyl sulphide (300–500 ppt) are more than adequate to cause tarnishing, the rate of which is increased as the RH and the levels of other pollutants (e.g. O_3, NO_2, Cl_2) rise. Silver–copper alloys tarnish faster than pure silver, with the tarnishing rate increasing with increasing copper content.

Untarnished silver is highly reflective and has a white colour (see the example in Figure 11.5). As the silver begins to tarnish, the initial film is essentially invisible until it is about 10 nm (100Å) thick. As the tarnish increases in thickness from about 10 nm to 100 nm (1000Å), the film appears coloured (e.g. yellow, red, blue) due to the formation of interference colours (i.e. interference between

Figure 11.5. A freshly cleaned silver-plated bowl (owned by L. Carlyle, CCI). (A colour version of Figure 11.5 is available on p. 87.)

Figure 11.6. The tarnish film on this silver-plated bowl (owned by L. Carlyle, CCI) has a yellow colour. (A colour version of Figure 11.6 is available on p. 87.)

light reflected from the outer and inner film surfaces). An example of tarnish with a yellow colour is given in Figure 11.6. Slight differences in thickness give rise to iridescent colours. As the tarnish layer becomes more than about 100 nm thick, the film colour becomes black — the true colour of silver sulphide.

Under more severe tarnishing conditions (e.g. high RH and high levels of sulphur-containing pollutants), silver sulphide may form as elongated crystals called whiskers. These can be grown under laboratory conditions, and have also been observed on museum objects (see the example in Figure 11.7).

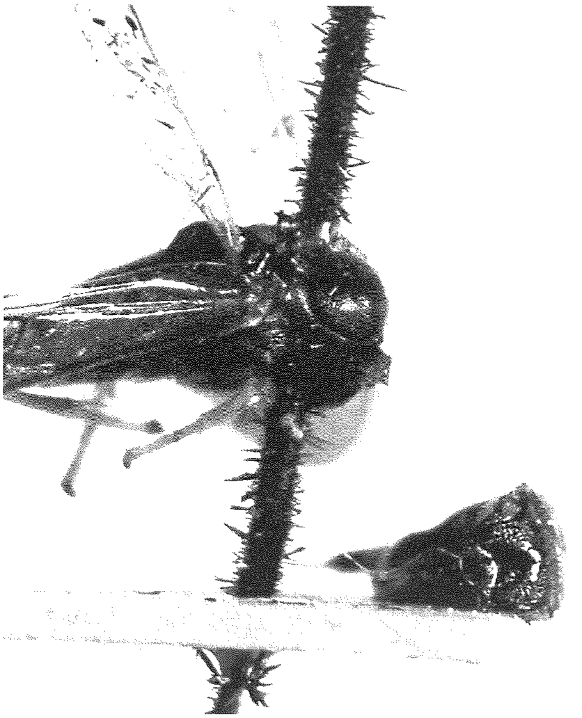

Figure 11.7. Black silver sulphide whiskers growing on a silver pin (used to mount an insect specimen). Photograph courtesy of the Natural History Museum, London.

Reference material: Ankersmit (2002); Ankersmit et al. (2000); Brimblecombe et al. (1992); De Witte (1973/74); Drott (1960); Eggert and Sobottka-Braun (1999); Evans (1981); Hatchett and White (1996); Heller (1983); MacLeod (1991); McNeil and Little (1999); Reedy et al. (1999); Sease et al. (1997); Selwyn (1990, 2000); Stirling et al. (2000); Weisser (1990); Wharton (1989).

Chloride contamination (fingerprints): Sodium chloride is a major component of human perspiration. When perspiration or other residues are left on silver, silver alloys, and silver-plated objects after handling, the sodium chloride reacts with the silver to form silver chloride — which is light-sensitive and can darken over time. This can result in fingerprint stains that are highly visible and distracting on highly polished pieces.

Reference material: Bailey and Zaccardi (1983).

Cleaning residue: Green material is sometimes observed in grooves, lines, or other decorations on silver objects. The most likely source of this green material is residual cleaning polish that can easily be trapped in decorations. Although most of the fine abrasive materials used in commercial silver polishes are white (e.g. calcium carbonate), one of the common components is ammonium hydroxide — which is known to form soluble complexes with copper. Therefore, when residues of silver polish remain after cleaning, the ammonium hydroxide reacts with the copper in sterling silver or with copper in the underlying metal (through porosity in silver plating). Once dissolved, the copper then diffuses through the polish residue and eventually reacts with gases in the air to form green copper salts (e.g. copper hydroxide sulphate or copper carbonate hydroxide), thus staining the polish residue green. For more information on the reaction between ammonia and copper, see "Chapter 6. Copper."

Commercial silver polishes often contain a tarnish inhibitor (i.e. a sulphur-containing organic compound with the formula RSH — where R represents an organic group (usually with a 16- to 18-carbon chain), S is sulphur, and H is hydrogen). The sulphur group of the inhibitor binds to silver atoms (exposed by polishing) and anchors the inhibitor molecules, allowing the inhibitor to form a film on the silver surface. This film has wax-like properties and acts as a barrier to tarnishing gases. The presence of a tarnish inhibitor on silver may result in uneven retarnishing because inhibitors do not bind as effectively to the copper component of silver–copper alloys as they do to the silver component. Also, the presence of an inhibitor film on silver may interfere with the application and adhesion of a lacquer.

Silver that is cleaned by a commercial process using a sodium or potassium cyanide solution can also suffer corrosion problems if any residual cyanide solution remains on the silver. For example, Strahan (see reference below) identified chalconatronite and toxic silver cyanide on a sterling silver object.

Reference material: Lins and McMahon (1993); Long (1999); Selwyn (1997); Selwyn and Costain (1991); Strahan (1986); Wharton et al. (1990).

Measles on daguerreotypes: Brown spots (referred to as measles) have been observed on daguerreotypes after they have been chemically cleaned to remove silver tarnish. When observed under magnification, these spots appear crystalline and resemble flowers. They are thought to form because of residual chemicals left on the surface after chemical cleaning, usually with thiourea-based acid cleaning solutions.

Reference material: Barger and White (1991); Barger et al. (1986); Jacobson and Leyshon (1972); Pobboravsky (1978).

CORROSION OUTDOORS

It is rare to find silver used outdoors. If it is exposed to outdoor conditions, it reacts with any reduced-sulphur pollutants in the air to form silver sulphide tarnish. It also forms silver chloride if exposed to chloride ions in a marine environment or in de-icing salts.

Reference material: Selwyn (2000).

CORROSION DURING BURIAL

Silver that is buried can suffer severe corrosion due to moist conditions and dissolved salts, especially dissolved chloride ions. The silver reacts with the dissolved chloride ions to form silver chloride, which exists in nature as the mineral chlorargyrite. Formerly known as cerargyrite, this material is also called horn silver; it melts at 455°C. Although pure silver chloride is white, when impure it can be gray, brown, or a dull lavender colour. It is also light-sensitive, which can be a particular problem after silver objects are excavated because exposure to light can cause the colour of the silver chloride to darken. Buried silver can also react with dissolved bromide ions (from decaying organic matter) to form silver bromide.

When buried under anaerobic conditions, silver forms silver sulphide in reaction with the hydrogen sulphide generated by sulphate-reducing bacteria.

It should be noted that silver chloride is more soluble than silver sulphide ($K_{sp} = 2 \times 10^{-10}$ for silver chloride).

Reference material: Cappel (1997); Costa (2001); Cronyn and Robinson (1990); Oddy and Bradley (1993); Šrámek et al. (1978); Thompson (1973).

Embrittlement: Archaeological silver can become brittle as a consequence of long-term burial, making it difficult to handle safely. This embrittlement may be the result of either microstructural changes or corrosion.

Microstructurally induced embrittlement is attributed to long-term aging at relatively low temperatures (e.g. those encountered during burial) where precipitation of impurities weakens the grain boundaries. Lead has been proposed as the most likely cause of microstructurally induced embrittlement.

Corrosion-induced embrittlement is attributed to segregation of copper at grain boundaries and subsequent intergranular corrosion caused by localized galvanic attack. The copper-enriched grain boundary regions are anodic, and so they corrode preferentially.

Reference material: Wanhill (2001).

GALVANIC CORROSION

Silver is more noble than most common metals. When it is plated onto less noble metals, these underlying metals can suffer galvanic corrosion if the silver layer is porous or not well adhered. The silver on the surface provides a large cathodic area; any small holes through it concentrate the anodic half-reaction in a small area and can result in large pits. If corrosion occurs beneath the silver, the expansion of corrosion products may lift the silver and detach it. If the base metal is a copper alloy, the result is usually green corrosion products, typical of copper corrosion. If a silver-plated copper alloy object has been buried, copper(I) chloride may have accumulated next to the surface of the copper alloy. Because copper(I) chloride is unstable in moist air, its presence may lead to bronze disease. For more information on bronze disease, see "Chapter 6. Copper."

DAMAGE BY SOLDERING

Repairing silver objects with lead–tin solder is not recommended. As with gold, silver dissolves readily and surprisingly rapidly in molten lead–tin solder. If the silver is thin, this rapid dissolution can result in the surprise formation of an unwanted hole (see the example in Figure 11.8). The rapid decrease in the melting point of silver–lead mixtures is shown in the silver–lead phase diagram (Figure 11.9). Silver also forms intermetallic compounds with tin (e.g. Ag_3Sn), and the formation of excess intermetallic compounds in a solder join can cause it to be rough, brittle, and subject to cracking.

Reference material: ASM International (1992); Selwyn (2000).

DELAMINATION OF MERCURY-GILDED SILVER

During mercury gilding of silver, prolonged heating may cause large numbers of silver atoms to diffuse from the underlying silver (leaving it porous) into the gold (causing blisters). The gilding may then delaminate from the silver. For more information on this problem, see "Chapter 7. Gold."

Reference material: van Langh (2000).

TOXICITY

Silver is an antimicrobial agent (being toxic to organisms such as *Escherichia coli*), but it is not toxic to humans. Silver foil is sometimes used on silver balls (known as silver dragees) for decorating cakes, and colloidal silver is used in alternative medicine. Although not toxic, the consumption of large amounts of silver can turn skin blue, a condition known as argyria.

Reference material: Etris (1997).

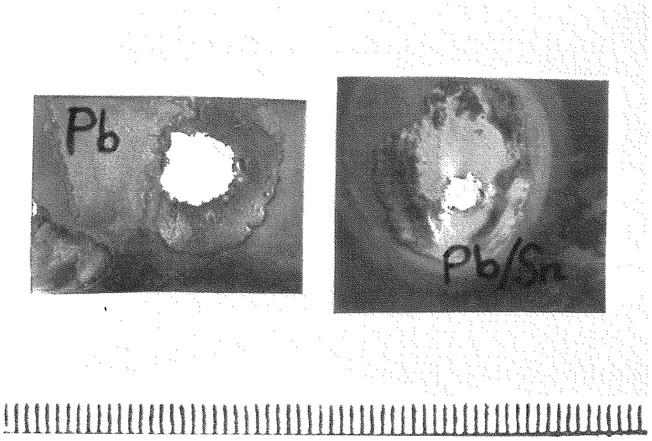

Figure 11.8. As demonstrated by this experiment, sterling silver is easily perforated when soldered with either pure lead (Pb) or a 50:50 lead–tin mixture (Pb/Sn).

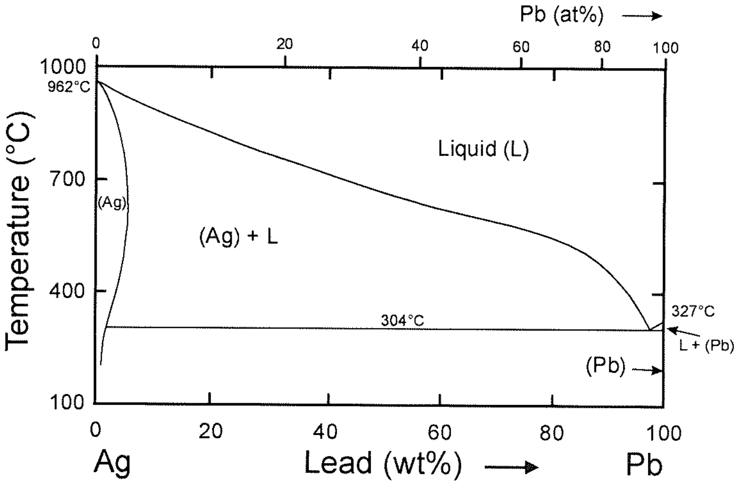

Figure 11.9. Equilibrium phase diagram for silver and lead. The bottom scale is weight percent and the top scale is atomic percent. Adapted from ASM International (1992).

12 TIN (Sn)

Principal oxidation number(s)	Atomic weight (g mol^{-1})	Density at 20°C (g cm^{-3})	Melting point (°C)	Boiling point (°C)	Linear expansivity (°C^{-1})	UNS range for alloys
Sn^{2+}(stannous) Sn^{4+}(stannic)	118.69	7.31	232	2602	22.0 x 10^{-6}	L13001– L13999

GENERAL DESCRIPTION

Tin is one of the world's most ancient metals. In its pure form it is silvery-white in colour, non-magnetic, soft, and malleable. It can be easily rolled and cold-worked, and has a lower melting point and a higher boiling point than other common metals. It is also non-poisonous and will not contaminate food. Because it is too soft for most uses, tin is usually alloyed with other metals.

For more information on tin, see the Web site of the International Tin Research Institute (www.itri.co.uk).

Reference material: Gaver (1997); Murphy (2000); Waite (1992).

PHASES IN PURE TIN

Tin exists in two different allotropes (i.e. physical forms) depending on the temperature: the β phase (white tin) exists between 13 and 232°C, and the α phase (gray tin) exists at temperatures below 13°C.

The β phase is the familiar form of tin. It is soft, malleable, lustrous, and has a highly crystalline structure. A rod or bar of white tin that is bent will emit a characteristic creaking or cracking sound called "tin cry" which is caused by the crystals rubbing against one another or breaking.

The α phase of tin is brittle and has little strength. It forms when white tin is cooled to low temperatures. This transformation theoretically takes place at 13°C, but in practice temperatures below 0°C are needed (usually with prolonged exposure at -40°C). The transformation is difficult to initiate and the rate is slow. The change is greatly delayed or even inhibited if small levels of certain impurities (e.g. bismuth, antimony, lead) are present in the tin. Lead levels as low as 0.1 wt% prevent the transformation.

When tin changes from the white β phase to the gray α phase, its density changes from 7.31 to 5.84 g cm^{-3}. Because the α phase is less dense than the β phase, the formation of the α phase causes the tin to expand and disintegrate into a coarse, friable gray powder, form local warts, or crack. The deterioration of tin as it undergoes this phase change is known as "tin pest," "tin plague," or "tin disease," and the appearance can closely resemble atmospheric corrosion. Indeed, reported cases of tin pest are generally due to normal atmospheric corrosion accelerated by the presence of high RH and pollutants. However, one occurrence of tin pest was recently confirmed by Lipcsei et al. (2002), who identified (using X-ray diffraction) α phase tin on tin ingots recovered from the cold waters surrounding the *Ulu Burun* shipwreck in Turkey.

Reference material: Gilberg (1991); Lihl (1962); Lipcsei et al. (2002); Payton (1987); Plenderleith and Organ (1953); Smith (1986).

ORIGIN

Tin is found in nature almost exclusively as cassiterite (tinstone), and is recovered by melting the cassiterite at 1127°C under reducing conditions in a blast or reverberatory furnace. Ancient tin mines can be found in Turkey, Germany, Spain, France, and England. In Canada, tin was first produced commercially in 1941 at Trail, BC. The tin minerals romarchite and hydroromarchite were first identified at the Royal Ontario Museum in Toronto in 1971, and are named after that institution.

Reference material: Earl (1991); Gaver (1997); Organ and Mandarino (1971).

USE

The use of tin dates back to 3200–3500 B.C. Tinned iron was first utilized in the Iron Age, and was common during Roman times. During the Middle Ages, the tin alloy pewter was used for utilitarian objects (e.g. dishes, lamps) and tin-plated steel was used by tinsmiths to make tableware (tinware). Commercial manufacturing of tinplate started around the 17th century.

Today, tin can be found in solders, and a range of white metals (bearing metals, pewter, Britannia metal). It is widely used as plating on copper and iron — particularly when manufacturing steel cans for food (because it is non-toxic) and also as a durable roofing material that can last for 50–100 years if kept well painted. (Note that the term "tin ceiling" tends to be a misnomer because most decorative sheets on ceilings are painted iron, not tinplate.) Tin compounds are also used to make glass opaque or colour it red (opaque white glass and glazes are made by adding powdered tin oxide; red ruby glass is made by adding a pigment of tin and gold called Purple of Cassius). Tin(IV) sulphide, with its golden colour, can be used to make a "gold" pigment called mosaic gold.

Reference material: Corfield (1985); Gaver (1997); Gayle and Look (1992); Hull (1992); Penhallurick (1986); Thornton (2000).

ALLOYS AND PLATING

Tin is often alloyed with other metals, one of the most common alloys being pewter. Old pewter is a tin–lead alloy and modern pewter is a tin–antimony alloy. Some general characteristics of tin–lead and tin–antimony alloys are discussed below, along with some examples of their use. Tin can also be added to copper to make the copper alloy known as bronze. For more information on bronze, see "Chapter 6. Copper."

TIN–LEAD ALLOYS

Lead is one of the most common metals alloyed with tin. A description of this alloy, along with the lead–tin phase diagram (Figure 9.1), was presented previously in "Chapter 9. Lead" (see p. 116).

Solder: Tin and lead are easily combined to form a group of alloys with relatively low melting points (i.e. alloys melting below 450°C) known as soft solders. Other elements (e.g. bismuth, cadmium, silver, and antimony) may also be present in small amounts. Two examples of tin–lead solders are given in Table 12.1.

Electronic components are commonly soldered with tin–lead solders that have a high tin content. These high-tin solders have the low soldering temperatures that are needed to avoid component damage. They also have higher electrical conductivities than high-lead soft solders, and they freeze rapidly — making assembly quick. Due to environmental concerns about lead toxicity, efforts are presently being made to phase out lead-based solders in electronics. For more information on high-lead solders, see "Chapter 9. Lead."

During the soldering process, the solder melts and flows over the underlying metal, wetting the surface. As a result of this action, some of the underlying metal dissolves in the molten solder. Several metals have an appreciable solubility in molten tin, especially gold and silver. As the layer of molten solder adjacent to the underlying metal becomes saturated with dissolving metal, intermetallic compounds start to precipitate. The tin in molten lead–tin solder reacts with many common soldered metals to form intermetallic compounds (see Table 1.3 on p. 8); in contrast, the lead-component does not react with most common metals, although it does form intermetallic compounds with gold (e.g. Au_2Pb, $AuPb_2$, and $AuPb_3$).

The formation of these intermetallic compounds at the soldering interface produces a strong metallurgical bond and a strong solder join. For example, when copper is soldered with a tin–lead solder, two layers of intermetallic compounds form: a layer of the ε phase (Cu_3Sn) adjacent to the copper and a layer of the η phase (Cu_6Sn_5) above the ε phase (for more information, see the copper–tin phase diagram in Figure 6.3 on p. 56). These intermetallic compounds grow at a substantial rate until the solder solidifies. Because intermetallic compounds tend to be brittle, the solder join may be rough and brittle if the intermetallic compound layers are too thick.

Reference material: Meeks (1993b); Murphy (2000); Tu and Zeng (2001).

TABLE 12.1. TIN-LEAD SOLDERS

Tin (wt%)	Lead (wt%)	Melting range (°C)	UNS number	Uses
63	37	183	L13630	electronic soldering (eutectic)
60	40	183–190	L13600	electronic soldering (fine solder)

Old pewter (leaded pewter): Early pewter was made with tin–lead alloys, and is sometimes referred to as leaded pewter to distinguish it from modern pewter (which should not contain lead). Ancient Roman pewter contained about 70 wt% tin and 30 wt% lead. Leaded pewter was easy to cast but not easy to shape. It became one of the most common metals for daily items in Europe during the Middle Ages, and was widely used for utilitarian objects such as dishes, lamps, candlesticks, and mugs (see, for example, Figure 12.1). Old pewter with a high lead content became known as black metal because it darkened greatly with age.

Figure 12.1. Leaded pewter mugs with varying capacities (1/4 gill, 1/2 pint, gill, and 1/2 gill) belonging to C. Gruchy (a former Director General of CCI). (Note: 1 gill = 1/4 pint.)

In 15th-century England, control of pewter production was granted to the Worshipful Company of Pewterers; English trade guilds subsequently enforced rigid standards on pewter production. Listed in Table 12.2 are the three basic grades they defined.

TABLE 12.2. GRADES OF OLD PEWTER

Grades of old pewter	Approximate composition	Uses
Fine or Plate	high tin (~85 wt%) low lead (~10 wt%) some copper	flatware (plates, dishes)
Trifle	high tin low lead (up to 4 wt%)	hollowware (bowls, drinking cups)
Lay or Ley	high tin high lead (up to 15 wt%)	non-food items (spirit measures)

In England and in the United States, pewter pieces were often marked on the base to identify the maker. Numerous books document old pewter makers and their marks. For more information on marking of pewter, see the Web site of the Pewter Society (www.members.aol.com/pewtrsocty/).

Leaded pewter continued to be used until the 19th century, when it was replaced by Britannia metal (a tin–antimony alloy).

Reference material: Child (1988); Cotterell (1963); Hull (1992); Laughlin (1969); Nadolski et al. (1987).

Organ pipes: Various tin–lead alloys are used for organ pipes, and it is common for the pipes of a single organ to be made from different materials, depending on the sound quality required. An alloy of 95 wt% tin and 5 wt% lead is often used for the largest pipes, with the tone of the other pipes changed by reducing the tin content and increasing the lead content. The molten metal is first cast into sheets which are then formed into cylindrical pipes and the seams soldered. In Canada, pipe organs are still being built by a century-old company called Casavant-Frères in St. Hyacinthe, QC. For more information on this company, see the Web site for Casavant-Frères (www.casavant.ca); for information on the conservation and maintenance of pipe organs in general, see the Web site for The New South Wales Heritage Office (www.heritage.nsw.gov.au/nav.htm).

Reference material: Friesel and Karlsson (1999); Kinsela (1983).

TIN–ANTIMONY ALLOYS

Antimony is another metal that is commonly alloyed with tin. Several examples of tin–antimony alloys, with their approximate composition, are listed in Table 12.3.

Tin–antimony alloys that are white in colour (e.g. casting and bearing alloys, modern pewter, and Britannia metal) are known as "white metal" although this term can also be used in a generic sense to describe white-coloured alloys with relatively low melting points.

Britannia metal: Around 1769, J. Vickers developed a new, improved pewter called Britannia metal. The new alloy contained mainly tin (~90 wt%) with some antimony and copper. It was more durable and had better moulding qualities than the older leaded pewter. It was

TABLE 12.3. TIN-ANTIMONY ALLOYS

Alloy name or description	UNS number	Tin (wt%)	Antimony (wt%)	Copper (wt%)	Zinc (wt%)
modern pewter	L13963	95–98	1–3	1–2	0.005 max
tin–antimony solder	L13950	95	4.5–5.5	0.08 max	0.005 max
modern pewter casting alloy	L13911	90–93	6–8	0.25–2	0.005 max
Britannia metal (Queen's metal)	—	88.5	7.1	3.5	0.9
white metal bearing alloy (babbitt metal)	L13840	83–85	7.5–8.5	7.5–8.5	0.005 max
tin die-casting alloy	L13820	80–84	12–14	4–6	0.01 max

malleable, ductile, could be worked from flat sheets by cold-shaping processes, and did not require annealing after fabrication.

Reference material: Child (1988); Hull (1992).

Modern pewter: The alloys used in modern pewter are similar to the older Britannia metal compositions. They typically contain 90–98 wt% tin, 1–8 wt% antimony, and 0.5–3 wt% copper. Modern pewter is used to make small items such as tankards, candlesticks, decorative plates, plaques, figurines or models, and jewelry (which for reasons of toxicity should definitely not contain any lead). Two examples (UNS L13911 and L13963) are listed in the above table.

Solder: The current environmental concerns about the use of lead-based soft solders have led to the development of new lead-free soft solders. One example of a lead-free solder now used for plumbing is a tin–antimony solder (UNS number L13950) that melts in the range 233–240°C.

Casting alloys: Tin–antimony alloys are easily cast at low temperatures and are especially suitable for small detailed work. Model soldiers and other miniatures are made with a tin die-casting alloy (i.e. alloys suitable for casting into permanent moulds) such as L13820. Other tin–antimony alloys are used for casting costume jewelry.

Bearing metal (babbitt metal): In 1839, I. Babbitt patented various white metal alloys that contained mainly tin alloyed with antimony and copper for use as bearing material to line steel or bronze shells. As a result of his work, a range of white bearing alloys (known commercially as babbitt metal) were developed. These alloys are commonly used for lubricant-film bearings; they reduce friction and allow for the movement of heavy rotating parts. Babbitt alloys may have high-tin or high-lead content, but all of them have a characteristic structure of hard intermetallic compounds within a relatively soft matrix, and all can be used at temperatures up to 175°C.

Modern tin babbitts usually contain 5–8 wt% antimony and 3–8 wt% copper. One example is the bearing alloy UNS L13840 listed in the above table. The microstructure consists of a soft matrix (a solid-solution of antimony in tin) filled with small hard particles (the copper–tin η phase). Increasing the copper content increases the amount of this intermetallic copper–tin phase whereas increasing the antimony concentration above 7.5 wt% promotes the formation of an intermetallic antimony–tin compound (SbSn).

Modern lead babbitts usually contain 9–16 wt% antimony and up to 12 wt% tin. The microstructure consists of a soft mixture of the three metals and hard particles of the intermetallic antimony–tin compound. Lead babbitts are often used as inexpensive substitutes for tin-based ones.

Reference material: Booser (1992); Gaver (1997).

TIN–MERCURY MIRRORS

Tin amalgams were once used as a reflective coating on glass to make mirrors. These mirrors were used from the 16th century until the beginning of the 20th century, when silver-backed glass mirrors became more popular. The reflective coating in tin–mercury mirrors contains two phases, a mercury-rich liquid and tin-rich solid (i.e. one of the tin–mercury intermetallic phases γ, δ, or ε). The tin–mercury phase diagram is shown in Figure 12.2. The reflection is due mainly to the mercury-rich liquid phase in contact with the glass. Tin amalgams have also been used to imitate silver inlay in wooden cabinets.

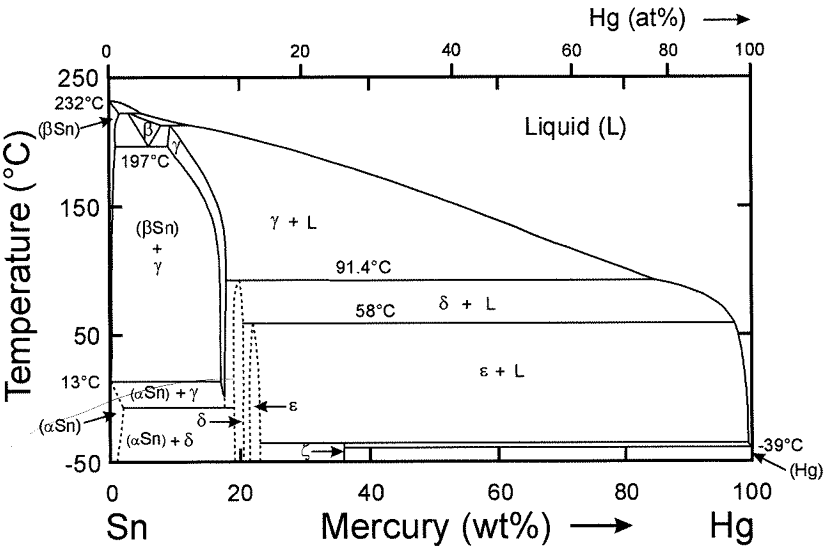

Figure 12.2. Equilibrium phase diagram for tin and mercury. The bottom scale is weight percent and the top scale is atomic percent. The intermetallic compounds have the following composition: γ phase = ~Sn_8Hg; δ phase = ~Sn_7Hg; and ε phase = ~Sn_6Hg. Adapted from ASM International (1992).

Reference material: ASM International (1992); Corbeil (1998); Hadsund (1993).

TIN-PLATED COPPER ALLOYS (TINNED COPPER)

Mercury tinning (fire tinning): Tin amalgams were used as early as Roman times to deposit a layer of tin onto copper alloys. This process was begun by heating tin and mercury to obtain a homogeneous mixture, and then cooling it. The amalgam that formed contained two phases: a mercury-rich liquid and a tin-rich solid (i.e. one of the intermetallic phases γ, δ, or ε). This amalgam was spread on the surface of a copper alloy and then heated to decompose the amalgam (at about 214°C) and drive off essentially all of the mercury (boiling point 357°C). The remaining molten tin then reacted with the copper alloy surface to form copper–tin intermetallic compounds (e.g. ε and η phases). (See the copper–tin phase diagram in Figure 6.3 on p. 56.)

Reference material: Kossolapov and Twilley (1994); Meeks (1986, 1993a, 1993b); Oddy and Bimson (1985).

Wiping and hot-dipping: In antiquity, copper cooking vessels were often tinned to prevent food from being tainted with copper. The tin could be applied by wiping or hot-dipping.

In wiping, tin is melted onto a copper surface that has been cleaned and flux-coated, and then the excess molten tin is wiped over the surface with a cloth. The surface copper reacts with the tin to form angular crystals of intermetallic compounds; the intermetallic ε phase precipitates next to the copper surface, and is then covered by a layer of the η phase. The resulting tinned surface is silvery in colour but dull and matte. Polishing produces a shiny, reflecting surface.

In hot-dipping, the copper alloy is first warmed, fluxed with rosin, and then heated to a temperature just above the melting point of tin. It is then dipped briefly into a bath of molten tin and the excess tin allowed to drain off. The intermetallic compounds (e.g. ε and η phases) that form are covered by a layer of unalloyed tin, which provides a smooth, reflective, and silvery surface. Because the surface is covered with this thin layer of soft tin metal overlying the harder intermetallic compounds, alloys tinned in this manner scratch easily.

Reference material: Meeks (1993b); Oddy and Bimson (1985).

Electroplating: The modern method for plating tin onto copper (e.g. tin plating on copper cooking utensils) is electroplating. There is some evidence that an electrochemical process was also used in the past to apply tin to brass pins. The process is thought to involve boiling a copper alloy in a solution of potassium tartrate together with granules of tin or pieces of tin foil.

Reference material: Meeks (1993b); Oddy and Bimson (1985).

Tin sweat: Tin-rich material that may appear on the surface of cast copper–tin alloys as they cool rapidly is known as tin sweat. Although this process is not intentional, the resulting surface is silver-coloured and can look like deliberate tinning. For more information about tin sweat, see "Chapter 6. Copper."

TIN-PLATED IRON

Wiping and hot-dipping: A layer of tin can be applied to the surface of iron by cleaning it, applying a coat of flux, and then dipping it into a bath of molten tin or a tin–lead alloy (note that pure lead cannot be applied to iron in this manner). An alternative process, known as "fusion" plating, is to sprinkle tin filings onto a cleaned and flux-coated iron surface and then heat it to melt the tin. Yet another variant, known as "wiping," is to wipe tin (in stick or powder form) over a prepared surface that is hot enough to melt the tin. Regardless of which method is used to apply the molten tin, the θ phase (the intermetallic compound $FeSn_2$) forms at the interface by diffusion of tin into the iron (see the tin–iron phase diagram in Figure 12.3). The resulting tin-plated iron is known as tinplate or tinned iron.

Reference material: ASM International (1992); Corfield (1988); Meeks (1993b); Murphy (2000).

Electroplating: The tinplate used in modern tin cans is made by electroplating, a process that began to replace hot-dipping in the 1930s. The iron is a sheet of mild, low-carbon steel. After plating, the tin undergoes momentary melting followed by quenching in water. This converts the matte, as-deposited coating to a bright, reflective surface, and also allows for the formation of a layer of the θ phase.

Reference material: Meeks (1993b); Murphy (2000).

CORROSION

When pure tin is exposed to air that is free of moisture and pollutants, it forms a stable oxide film that allows it to maintain its lustrous silvery-white brightness for a long time. However, if the air is moist, the surface oxide layer thickens and the tin turns a dull gray colour. Some of the tin minerals and tin corrosion products discussed in this chapter are listed in Table 12.4.

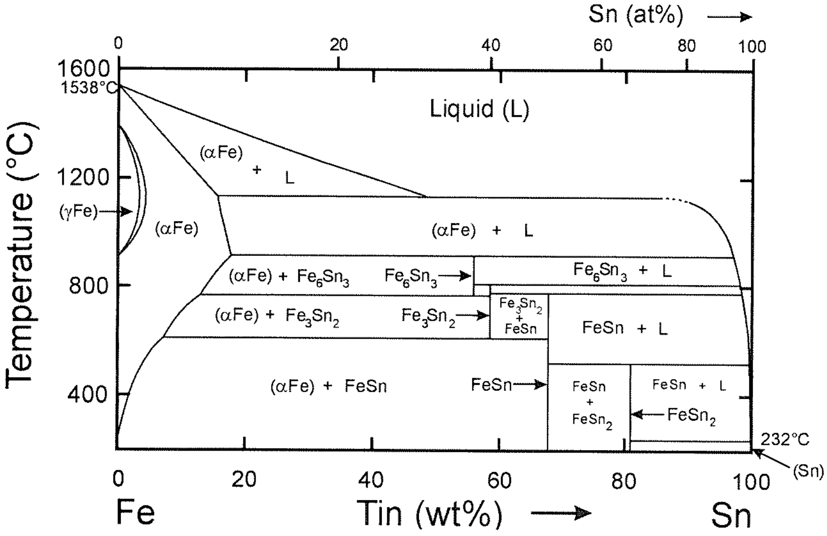

Figure 12.3. Equilibrium phase diagram for iron and tin. The bottom scale is weight percent and the top scale is atomic percent. $FeSn_2$ is sometimes called the θ phase, and FeSn is sometimes called the η phase. Adapted from ASM International (1992).

Reference material: Gaver (1997); Organ and Mandarino (1971); Turgoose (1985).

SOLUTION CHEMISTRY

The principal oxidation states of tin are +2 (Sn^{2+}) and +4 (Sn^{4+}). The initial anodic and cathodic half-reactions are usually given by:

Anodic half-reaction: $Sn(s) \rightarrow Sn^{2+} + 2e^-$
Cathodic half-reaction: $\frac{1}{2}O_2(g) + H_2O + 2e^- \rightarrow 2OH^-$
Net reaction: $Sn(s) + \frac{1}{2}O_2(g) + H_2O \rightarrow Sn^{2+} + 2OH^-$

Tin is reasonably stable when exposed to aqueous solutions with pH 3–10 (the surface is initially covered with a thin layer of tin(II) oxide, which can be further oxidized to tin(IV) oxide). However, being amphoteric, it corrodes at either lower or higher pH levels. At lower pH (acidic conditions), it dissolves as Sn^{2+} or Sn^{4+} ions, and at higher pH (alkaline conditions) it dissolves as $Sn(OH)_6^{2-}$ or $Sn(OH)_3^-$ ions. Tin is also susceptible to corrosion when exposed to chloride ions, which form soluble complexes with both tin(II) and tin(IV) ions.

Reference material: Gaver (1997); Turgoose (1985).

INDOOR EXPOSURE

The colour of tin and high-tin alloys is generally gray (this includes leaded pewter which tends to be a duller gray). The shade of gray depends on the amounts of the two tin oxides, the black tin(II) oxide and the white tin(IV) oxide. The colour can also darken when tin is exposed to pollution, especially hydrogen sulphide, because of the formation of coloured tin sulphides. The presence of chloride ions may encourage local corrosion of tin and result in the formation of black spots of tin oxide. Tin is not generally susceptible to the serious corrosion problems suffered by many other metals when exposed to volatile organic acids, although the lead component in tin–lead alloys (e.g. leaded pewter) is. This may take the form of active corrosion, with white powdery material (usually lead carbonate hydroxide) forming as a result of exposure to moisture and volatile organic acids. For more information on active corrosion on lead, see "Chapter 9. Lead."

TABLE 12.4. TIN MINERALS AND CORROSION PRODUCTS

Chemical name	Mineral name	Chemical formula	Colour
tin(II) oxide	romarchite	SnO	black
tin(II) hydroxide oxide	hydroromarchite	$Sn_3O_2(OH)_2$	white
tin(IV) oxide	cassiterite	SnO_2	white
tin(II) sulphide	herzenbergite	SnS	black
tin(II,IV) sulphide	ottemannite	Sn_2S_3	gray
tin(IV) sulphide	berndtite	SnS_2	yellow-brown
magnesium tin(IV) hydroxide	schoenfliesite	$MgSn(OH)_6$	white

Reference material: Child (1988); Leidheiser (1971); Murphy (2000); Turgoose (1985).

OUTDOOR EXPOSURE

Pure tin and tin alloys are rarely found outdoors. However, tin-plated iron is used as roofing and the tin–lead alloys in organ pipes in churches may be exposed to damp, cold conditions where moisture can condense on their surface. When tin alloys are exposed to high moisture levels, they corrode and become covered with a mixture of black tin(II) oxide and white tin(IV) oxide. The initial shiny surface dulls to a gray colour and the texture can be granular. Tin alloys tend to retain their bright appearance longer in rural areas than they do in marine and industrial environments, where they are more likely to be exposed to chloride ions and pollution. White corrosion products (presumably tin(IV) oxide) have been observed in areas sheltered from rain. If the tin oxides form within cracks or pores in the metal, the increase in volume may stress the surrounding material, causing it to split away from the relatively soft underlying metal. Figures 12.4 and 12.5 show a corroded tin sundial (dating from ~1512) after prolonged outdoor exposure.

Reference material: Leidheiser (1971); Warwick (1982).

CORROSION DURING BURIAL

Tin alloys from burial sites are usually covered with characteristic pustules or wart-like blisters overlying holes or deep corrosion pits. Blisters are thought to be produced by the expansion of corrosion products that have formed in crevices and cracks in the metal, which causes the surrounding relatively soft material to expand. The tin corrosion may also appear as laminar exfoliation of surface layers, fractures and cracks, and crater-like holes filled with powdery corrosion.

When lead-free tin alloys (tin alloyed with antimony and copper) are recovered from well-aerated marine sites, they have usually corroded extensively to tin(IV) oxide, copper corrosion products, and

Figure 12.4. A corroded tin sundial (dating from ~1512) after being removed from an outdoor environment and placed into storage at Arc'Antique in Nantes, France.

Figure 12.5. Close-up photograph of the cracking and corrosion on the tin sundial shown in Figure 12.4. Photograph by J.G. Aubert 10/96. Courtesy of Arc'Antique.

residual uncorroded tin–antimony intermetallic compounds (the corrosion is extensive because the initial tin oxide was not an effective barrier and allowed corrosion to continue unabated). On occasion, the mineral schoenfliesite has also been identified on corroded tin from aerobic marine sites. If oxygen access was restricted, tin(II) or mixed tin(II)–tin(IV) compounds may be present (see MacLeod 1991; MacLeod and Wozniak 1997). If the site was anaerobic, the tin alloys are often well preserved by a protective layer of tin sulphides.

Leaded tin alloys (e.g. leaded pewter) are relatively resistant to corrosion in marine environments. They are often protected by lead corrosion products — either lead sulphate (under aerobic conditions) or lead sulphide (under anaerobic conditions).

Reference material: Child (1988); Leidheiser (1971); Lihl (1962); MacLeod (1984, 1991); MacLeod and Wozniak (1997); Murphy (2000); North (1987); North and MacLeod (1987); Payton (1987); Turgoose (1985).

YELLOW STAIN

If sheets of tin or tin-plated iron are left stacked on one another for several months under conditions of high RH, an adherent yellow film forms on the surface (industry calls this yellow stain). The yellow stain is due to the formation of tin oxide in oxygen concentration cells.

Reference material: Murphy (2000).

GALVANIC CORROSION

Tinned iron: As long as there are no imperfections in the tin layer, it corrodes in the same way as pure tin (i.e. it is relatively stable) and acts as a physical barrier that protects the iron underneath from rusting. However, because tin is more noble than iron, a galvanic cell will be established if the tin plating has imperfections or is damaged so as to expose the iron. In this case, the iron suffers accelerated corrosion in the presence of moisture due to galvanic action between the tin and iron. The iron behaves as the anode and forms rust as shown in Figure 12.6.

Reference material: Murphy (2000).

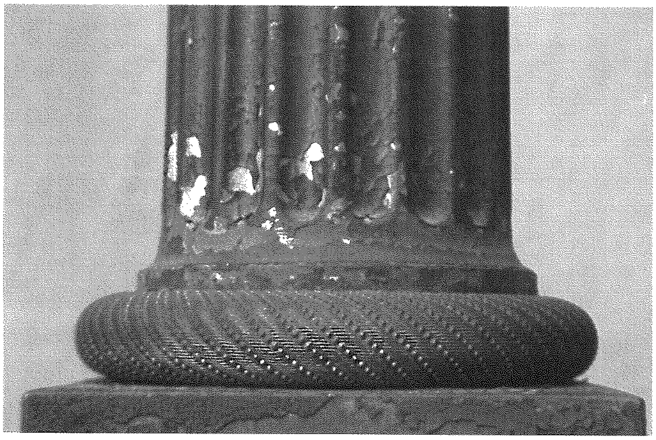

Figure 12.6. Iron corrosion on a painted tinware lamp from a room in a historic house overlooking the sea. Photograph by Lisa Ellis. Courtesy of the Collections Department of the Society for the Preservation of New England Antiquities (SPNEA). (A colour version of Figure 12.6 is available on p. 88.)

Inside tinned iron cans: There is usually a reversal of the relative potentials of the tin and iron inside a sealed tinned iron container, especially when the contents are acidic (e.g. fruit acids such as citric, tartaric, malic). Under the pH and anaerobic conditions inside the container, the tin coating acts as an anode and it is the tin rather than the iron that corrodes. Although tin and iron are both non-toxic, they can alter the flavour and appearance of food so it is important for the canning industry to maintain low levels of dissolved ions. Therefore, even though the tin coating corrodes very slowly, the inside of tinned iron cans is often lacquered to further reduce corrosion.

Reference material: Murphy (2000).

CORROSION OF TIN AMALGAMS

Tin amalgams can also suffer from galvanic corrosion. The mercury-rich liquid phase (the more noble component) accelerates the corrosion of the tin-rich solid phase (the more active component). As the tin-rich intermetallic phase corrodes, it forms tin oxides (tin(II) oxide and/or tin(IV) oxide) and releases more liquid mercury to the mixture, which perpetuates the corrosion.

Reference material: Corbeil (1998); Hadsund (1993).

13

ZINC (Zn)

Principal oxidation number(s)	Atomic weight (g mol^{-1})	Density at 20°C (g cm^{-3})	Melting point (°C)	Boiling point (°C)	Linear expansivity (°C^{-1})	UNS range for alloys
Zn^{2+}(zincic)	65.39	7.13	420	907	30.2×10^{-6}	Z00001–Z99999

GENERAL DESCRIPTION

Zinc is a non-magnetic, bluish-white, lustrous metal. Softer than iron, it has low strength and is subject to creep (slow deformation under constant load). Zinc has a fairly high coefficient of thermal expansion; it is brittle at 25°C but becomes malleable when heated to about 100°C. Zinc's corrosion products are white if finely divided, but are otherwise colourless.

For more information on zinc, see the Web site for the International Lead Zinc Research Organization (www.ilzro.org).

Reference material: Dawkins (1950); Gayle and Look (1992); Porter (1991); Waite (1992).

ORIGIN

Zinc ores generally contain one or more of the minerals smithsonite, hemimorphite, and hydrozincite, although another principal source is the mineral sphalerite (also known as zinc blend or wurtzite). Some confusion may arise when reading the literature on zinc because zinc ores have often been collectively termed "calamine" — a term used in England to describe zinc carbonate ores and in the United States to describe zinc silicate ores.

Collecting zinc metal after it has been reduced from ore is more difficult than collecting many other metals. Zinc boils at 907°C; therefore, during the smelting of zinc-containing ores, the zinc evaporates and reoxidizes in the upper parts of the furnace instead of simply melting and collecting at the base of the furnace as happens with metals such as copper and lead. Special procedures are therefore required to collect the evaporated zinc metal in a condenser and convert it to liquid zinc by cooling. Due to the difficulties in collecting the metal, the metallic properties of zinc were not recognized until the 17th century and the industrial scale smelting of zinc ore was not performed until 1738 (by W. Champion).

In Canada, there are presently zinc mines in every province and territory except Alberta and Prince Edward Island.

Reference material: Craddock (1998); Dawkins (1950); Dutrizac and O'Reilly (1984); Goodwin (1998a); Porter (1991); Tylecote (1987).

USE

Zinc became popular as a roofing material in Europe in the early 1800s. By the latter part of that century, it could also be found in architectural decorations such as mouldings, animal heads, and gargoyles. Over the years zinc has been used for many coins, either as a plating over steel (e.g. in the United States in the 1940s) or as a zinc alloy (e.g. during World War I and World War II in Germany and in German-occupied countries such as Belgium and the Netherlands). Zinc compounds have also been used as white pigments (e.g. zinc oxide, zinc sulphide, and zinc sulphide mixed with barium sulphate in the pigment lithopone).

Reference material: Ashurst and Ashurst (1988a); Gayle and Look (1992); Krause and Mishler (1991).

SCULPTURES

Zinc was first cast into sculptures in 1832 in Germany. Between 1850 and 1920, it was used as a low-cost alternative to bronze (and sometimes marketed as "white bronze") for sculptures, cemetery monuments, and tombstones.

Zinc sculptures could be produced by slush or sand casting (in slush casting, molten zinc was poured into small moulds, sloshed around, and the excess poured out, leaving a thin coating of zinc; in sand casting, a model was pressed into sand to form a mould for the molten zinc) or by bolting together or soft soldering stamped zinc sheets (an example of an architectural decorative element created from stamped zinc sheet is shown in Figure 13.1). The different methods produced sculptures with different thicknesses. In general, sand-cast pieces were 9.5–12.7 mm ($^{3}/_{8}$–$^{1}/_{2}$") thick, slush-cast pieces were 6.3–9.5 mm ($^{1}/_{4}$–$^{3}/_{8}$") thick, and stamped sheets were about 1.25 mm ($^{1}/_{20}$") thick. Once completed, zinc pieces were often finished to imitate other materials (more expensive materials such as marble, sandstone, granite, polychromed wood, bronze, and even gold), either by painting, electroplating with copper and patinating to resemble bronze, or being left uncoated and allowed to develop a light gray or white patina.

The use of zinc in sculptures started to decline around 1920 when foundries began to recognize its poor durability outdoors (large sculptures tended to creep under their own weight and zinc sheets in sculpture broke or were torn over time).

Figure 13.1. Stamped zinc decorative element on the 1898 Aberdeen Pavilion, Ottawa.

Reference material: Ashurst and Ashurst (1988b); Gayle and Look (1992); Grissom (1994); Grissom and Harvey (2003); Holm (1994); Lins (1985); Mottner et al. (1997, 1998); Riederer (1993).

ZINC OXIDE

Zinc oxide has many useful properties. It is a strong absorber of ultraviolet (UV) radiation, and is often used as a UV absorber in paints, plastics, rubber, and suntan lotion. It is photoconductive, and was used in coated paper in the first photocopying process patented in 1956 by RCA. Finally, it is amphoteric (i.e. soluble in both acids and bases). This property is sometimes undesirable (e.g. zinc oxide reacts with fatty acids in alkyd paints to form zinc soaps) but can also be used to advantage (e.g. zinc oxide is sometimes added to products to neutralize acid byproducts). The Library of Congress in the United States, for example, developed a gas-phase process based on the zinc compound diethyl zinc for mass deacidification of paper; this process left zinc oxide on the paper after treatment.

Reference material: Brown (1976); Goodwin (1998b); Porter (1991).

ALLOYS AND PLATING

ZINC–ALUMINUM ALLOYS

Today's traditional die-casting alloys are primarily zinc–aluminum alloys that contain 4 wt% aluminum. In die casting, molten metal flows under gravity or is forced under pressure into the cavity within two halves of a permanent casting die (i.e. mould) held tightly together. Such die-casting alloys can be readily cast into intricate forms and shapes because they have a low melting point and good fluidity. Some examples are shown in Table 13.1.

Although these zinc alloys can be polished to a reflective surface, this is not normally done unless they are to be plated (e.g. with chrome or silver) for decorative elements such as automobile trim or household goods. The level of impurities in these alloys is carefully controlled; if impurity levels become too high, these alloys become susceptible to intergranular corrosion.

TABLE 13.1. ZINC-ALUMINUM ALLOYS

Cast zinc alloys	Other name(s)	UNS number	Approximate composition
die casting	Alloy No. 3, AG40A, Zamak 3, Mazak 3	Z33520	96 wt% zinc, 4 wt% aluminum, 0.04 wt% magnesium
foundry alloy	ZA-8	Z35635	91 wt% zinc, 8 wt% aluminum, 1 wt% copper, 0.02 wt% magnesium
slush casting	Alloy B	Z30500	94.7 wt% zinc, 5.3 wt% aluminum

Reference material: Barnhurst (1990); Goodwin (1998a); Porter (1991); Street (1985); Zahner (1995).

ZINC–COPPER ALLOYS

Zinc is often alloyed with small amounts of copper and titanium for modern roofing (the presence of copper and titanium help to make the zinc more resistant to creep). Listed in Table 13.2 is an example of rolled zinc used for roofing.

Reference material: Barnhurst (1990); Zahner (1995).

Bidri ware: Zinc alloyed with 2–10 wt% copper is used to make Indian metal objects known as Bidri ware. These are usually patinated black to contrast with inlays of brass, silver, or gold.

Reference material: Craddock et al. (1998); La Niece and Martin (1987); Scott (2002); Strong (1993).

Brass: Up to 45 wt% zinc can be added to copper to make the copper alloy known as brass. For more information on brass, see "Chapter 6. Copper."

ZINC–MERCURY ALLOYS

Early Indian literature mentions the use of zinc amalgams for making objects or decorative inlays. Few examples exist today.

Figure 13.2. Characteristic crystalline spangle pattern on hot-dip galvanized steel.

Reference material: Craddock et al. (1998).

GALVANIZING

A layer of metallic zinc is sometimes applied to iron or steel to protect it from rusting (because the zinc corrodes preferentially). There are several methods of application — hot-dip galvanizing, electroplating, sherardizing, zinc spraying, and painting with a zinc-rich coating — each of which provides a different thickness of zinc. More information on applying zinc coatings to iron can be found on the Web site of the American Galvanizers Association (www.galvanizeit.org).

Hot-dip galvanizing: In hot-dip galvanizing, the iron or steel is completely immersed in molten zinc (~450°C). This process was patented around 1837 by S. Sorel — who introduced the term "galvanize" because he thought the bond between the zinc and iron was from galvanic action. The surface of hot-dip galvanized steel usually has a characteristic silvery crystalline spangle pattern which is created by the crystallization of zinc as it cools following removal from the galvanizing bath. An example of this spangle pattern is shown in Figure 13.2.

The coating formed by dipping iron or steel into molten zinc is metallurgically bonded to the underlying metal through a series of zinc–iron intermetallic compounds with approximate compositions $FeZn_{13}$ (the ζ phase), $FeZn_{10}$ (the δ phase), and $FeZn_3$ (the Γ_1 phase). These phases are shown in the zinc–iron phase diagram (Figure 13.3). Each successive layer in hot-dip galvanized iron from the iron outward contains a higher portion of zinc. The intermediate layers are harder than the underlying iron so they help protect it from abrasive damage. This is illustrated in Figure 13.4. For more information on intermetallic compounds, see "Chapter 1. Metals."

Modified galvanized steel products in which a zinc–aluminum alloy (rather than pure zinc) is applied to the steel were recently introduced. Examples of these alloys include Galfan (95 wt% zinc + 5 wt% aluminum) and Galvalume (45 wt% zinc + 55 wt% aluminum). These new galvanized steel products are said to be more corrosion-resistant than traditional galvanized steel.

TABLE 13.2. ZINC-COPPER ALLOY

Wrought zinc alloy	Other name	UNS number	Approximate composition
rolled zinc	Alloy 700	Z41320	99 wt% zinc, 0.8 wt% copper, 0.15 wt% titanium

The term "duplex system" is sometimes associated with galvanized steel. This term refers to hot-dip galvanized steel that has been painted (the paint layer extends the life of the galvanized steel).

Reference material: ASM International (1992); Porter (1991); Zhang (2000).

Electroplating: Zinc can also be plated onto a prepared steel surface by electrodeposition using an electrolyte containing zinc salt. The most widely used electrolytes are acidified zinc sulphate solutions and alkaline cyanide solutions. The first patents for electroplating zinc appeared in England in 1852–1855. Today zinc electroplated onto steel is widely used for car body panels which are then painted.

Reference material: Porter (1991).

Sherardizing: Sherardizing is an industrial process that creates an even dull gray coating of zinc on small iron or steel objects. It was discovered in 1900 by Sherard Cowper-Coles, but not widely used until 1923. The iron pieces are heated with zinc dust and sand in a slowly rotating drum at a temperature just below the melting point of zinc. The zinc forms a metallurgical bond with the steel by a diffusion process which allows a hard, even layer of zinc–iron intermetallic compounds to form (as in hot-dip galvanizing).

Reference material: Porter (1991).

Zinc spraying: Zinc spraying is another industrial process for applying zinc to steel surfaces (it is often used to coat structural steel pieces that are too large to dip into a galvanizing bath). In this case, molten zinc is sprayed onto a blast-cleaned steel surface. Also called metallizing, the process was first described in 1909.

Reference material: Porter (1991).

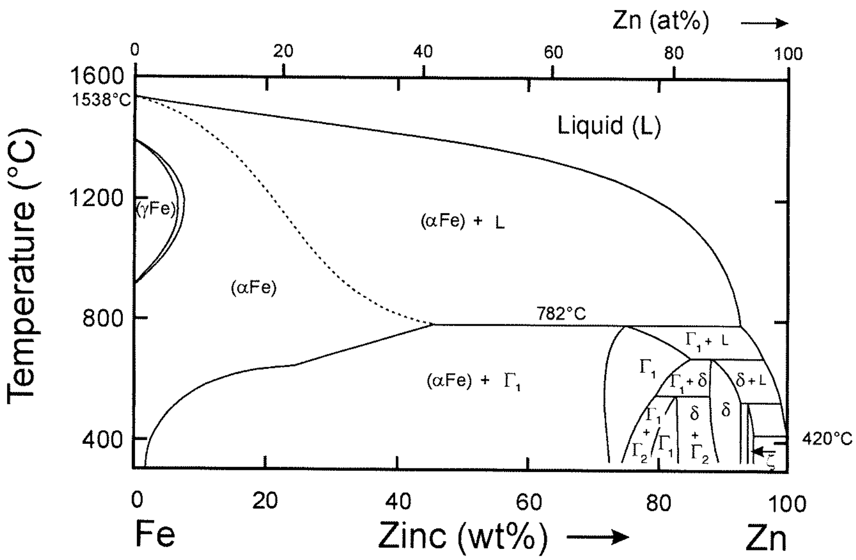

Figure 13.3. Equilibrium phase diagram for iron and zinc. The bottom scale is weight percent and the top scale is atomic percent. The approximate compositions of some of the intermetallic compounds are as follows: the ζ phase is ~ $FeZn_{13}$; the δ phase is ~ $FeZn_{10}$; and the Γ_1 phase is ~$FeZn_3$. Adapted from ASM International (1992).

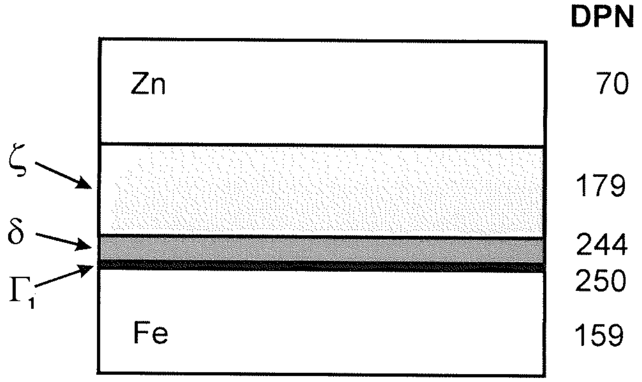

Figure 13.4. Intermetallic zinc–iron phases on hot-dip galvanized iron. The relative hardness of each phase is indicated by its diamond pyramid number (DPN). The higher the number, the greater the hardness. Adapted from the Web site of the American Galvanizers Association (www.galvanizeit.org).

Zinc-rich paints: Zinc can also be applied to steel surfaces using zinc-rich paints, which were largely developed at Cambridge, England, in the 1930s and early 1940s. Zinc-rich paints contain a high fraction of zinc dust particles and are best applied to rust-free iron surfaces. If the zinc-rich paint contains more than 90 wt% metallic zinc (enough to ensure that the paint film is electrically conducting when dry), it can protect the steel from rusting by a galvanic process.

Zinc-rich paints can be divided into two main groups (depending on whether the medium is organic or inorganic): organic-based paints are generally based on epoxy resins, polystyrene, or chlorinated rubber whereas inorganic-based paints generally contain a silicate. (The original zinc silicate paints were developed in Australia about 1940; they were a mixture of zinc dust and sodium silicate, and the film was formed by baking at 250°C for 2 hours.)

Reference material: Porter (1991).

CORROSION

A new piece of metallic zinc maintains a lustrous appearance because the freshly exposed metal reacts with air to form a thin transparent film of zinc oxide. Some common zinc minerals and zinc corrosion products are listed in Table 13.3.

Reference material: Goodwin (1998b); Graedel (1989); Zhang (2000).

SOLUTION CHEMISTRY

The principal oxidation state of zinc is +2 (Zn^{2+}). Under moist conditions, zinc corrodes electrochemically according to:

Anodic half-reaction: $Zn(s) \rightarrow Zn^{2+} + 2e^-$
Cathodic half-reaction: $\frac{1}{2}O_2(g) + H_2O + 2e^- \rightarrow 2OH^-$
Net reaction: $Zn(s) + \frac{1}{2}O_2(g) + H_2O \rightarrow Zn^{2+} + 2OH^-$

The zinc ions react with water to form either zinc oxide or zinc hydroxide, both of which are only slightly soluble. As long as the solution pH remains in the range 6–12, these compounds remain stable and, because of their low solubility, tend to form a relatively adherent film on the zinc surface. However, these zinc oxides and hydroxides may be converted chemically to other compounds — depending on the composition of the surrounding electrolyte. Zinc is amphoteric and suffers accelerated corrosion when the conditions become too acidic or too alkaline. At pH < 6 (acidic), zinc dissolves as Zn^{2+} ions; at pH > 12 (alkaline), it dissolves as $Zn(OH)_4^{2-}$ ions.

Reference material: Goodwin (1998b); Graedel (1989); Porter (1991); Zhang (2000).

INDOOR EXPOSURE

Zinc does not generally corrode in a clean indoor environment until the RH is above 70%. As it slowly loses its original lustre, the tarnish begins in places where dust particles have fallen and gradually spreads over the entire surface. Over time, the carbon dioxide in air reacts with surface zinc oxide and zinc hydroxide, converting them into carbonates, mainly zinc carbonate hydroxides.

The formation of a relatively adherent layer of zinc carbonate hydroxides keeps the corrosion rate of zinc slow in uncontaminated atmospheres. However, if the atmosphere is contaminated with organic acids such as acetic (ethanoic) or formic (methanoic) acids, the zinc forms water-soluble zinc acetate (zinc ethanoate) and zinc formate (zinc methanoate) — and corrosion

TABLE 13.3. ZINC MINERALS AND CORROSION PRODUCTS

Chemical name	Mineral name	Chemical formula	Colour
zinc(II) oxide	zincite	ZnO	white
zinc(II) hydroxide	—	$Zn(OH)_2$	white
zinc(II) carbonate	smithsonite	$ZnCO_3$	white
zinc(II) carbonate hydroxide	hydrozincite	$Zn_5(CO_3)_2(OH)_6$	white
zinc(II) carbonate hydroxide monohydrate	—	$Zn_4CO_3(OH)_6 \cdot H_2O$	probably white
zinc(II) sulphate heptahydrate	goslarite	$ZnSO_4 \cdot 7H_2O$	white
zinc(II) hydroxide sulphate hydrate	—	$Zn_4(OH)_6SO_4 \cdot xH_2O$*	probably white
zinc(II) chloride hydrate	—	$ZnCl_2 \cdot xH_2O$*	white
zinc(II) chloride hydroxide monohydrate	simonkolleite	$Zn_5Cl_2(OH)_8 \cdot H_2O$	white
zinc(II) formate hydrate	—	$Zn(HCO_2)_2 \cdot xH_2O$*	white
zinc(II) acetate dihydrate	—	$Zn(CH_3CO_2)_2 \cdot 2H_2O$	white
zinc(II) hydroxide silicate monohydrate	hemimorphite	$Zn_4(OH)_2Si_2O_7 \cdot H_2O$	white
zinc(II) sulphide	sphalerite	ZnS	white

*x can vary, depending on the number of waters of hydration.

proceeds. Zinc formate hydrate, for example, has been identified on indoor zinc-rich copper alloys, and zinc acetate dihydrate has been identified in the white corrosion on zinc coins (see Figure 13.5). Other indoor contaminants (e.g. chloride ions, sulphate ions, ammonia) also stimulate corrosion on zinc. Zinc reacts with ammonia to form water-soluble zinc–ammonia complex ions. Similarly, it reacts with chloride or sulphate ions to form water-soluble zinc chlorides and zinc sulphates. Zinc chloride is hygroscopic, picking up moisture at about 10% RH. If polished zinc is touched or handled with bare hands, it can be etched by the perspiration salts left behind. Although the fingerprints may hardly be visible initially, they develop slowly over the next few days and remain conspicuous. Zinc is also corroded by nitrogen oxides, which are given off by degrading cellulose nitrate.

Reference material: Graedel (1989); Green and Thickett (1993); Oddy and Bradley (1993); Persson and Leygraf (1995); Sirois and Moffatt (2001); Wypyski (1990); Zhang (2000).

OUTDOOR EXPOSURE

Zinc exposed outdoors is generally protected by an adherent layer of zinc carbonates (e.g. smithsonite, hydrozincite, zinc carbonate hydroxide hydrate), but certain conditions interfere with the formation of this insoluble zinc carbonate film. In the presence of acidic moisture (e.g. acid rain), the acid dissolves the zinc corrosion products and increases the zinc's rate of corrosion. In polluted or marine environments, zinc can form soluble zinc compounds (e.g. zinc sulphate, zinc chloride) which can be easily washed away by rain (although in the absence of rain these compounds may be slowly converted into relatively insoluble zinc hydroxide sulphates and zinc chloride hydroxides). Zinc also suffers corrosion when exposed to high pH — so it should not be embedded in alkaline material such as limestone.

Reference material: Graedel (1989); Mottner et al. (1995); Riederer (1993); Zhang (2000).

White rust: White rust, also called white stain or wet storage stain, is a type of surface corrosion that appears on stacked zinc sheets. It is a bulky, non-adherent white powder that forms when zinc is left closely stacked and stored under damp and poorly ventilated conditions. In such cases, moisture is retained between surfaces in contact. The outer edges of the water film are exposed to oxygen and become cathodic (oxygen is reduced) while the central areas where oxygen (and carbon dioxide) is restricted become anodic (zinc corrodes). The low level of carbon dioxide interferes with the usual formation of a dense gray film that takes place under normal atmospheric exposure. Instead of forming this passivating layer, the zinc corrosion products (zinc oxide, zinc hydroxide, zinc carbonate hydroxides) precipitate as non-adherent, white material at the outer edges of the water film. A close-up photograph of white corrosion (white rust) forming on a piece of galvanized steel is shown in Figure 13.6.

Reference material: Falk et al. (1998); Graedel (1989); Zhang (2000).

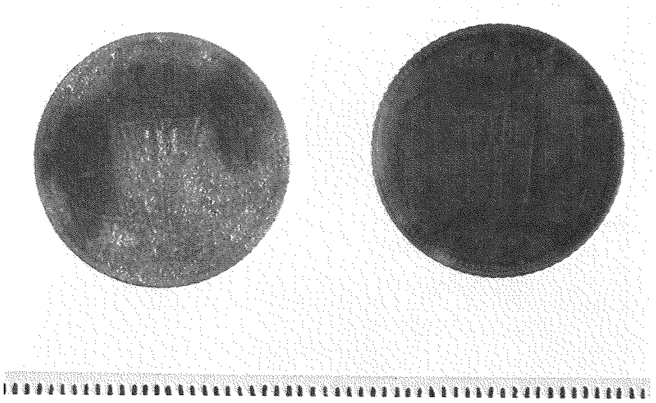

Figure 13.5. Two Belgian zinc coins (1942–1947) (owned by T. Stone and L. Carlyle, CCI). The white corrosion on the left-hand coin is a mixture of hydrozincite and zinc acetate dihydrate. Analysis of the dark even patina on the right-hand coin identified only metallic zinc.

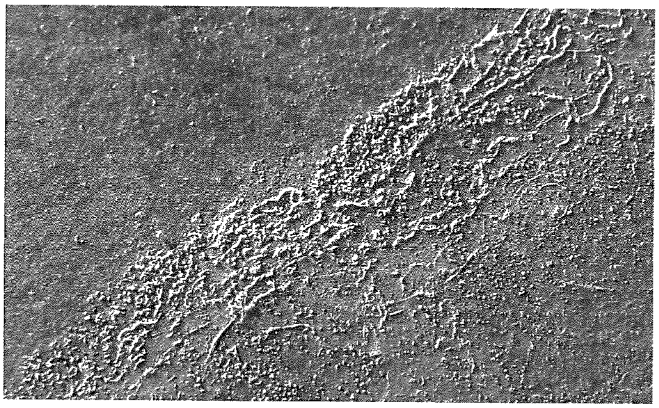

Figure 13.6. The light-coloured corrosion (known as white rust) on the surface of this piece of galvanized steel is composed of various corrosion products (e.g. zinc oxide, zinc hydroxide, zinc carbonate hydroxides) that formed when the zinc corroded under humid conditions.

Underside corrosion (also called condensation corrosion): The rate of corrosion is also influenced by the rate of drying, as a thin film of moisture with a high concentration of dissolved oxygen promotes rapid corrosion. Moisture films on outdoor zinc generally dry rapidly, but in sheltered areas the drying times may be longer and the corrosion rate slightly higher compared to non-sheltered areas. If water condenses, pools, or otherwise becomes trapped on the underside of outdoor zinc installations (e.g. roofs, sheets), there can be rapid and severe corrosion, especially if pollutants or other materials increase the acidity of the water. The corrosion often shows up as pitting, including perforation. In roofing, this problem can usually be prevented by ensuring adequate ventilation of the underside or non-exposed surface of the zinc.

Reference material: Porter (1991); Zahner (1995).

Zinc soaps: Zinc and zinc oxide react with fatty acids to form zinc soaps in a process known as saponification. When zinc is painted with an alkyd- or oil-based paint, zinc soaps can form as the zinc reacts with free fatty acids in the paint. Because these soaps form at the interface between the metal and the paint, they can dramatically reduce paint film adhesion and result in peeling and flaking of the paint system. For this reason, any time zinc or galvanized steel is to be painted, it is important to ensure that the intended paint system (especially the primer) has been specifically designed for a zinc surface. Similarly, zinc-rich primers should not be topcoated with an alkyd- or oil-based paint. For more information on metal soaps, see "Chapter 3. Specific Corrosion Problems."

Reference material: Goodwin (1998b); Graedel (1989); Green and Thickett (1993); Mottner et al. (1995); Persson and Leygraf (1995); Riederer (1993); Robinet and Corbeil (2003); Zhang (2000).

CORROSION DURING BURIAL

Zinc-containing metals submersed in marine environments may form a variety of corrosion products (mainly sulphates), e.g. MacLeod (1991) identified goslarite on a recovered bronze cannon. Zinc alloys exposed to soils containing high concentrations of chloride ions can suffer from deep pitting.

Reference material: MacLeod (1991); Zhang (2000).

GALVANIC CORROSION

Zinc is more active than all other common metals except magnesium. Therefore, when in contact with these common metals, zinc corrodes faster than if it were isolated. In general, the acceleration of the corrosion rate is not too much when zinc is in contact with lead, tin, or stainless steel. However, contact with copper alloys causes rapid corrosion of zinc. Copper-plated zinc sculptures, for example, suffer from serious pitting as a result of the accelerated galvanic corrosion of zinc at imperfections in the copper plating, especially outdoors. The surface can often be completely covered with tiny holes filled with white corrosion products. Even trace amounts of copper in water (as little as 0.1 ppm) can substantially increase the corrosion of zinc because metallic copper plates onto the zinc surface, thus providing ideal sites for the cathodic half-reaction of oxygen reduction. For this reason, it is important to prevent the transfer of water from a copper surface onto a zinc surface. The zinc surface will first discolour in streaks as the copper plates, and then the zinc will corrode preferentially.

Galvanized steel: The protective effect of plating iron or steel with zinc is twofold. First, zinc corrodes more slowly than the steel under it. In fact, the corrosion rate of zinc in most outdoor atmospheres is at least 10 times lower than that of steel, and the presence of zinc corrosion products (e.g. zinc oxides, zinc hydroxides, and zinc carbonate hydroxides) helps maintain a low zinc corrosion rate. As long as the zinc layer is present and continuous, it provides barrier protection to the underlying steel, isolating it from the environment and potential electrolytes. Second, if the zinc coating is damaged and the underlying iron is exposed to the environment, the zinc (being anodic to iron) will preferentially corrode and protect the iron or steel from rusting. Rust is not usually seen on galvanized items until the zinc plating has corroded extensively. An example of rusting and zinc corrosion on galvanized steel is shown in Figure 13.7.

Reference material: Goodwin (1998b); Zahner (1995); Zhang (2000).

INTERGRANULAR CORROSION

Certain zinc alloys, especially zinc–aluminum alloys, suffer from intergranular corrosion when exposed to moisture and aggressive conditions such as high temperatures, acids (pH < 5), or alkalis (pH > 10). When this happens the alloys lose strength, crack, and eventually disintegrate. Such disintegration problems were first noted in the first quarter of the

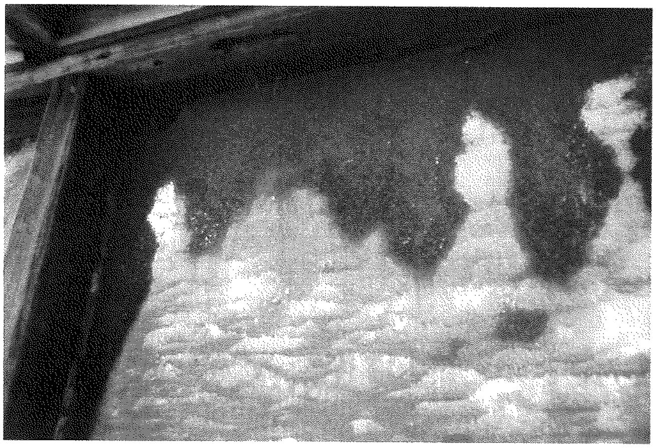

Figure 13.7. This piece of galvanized iron was exposed outdoors. The zinc on the top has corroded away, and the exposed iron is suffering from serious damage, including loss. The zinc on the lower part has corroded and become covered with white zinc corrosion products. Photograph by S. Maltby. (A colour version of Figure 13.7 is available on p. 88.)

20th century, and were attributed to the precipitation of certain impurities (e.g. lead, cadmium, tin, iron) at grain boundaries. An example of intergranular corrosion in an ice skate blade is shown in Figure 13.8. Corrosion is caused by preferential attack of an aluminum-rich phase and other impurity metal phases precipitated at the grain boundaries. Today this problem is minimized by carefully controlling the impurity levels in modern zinc alloys.

Reference material: Barnhurst (1990); Goodway (1985); Goodwin (1998a); Helwig (1992); Zhang (2000).

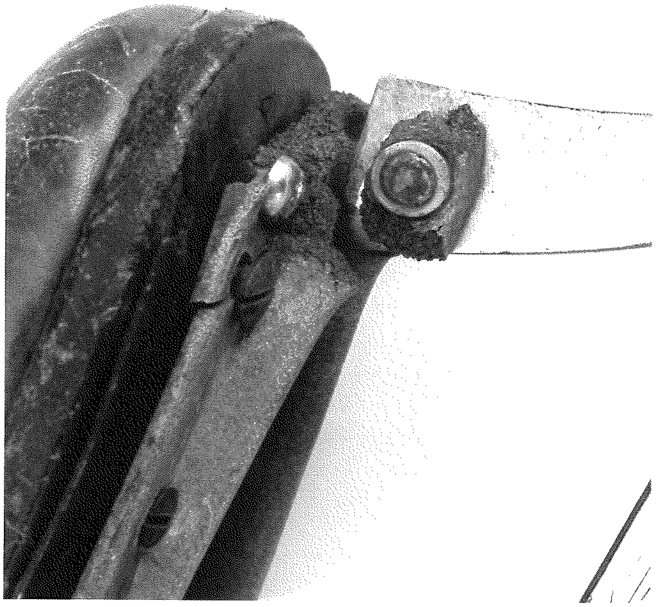

Figure 13.8. The zinc–aluminum alloy in this ice skate blade dating from the 1920s (Glenbow C-16899 A) is suffering from intergranular corrosion caused by impurities. Photo courtesy Glenbow Museum, Calgary.

TOXICITY

Zinc is not considered to pose any significant hazards to humans, although a disorder known as zinc chills (also called metal fume fever) can occur if freshly formed zinc oxide, produced by heating zinc, is inhaled.

Reference material: Rossol (2002).

BIBLIOGRAPHY

CHAPTER 1. METALS

ASM International. *ASM Handbook. Vol. 1. Properties and Selection: Iron, Steels, and High-performance Alloys*. Materials Park, OH: ASM International, 1990a.

ASM International. *ASM Handbook. Vol. 2. Properties and Selection: Nonferrous Alloys and Special-purpose Materials*. Materials Park, OH: ASM International, 1990b.

ASM International. *ASM Handbook. Vol. 3. Alloy Phase Diagrams*. Materials Park, OH: ASM International, 1992.

ASTM. "E527-83 (Reapproved 1997). Standard Practice for Numbering Metals and Alloys (UNS)." pp. 764–768 in *Annual Book of ASTM Standards 2001. Vol. 01.01. Steel — Piping, Tubing, Fittings*. West Conshohocken, PA: American Society for Testing and Materials, 2001a.

ASTM. "G1-90 (Reapproved 1999). Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens." pp. 15–22 in *Annual Book of ASTM Standards 2001. Vol. 03.02. Wear and Erosion; Metal Corrosion*. West Conshohocken, PA: American Society for Testing and Materials, 2001b.

Barclay, R.L. "The Metal." pp. 33–66 in *The Art of the Trumpet-maker: The Materials, Tools, and Techniques of the Seventeenth and Eighteenth Centuries in Nuremberg*. Early Music Series, No. 14. Oxford, UK: Oxford University Press, 1992.

Barraclough, K.C. "The Chemistry of Metal Extraction." pp. 307–311 in *The Industrial Revolution in Metals* (edited by J. Day and R.F. Tylecote). London, UK: The Institute of Metals, 1991.

Bewer, F.G., and D.A. Scott. "A Bronze Sculpture attributed to Louis-Simon Boizot and Platinum Coating Methods." *Archaeometry* 37 (1995), pp. 351–361.

Canadian Conservation Institute. *Storage of Metals*. CCI Notes, No. 9/2. Ottawa, ON: Canadian Conservation Institute, 1995.

Canadian Conservation Institute. *Recognizing Active Corrosion*. CCI Notes, No. 9/1. Ottawa, ON: Canadian Conservation Institute, 1997.

Canadian Conservation Institute. *Trade Literature for Industrial Collections*. CCI Notes, No. 15/6. Ottawa, ON: Canadian Conservation Institute, 2002a.

Canadian Conservation Institute. *Identifying Archaeological Metal*. CCI Notes, No. 4/1. Ottawa, ON: Canadian Conservation Institute, 2002b.

Carter, G.F. *Principles of Physical and Chemical Metallurgy*. Materials Park, OH: ASM International, 1979.

Child, R. "The Identification of Post-Industrial Revolution Metals." pp. 7–14 in *Modern Metals in Museums* (edited by R.E. Child and J.M. Townsend). London, UK: Institute of Archaeology, 1988.

Child, R. "Modern Electroplating and Electrofinishing Techniques." pp. 291–300 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Cronyn, J.M., and W.S. Robinson. *The Elements of Archaeological Conservation*. London, UK: Routledge, 1990.

Day, J., and R.F. Tylecote (editors). *The Industrial Revolution in Metals*. London, UK: The Institute of Metals, 1991.

Feigl, F., and V. Anger. *Spot Tests in Inorganic Analysis, 6th ed.* New York, NY: Elsevier, 1972.

Franklin, U.M., E. Badone, R. Gotthardt, and B. Yorga. *An Examination of Prehistoric Copper Technology and Copper Sources in Western Arctic and Subarctic North America*. National Museum of Man Mercury Series, Archaeological Survey of Canada Paper No. 101. Ottawa, ON: National Museums of Canada, 1981.

Hamilton, M.W. *Silver in the Fur Trade: 1680–1820* (edited by J.D. Hamilton and R.P. Lydick). Chelmsford, MA: Martha Hamilton Publishing, 1995.

Hancock, R.G.V., L.A. Pavlish, R.M. Farquhar, R. Salloum, W.A. Fox, and G.C. Wilson. "Distinguishing European Trade Copper and North-eastern North American Native Copper." *Archaeometry* 33 (1991), pp. 69–86.

Hodges, H. *Artifacts; An Introduction to Early Materials and Technology*. London, UK: John Baker, 1964.

Jenness, D. *Indians of Canada, 2nd ed.* Ottawa, ON: National Museums of Canada, 1934.

Killick, D. "Science, Speculation and the Origins of Extractive Metallurgy." pp. 483–492 in *Handbook of Archaeological Sciences* (edited by D.R. Brothwell and A.M. Pollard). Chichester, UK: John Wiley & Sons, 2001.

Krulik, G.A. "Electroless Plating." pp. 198–218 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 9*. New York, NY: John Wiley & Sons, 1994.

Lambert, J.B. "Metals." pp. 168–213 in *Traces of the Past; Unraveling the Secrets of Archaeology through Chemistry*. Reading, MA: Perseus Books, 1997.

Larsen, E.B. *Electroplating*. Copenhagen, Denmark: School of Conservation, 1984.

Laver, M.E. "Spot Tests in Conservation: Metals and Alloys." pp. 78/23/8/1–11 in *ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb*. Paris, France: International Council of Museums, 1978.

Lewis, L. "Properties and Applications of Electro-plated Coatings." pp. 39–40 in *Modern Metals in Museums* (edited by R.E. Child and J.M. Townsend). London, UK: Institute of Archaeology, 1988.

Maryon, H. *Metalwork & Enamelling, 5th revised ed.* New York, NY: Dover Publications, 1971.

Mouat, J. *Metal Mining in Canada, 1840–1950*. Transformation Series, No. 9. Ottawa, ON: National Museum of Science and Technology, 2000.

Nassau, K. *The Physics and Chemistry of Color: The Fifteen Causes of Color*. New York, NY: John Wiley & Sons, 1983.

Odegaard, N., S. Carroll, and W.S. Zimmt. *Material Characterization Tests for Objects of Art and Archaeology*. London, UK: Archetype Publications, 2000.

Pearson, C. (editor). *Conservation of Marine Archaeological Objects*. London, UK: Butterworths, 1987.

Raub, C. "The History of Electroplating." pp. 284–290 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Raymond, R. *Out of the Fiery Furnace; The Impact of Metals on the History of Mankind.* University Park, PA: Pennsylvania State University Press, 1984.

Roberts, S. *Construction of a Constant-current Power Supply for Spot Electrolysis.* Technical Bulletin, No. 20. Ottawa, ON: Canadian Conservation Institute, 1999.

Society of Automotive Engineers (SAE) and American Society for Testing and Materials (ASTM). *Metals & Alloys in the Unified Numbering System, 9th ed.* Warrendale, PA: Society of Automotive Engineers, 2001.

Score, R., and I.J. Cohen. "Stainless Steel." pp. 64–71 in *Twentieth-century Building Materials* (edited by T.C. Jester). Toronto, ON: McGraw-Hill, 1995.

Scott, D.A. *Metallography and Microstructure of Ancient and Historic Metals.* Marina del Rey, CA: Getty Conservation Institute and J. Paul Getty Museum, 1991.

Scott, D.A. *Copper and Bronze in Art: Corrosion, Colorants, Conservation.* Marina del Rey, CA: Getty Conservation Institute, 2002.

Selwyn, L. "Corrosion Chemistry of Gilded Silver and Copper." pp. 21–47 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Singer, C. (editor). *A History of Technology. Vols. I–V.* Oxford, UK: Clarendon Press, 1954.

Smithells, C.J. (editor). *Metals Reference Book, 5th ed.* London, UK: Butterworths, 1976.

Street, A., and W. Alexander. *Metals in the Service of Man, 10th ed.* London, UK: Penguin Books, 1995.

Thompson, D.H. "General Tests and Principles." pp. 115–141 in *Handbook on Corrosion Testing and Evaluation* (edited by W.H. Ailor). New York, NY: John Wiley & Sons, 1971.

Townsend, J.H. "The Identification of Metals: Chemical Spot Tests." pp. 15–22 in *Modern Metals in Museums* (edited by R.E. Child and J.M. Townsend). London, UK: Institute of Archaeology, 1988.

Tylecote, R.F. *A History of Metallurgy.* London, UK: The Metals Society, 1976.

Tylecote, R.F. *The Early History of Metallurgy in Europe.* London, UK: Longman, 1987.

Unglik, H., and J. Stewart. *The Metallurgy of Norse Material from L'Anse aux Meadows, Newfoundland.* Report No. 92-2216 (unpublished). Ottawa, ON: Ontario Service Centre, Parks Canada, 1999. 2 volumes, 490 pp.

Wainwright, I.N.M. "Examination of Paintings by Physical and Chemical Methods." pp. 79–102 in *Shared Responsibility, Proceedings of a Seminar for Curators and Conservators* (edited by B.A. Ramsay-Jolicoeur and I.N.M. Wainwright). Ottawa, ON: National Gallery of Canada, 1990.

Wayman, M.L. "Determining the Origin and Age of Metal Artifacts." *MRS Bulletin* 14 (1989), pp. 31–35.

Weaver, J.H., and H.P.R. Frederikse. "Optical Properties of Metals and Semiconductors." pp. 12-127–12-150 in *CRC Handbook of Chemistry and Physics, 79th ed.* Boca Raton, FL: CRC Press, 1998.

Wells, A.F. *Structural Inorganic Chemistry, 5th ed.* Oxford, UK: Clarendon Press, 1984.

Wilson, M.L. *Nondestructive Rapid Identification of Metals and Alloys by Spot Test.* ASTM Special Technical Publication, No. 550. Philadelphia, PA: American Society for Testing and Materials, 1974.

Young, R.D., and R.A. Fennell. *Methods for Modern Sculptors.* Escondido, CA: Sculpt Nouveau, 1980.

CHAPTER 2. CORROSION

ASM International. *Metals Handbook, 9th ed. Vol. 13. Corrosion.* Materials Park, OH: ASM International, 1987.

ASTM. "G15-99b. Standard Terminology Relating to Corrosion and Corrosion Testing." pp. 70–74 in *Annual Book of ASTM Standards 2001. Vol. 03.02. Wear and Erosion; Metal Corrosion.* West Conshohocken, PA: American Society for Testing and Materials, 2001a.

ASTM. "G3-89 (Reapproved 1999). Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing." pp. 39–48 in *Annual Book of ASTM Standards 2001. Vol. 03.02. Wear and Erosion; Metal Corrosion.* West Conshohocken, PA: American Society for Testing and Materials, 2001b.

ASTM. "G82-98. Standard Guide for Development and Use of a Galvanic Series for Predicting Galvanic Corrosion Performance." pp. 360–366 in *Annual Book of ASTM Standards 2001. Vol. 03.02. Wear and Erosion; Metal Corrosion.* West Conshohocken, PA: American Society for Testing and Materials, 2001c.

Baboian, R. "Galvanic Corrosion on the Statue of Liberty." pp. 93–99 in *The Statue of Liberty Restoration* (edited by R. Baboian, E.B. Cliver, and E.L. Bellante). Houston, TX: National Association of Corrosion Engineers, 1990.

Beale, A., H. Bump, W.T. Chase, T.E. Graedel, J. Kruger, P.D. Weil, and T.D. Weisser. *Conservation of Metallic Artistic and Historic Works: Glossary of Terms.* Houston, TX: National Association of Corrosion Engineers, 1988.

Böhni, H. "Localized Corrosion of Passive Metals." pp. 173–190 in *Uhlig's Corrosion Handbook, 2nd ed.* (edited by R.W. Revie). New York, NY: John Wiley & Sons, 2000.

Brown, B.F., H.C. Burnett, W.T. Chase, M. Goodway, J. Kruger, and M. Pourbaix (editors). *Corrosion and Metal Artifacts — A Dialogue Between Conservators and Archaeologists and Conservation Scientists.* National Bureau of Standards Special Publication, No. 479. Washington, DC: U.S. Government Printing Office, 1977.

Canadian Conservation Institute. *Recognizing Active Corrosion.* CCI Notes, No. 9/1. Ottawa, ON: Canadian Conservation Institute, 1997.

Coburn, S.K. "Corrosion in Fresh Water." pp. 733–738 in *Metals Handbook, 9th ed. Vol. 1. Properties and Selection: Irons and Steels.* Materials Park, OH: ASM International, 1978.

Cook, A.R., and R. Smith. "Atmospheric Corrosion of Lead and its Alloys." pp. 393–404 in *Atmospheric Corrosion* (edited by W.H. Ailor). New York, NY: John Wiley & Sons, 1982.

Fontana, M.G. *Corrosion Engineering, 3rd ed.* New York, NY: McGraw-Hill, 1986.

Garrels, R.M., and C.L. Christ. *Solutions, Minerals, and Equilibria*. Boston, MA: Jones and Bartlett Publishers, 1990.

Gu, J.-D., T.E. Ford, and R. Mitchell. "Microbiological Corrosion of Metals." pp. 915–927 in *Uhlig's Corrosion Handbook, 2nd ed.* (edited by R.W. Revie). New York, NY: John Wiley & Sons, 2000.

Hughes, J. "Ten Myths about the Preservation of Historic Sites in Antarctica and Some Implications for Mawson's Huts at Cape Denison." *Polar Record* 36 (2000), pp. 117–130.

Hughes, J., G. King, and W. Ganther. "Application of Corrosion Data to develop Conservation Strategies for a Historic Building in Antarctica." pp. 865–870 in *ICOM Committee for Conservation, 13th Triennial Meeting, Rio de Janeiro, Brazil* (edited by R. Vontobel). London, UK: James & James Science Publishers, 2002.

Hughes, R., and M. Rowe. *The Colouring, Bronzing and Patination of Metals.* London, UK: Crafts Council, 1982.

Junge, C.E., and R.T. Werby. "The Concentration of Chloride, Sodium, Potassium, Calcium, and Sulfate in Rain Water over the United States." *Journal of Meteorology* 15 (1958), pp. 417–425.

King, G.A. "Atmospheric Corrosion in Cold Regions." pp. 323–328 in *Uhlig's Corrosion Handbook, 2nd ed.* (edited by R.W. Revie). New York, NY: John Wiley & Sons, 2000.

LaQue, F.L. *Marine Corrosion: Causes and Prevention.* New York, NY: John Wiley & Sons, 1975.

Lobnig, R.E., R.P. Frankenthal, D.J. Siconolfi, and J.D. Sinclair. "The Effect of Submicron Ammonium Sulfate Particles on the Corrosion of Copper." pp. 336–356 in *Corrosion and Reliability of Electronic Materials and Devices.* Pennington, NJ: The Electrochemical Society, 1993.

MacLeod, I.D. "Shipwrecks and Applied Electrochemistry." *Journal of Electroanalytical Chemistry* 118 (1981), pp. 291–303.

Marek, M.I., C.A. Natalie, and D.L. Piron. "Thermodynamics of Aqueous Corrosion." pp. 18–28 in *Metals Handbook, 9th ed. Vol. 13. Corrosion.* Materials Park, OH: ASM International, 1987.

Mattsson, E. "The Atmospheric Corrosion Properties of Some Common Structural Metals — A Comparative Study." *Materials Performance* 21 (1982), pp. 9–19.

Mattsson, E., and R. Holm. "Atmospheric Corrosion of Copper and its Alloys." pp. 365–381 in *Atmospheric Corrosion* (edited by W.H. Ailor). New York, NY: John Wiley & Sons, 1982.

McNeil, M., and L.S. Selwyn. "Electrochemical Processes in Metallic Corrosion." pp. 605–614 in *Handbook of Archaeological Sciences* (edited by D.R. Brothwell and A.M. Pollard). Chichester, UK: John Wiley & Sons, 2001.

Payer, J.H. "Bronze Corrosion: Rates and Chemical Processes." pp. 103–121 in *Dialogue 89 — The Conservation of Bronze Sculpture in the Outdoor Environment* (edited by T. Drayman-Weisser). Houston, TX: National Association of Corrosion Engineers, 1992.

Payer, J.H., G. Ball, B.I. Rickett, and H.S. Kim. "Role of Transport Properties in Corrosion Product Growth." *Materials Science and Engineering* A198 (1995), pp. 91–102.

Pearson, C. (editor). *Conservation of Marine Archaeological Objects*. London, UK: Butterworths, 1987.

Phipps, P.B.P., and D.W. Rice. "The Role of Water in Atmospheric Corrosion." pp. 235–261 in *Corrosion Chemistry* (edited by G.R. Brubaker and P.B.P. Phipps). ACS Symposium Series, No. 89. Washington, DC: American Chemical Society, 1979.

Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd ed.* Houston, TX: National Association of Corrosion Engineers, 1974.

Raiswell, R. "Defining the Burial Environment." pp. 595–604 in *Handbook of Archaeological Sciences* (edited by D.R. Brothwell and A.M. Pollard). Chichester, UK: John Wiley & Sons, 2001.

Revie, R.W. (editor). *Uhlig's Corrosion Handbook, 2nd ed.* New York, NY: John Wiley & Sons, 2000.

Ruggeri, R.T., and T.R. Beck. "An Analysis of Mass Transfer in Filiform Corrosion." *Corrosion* 39 (1983), pp. 452–465.

Scott, D.A. *Copper and Bronze in Art: Corrosion, Colorants, Conservation.* Marina del Rey, CA: Getty Conservation Institute, 2002.

Selwyn, L. *Analysis of the Chloride Ion Concentration in Aqueous Solutions by Potentiometric Titration.* CCI Research Report, No. 2. Ottawa, ON: Canadian Conservation Institute, 2001.

Skoog, D.A., D.M. West, and F.J. Holler. *Fundamentals of Analytical Chemistry, 5th ed.* New York, NY: Saunders College Publishing, 1988.

Tullmin, M., and P.R. Roberge. "Atmospheric Corrosion." pp. 305–321 in *Uhlig's Corrosion Handbook, 2nd ed.* (edited by R.W. Revie). New York, NY: John Wiley & Sons, 2000.

Vanýsek, P. "Electrochemical Series." pp. 8-21–8-31 in *CRC Handbook of Chemistry and Physics, 79th ed.* Boca Raton, FL: CRC Press, 1998.

Young, R.D. *Contemporary Patination, 5th ed.* Escondido, CA: Sculpt Nouveau, 2000.

CHAPTER 3. SPECIFIC CORROSION PROBLEMS

Bacon, L. "The Deterioration of Four Giorgi Flutes made of Ebonite and a Possible Method for their Conservation." pp. 96–100 in *Conservation Today: Papers presented at the UKIC 30th Anniversary Conference, 1988* (edited by V. Todd). London, UK: United Kingdom Institute for Conservation of Historic and Artistic Works, 1988.

Bailey, R.A., and J.A. Zaccardi. "Corrosion of Copper and Other Metals by Perspiration." *Journal of Electroanalytical Chemistry* 144 (1983), pp. 443–448.

Bamberger, J.A., E.G. Howe, and G. Wheeler. "A Variant Oddy Test Procedure for evaluating Materials used in Storage and Display Cases." *Studies in Conservation* 44 (1999), pp. 86–90.

Banik, G. "Decay caused by Iron-gall Inks." pp. 21–26 in *Iron-gall Ink Corrosion; Proceedings European Workshop on Iron-gall Ink Corrosion.* Amsterdam, Netherlands: Netherlands Institute for Cultural Heritage, 1997.

Banik, G., H. Stachelberger, and O. Wächter. "Investigation of the Destructive Action of Copper Pigments on Paper and Consequences for Conservation." pp. 75–78 in *Science and Technology in the Service of Conservation* (edited by N.S. Brommelle and G. Thomson). London, UK: International Institute for Conservation, 1982.

Bicchieri, M., and S. Pepa. "The Degradation of Cellulose with Ferric and Cupric Ions in a Low-acid Medium." *Restaurator* 17 (1996), pp. 165–183.

Bradley, S., and D. Thickett. "The Pollution Problem in Perspective." pp. 8–13 in *ICOM Committee for Conservation, 12th Triennial Meeting, Lyon, France* (edited by J. Bridgland). London, UK: James & James Science Publishers, 1999.

Burmester, A., and J. Koller. "Known and New Corrosion Products on Bronzes: Their Identification and Assessment, particularly in relation to Organic Protective Coatings." pp. 97–103 in *Recent Advances in the Conservation and Analysis of Artifacts.* London, UK: Summer Schools Press, 1987.

Canadian Conservation Institute. *The Beilstein Test: Screening Organic and Polymeric Materials for the presence of Chlorine, with Examples of Products Tested.* CCI Notes, No. 17/1. Ottawa, ON: Canadian Conservation Institute, 1993.

Canadian Conservation Institute. *Storage of Metals.* CCI Notes, No. 9/2. Ottawa, ON: Canadian Conservation Institute, 1995.

Corbeil, M.-C., and E. Moffatt. *Analysis of a Corrosion Sample.* CCI Analytical Report ARS 3513. Ottawa, ON: Canadian Conservation Institute, 1996.

Coxon, H.C. "Practical Pitfalls in the Identification of Plastics." pp. 395–409 in *Saving the Twentieth Century: The Conservation of Modern Materials* (edited by D.W. Grattan). Ottawa, ON: Canadian Conservation Institute, 1993.

Daniels, V., and M. Leese. "The Degradation of Silk by Verdigris." *Restaurator* 16 (1995), pp. 45–63.

Daniels, V., and S. Ward. "A Rapid Test for the detection of Substances which will Tarnish Silver." *Studies in Conservation* 27 (1982), pp. 58–60.

Deasy, C.L. "Degradation of Collagen by Metal Ion – Hydrogen Peroxide Systems. I. Evidence for a Free Radical-catalyzed Depolymerization Mechanism." *Journal of American Leather Chemists Association* 62 (1967), pp. 258–269.

Dignard, C., and G. Gordon. "Metal Ion Catalysed Oxidation of Skin: Treatment of the Fur Trim and Collar on a Velvet Cape." *Journal of the Canadian Association for Conservation* 24 (1999), pp. 11–22.

Donovan, P.D., and J. Stringer. "Corrosion of Metals and their Protection in Atmospheres containing Organic Acid Vapours." *British Corrosion Journal* 6 (1971), pp. 132–138.

Emery, J.A., and H.A. Schroeder. "Iron-catalyzed Oxidation of Wood Carbohydrates." *Wood Science and Technology* 8 (1974), pp. 123–137.

Fenn, J. "The Cellulose Nitrate Time Bomb: Using Sulphonephthalein Indicators to Evaluate Storage Strategies." pp. 87–92 in *From Marble to Chocolate: The Conservation of Modern Sculpture* (edited by J. Heuman). London, UK: Archetype Publications, 1995.

Gent, M., and J. Rees. "A Conservation Treatment to Remove Residual Iron from Platinum Prints." *The Paper Conservator* 18 (1994), pp. 90–95.

Gilberg, M. "The Use of Camphor to Protect Silver Against Tarnishing." *International Institute for Conservation - Canadian Group Newsletter* 12 (1987), p. 19.

Graf, E., J.R. Mahoney, R.G. Bryant, and J.W. Eaton. "Iron-catalyzed Hydroxyl Radical Formation." *The Journal of Biological Chemistry* 259 (1984), pp. 3620–3624.

Green, L.R., and D. Thickett. "Testing Materials for Use in the Storage and Display of Antiquities — A Revised Methodology." *Studies in Conservation* 40 (1995), pp. 145–152.

Hatchfield, P.B. *Pollutants in the Museum Environment.* London, UK: Archetype Publications, 2002.

Helwig, K., G. Sansoucy, and J. Sirois. *Analysis of Corrosion on a Set of Pastel Crayons.* CCI Analytical Report ARL 3899. Ottawa, ON: Canadian Conservation Institute, 2001.

Lee, L.R., and D. Thickett. "The Oddy Test — An Accelerated Corrosion Test for Effects on Metals." pp. 14–21 in *Selection of Materials for the Storage or Display of Museum Objects*. British Museum Occasional Paper, No. 111. London, UK: British Museum Publications Ltd., 1996a.

Lee, L.R., and D. Thickett. "The Azide Test — For Sulphur Containing Materials." pp. 22–24 in *Selection of Materials for the Storage or Display of Museum Objects.* British Museum Occasional Paper, No. 111. London, UK: British Museum Publications Ltd., 1996b.

Lee, L.R., and D. Thickett. "Why is Testing Necessary?" pp. 1–10 in *Selection of Materials for the Storage or Display of Museum Objects.* British Museum Occasional Paper, No. 111. London, UK: British Museum Publications Ltd., 1996c.

Lewis, S. (Lead Curator, Department of Entomology, Natural History Museum, London, United Kingdom). Personal communication, February 2002.

Lind, S.E. "Corrosion of Metals by Human Sweat and its Prevention." *Corrosion Science* 12 (1972), pp. 749–755.

Lobnig, R.E., R.P. Frankenthal, D.J. Siconolfi, and J.D. Sinclair. "The Effect of Submicron Ammonium Sulfate Particles on the Corrosion of Copper." pp. 336–356 in *Corrosion and Reliability of Electronic Materials and Devices*. Pennington, NJ: The Electrochemical Society, 1993.

Lunning, E. "Silver Safe." *AIC Newsletter* 5 (1980), p. 13.

Mairinger, F., G. Banik, H. Stachelberger, A. Vendl, and J. Ponahlo. "The Destruction of Paper by Green Copper Pigments, Demonstrated by a Sample of Chinese Wallpaper." pp. 180–185 in *Conservation Within Historic Buildings* (edited by N.S. Brommelle, G. Thomson, and P. Smith). London, UK: International Institute for Conservation, 1980.

Miller, J.E., and B.M. Reagan. "Degradation in Weighted and Unweighted Historic Silks." *Journal of the American Institute for Conservation* 28 (1989), pp. 97–115.

Nagy, E. "Corrosion Intercept Tent Packing and Handling System for Donald Judd's Brass and Copper Sculptures: Experiences with Packing and Handling Methods." *AIC Objects Specialty Group Postprints* 6 (1999), pp. 11–35.

Neevel, J.G. "Phytate: A Potential Conservation Agent for the Treatment of Ink Corrosion caused by Irongall Inks." *Restaurator* 16 (1995), pp. 143–160.

Oddy, A. "An Unsuspected Danger in Display." *Museums Journal* 73 (1973), pp. 27–28.

Oddy, A. "The Corrosion of Metals on Display." pp. 235–237 in *Conservation in Archaeology and the Applied Arts*. London, UK: International Institute for Conservation, 1975.

Odegaard, N., S. Carroll, and W.S. Zimmt. *Material Characterization Tests for Objects of Art and Archaeology*. London, UK: Archetype Publications, 2000.

Reissland, B. "Ink Corrosion: Aqueous and Non-aqueous Treatment of Paper Objects — State of the Art." *Restaurator* 20 (1999), pp. 167–180.

Richardson, G.M., and R.S. Malthus. "Salts for Static Control of Humidity at Relatively Low Levels." *Journal of Applied Chemistry* 5 (1955), pp. 557–567.

Schrenk, J.L. "Corrosion and Past "Protective" Treatments of the Benin "Bronzes" in the National Museum of African Art." pp. 805–812 in *Materials Issues in Art and Archaeology. II* (edited by P.B. Vandiver, J. Druzik, and G.S. Wheeler). Materials Research Society Symposium Proceedings. Vol. 185. Warrendale, PA: Materials Research Society, 1991.

Schrenk, J.L. "The Royal Art of Benin: Surfaces, Past and Present." pp. 51–62 in *Ancient & Historic Metals, Conservation and Scientific Research* (edited by D.A. Scott, J. Podany, and B. Considine). Marina del Rey, CA: Getty Conservation Institute, 1994.

Scott, D.A. *Copper and Bronze in Art: Corrosion, Colorants, Conservation.* Marina del Rey, CA: Getty Conservation Institute, 2002.

Scott, D.A., Y. Taniguchi, and E. Koseto. "The Verisimilitude of Verdigris: A Review of the Copper Carboxylates." *Reviews in Conservation* 2 (2001), pp. 73–91.

Selwyn, L. *Analysis of the Chloride Ion Concentration in Aqueous Solutions by Potentiometric Titration.* CCI Research Report, No. 2. Ottawa, ON: Canadian Conservation Institute, 2001.

Semczak, C.M. "A Comparison of Chloride Tests." *Studies in Conservation* 22 (1977), pp. 40–41.

Shashoua, Y.R. *Inhibiting the Deterioration of Plasticized Poly(vinyl chloride) — A Museum Perspective.* Ph.D. Thesis. Copenhagen, Denmark: The National Museum of Denmark, 2001.

Sirois, J. *Analysis of Corrosion Wavemeter Coil: Copper and Ebonite Interface.* CCI Analytical Report ARS 3452. Ottawa, ON: Canadian Conservation Institute, 1995.

Sirois, J., and E. Moffatt. *Analysis of Green Corrosion and Pin Associated with an Insect Specimen.* CCI Analytical Report ARL 4084. Ottawa, ON: Canadian Conservation Institute, 2002.

Sirois, J., E. Moffatt, and L. Selwyn. *Analysis of Corrosion Products on Bronze Sculptures (Phase III).* CCI Analytical Report ARL 3864. Ottawa, ON: Canadian Conservation Institute, 2002.

Sirois, J., E. Moffatt, and L. Selwyn. *Analysis of Corrosion Products on Bronze Sculptures (Phase IV).* CCI Analytical Report ARL 4153. Ottawa, ON: Canadian Conservation Institute, 2003.

Tang, L.C. "Determination of Iron and Copper in 18th and 19th Century Books by Flameless Atomic Absorption Spectroscopy." *Journal of the American Institute for Conservation* 17 (1978), pp. 19–32.

Tétreault, J. "Display Materials: The Good, The Bad and The Ugly." pp. 79–87 in *Exhibitions and Conservation.* Edinburgh, UK: Scottish Society for Conservation and Restoration, 1994.

Tétreault, J. *Coatings for Display and Storage in Museums.* CCI Technical Bulletin, No. 21. Ottawa, ON: Canadian Conservation Institute, 1999.

Tétreault, J. *Airborne Pollutants in Museums, Galleries, and Archives: Risk Assessment and Control Strategies.* Ottawa, ON: Canadian Conservation Institute, 2003.

Thickett, D., S. Bradley, and L. Lee. "Assessment of the Risks to Metal Artifacts posed by Volatile Carbonyl Pollutants." pp. 260–264 in *Metal 98* (edited by W. Mourey and L. Robbiola). London, UK: James & James Science Publishers, 1998.

Tilbrooke, D. "The Fatty Acid Corrosion of Copper Alloys and its Treatment." *ICCM Bulletin* 6 (1980), pp. 46–52.

Williams, J.C., C.S. Fowler, M.S. Lyon, and T.L. Merrill. "Metallic Catalysts in the Oxidative Degradation of Paper." pp. 37–61 in *Preservation of Paper and Textiles of Historic and Artistic Value* (edited by J.C. Williams). Advances in Chemistry Series, No. 164. Washington, DC: American Chemical Society, 1977.

Williams, R.S. *Accretion on Marconi Magnetic Metal Detector.* CCI Analytical Report ARS 1855. Ottawa, ON: Canadian Conservation Institute, 1982.

Williams, R.S. *Accretion on Accumulator Wheels of Van de Graaf Generator.* CCI Analytical Report ARS 2765. Ottawa, ON: Canadian Conservation Institute, 1988.

Williams, R.S. *The Diphenylamine Spot Test for Cellulose Nitrate in Museum Objects.* CCI Notes, No. 17/2. Ottawa, ON: Canadian Conservation Institute, 1994a.

Williams, R.S. *Display and Storage of Museum Objects Containing Cellulose Nitrate.* CCI Notes, No. 15/3. Ottawa, ON: Canadian Conservation Institute, 1994b.

Williams, R.S. *Care of Objects made from Rubber and Plastic.* CCI Notes, No. 15/1. Ottawa, ON: Canadian Conservation Institute, 1997.

Williams, R.S. "Care of Plastics: Malignant Plastics." *WAAC Newsletter* 24 (2002), pp. 10–15.

Wypyski, M.T. "Technical Examination of a 19th C. Zinc Outdoor Sculpture." In *Papers presented by Trainees at the Fifteenth Annual Art Conservation Training Programs Conference, 1989.* Cambridge, MA: Harvard University Art Museums, 1990.

CHAPTER 4. INTRODUCTION TO SPECIFIC METALS

ASM International. *ASM Handbook. Vol. 3. Alloy Phase Diagrams.* Materials Park, OH: ASM International, 1992.

CRC Press. *CRC Handbook of Chemistry and Physics, 79th ed.* Boca Raton, FL: CRC Press, 1998.

Rossol, M. *The Artist's Complete Health and Safety Guide, 3rd ed.* New York, NY: Allworth Press, 2002.

Scott, D.A. *Metallography and Microstructure of Ancient and Historic Metals.* Marina del Rey, CA: Getty Conservation Institute and J. Paul Getty Museum, 1991.

Wanhill, R.J.H. *Microstructurally-induced Embrittlement of Archaeological Silver.* Report NLR-TP-2001-032. Amsterdam, Netherlands: National Aerospace Laboratory, 2001.

CHAPTER 5. ALUMINUM

Adams, C., and D. Hallam. "Finishes on Aluminium — A Conservation Perspective." pp. 273–286 in *Saving the Twentieth Century: The Conservation of Modern Materials* (edited by D.W. Grattan). Ottawa, ON: Canadian Conservation Institute, 1993.

Aluminum Association. *Care of Aluminum, 5th ed.* Washington, DC: The Aluminum Association, 1983.

ASM International. *ASM Handbook. Vol. 3. Alloy Phase Diagrams.* Materials Park, OH: ASM International, 1992.

Burns, R.M., and W.W. Bradley. *Protective Coatings for Metals, 3rd ed.* American Chemical Society Monograph Series, No. 163. London, UK: Reinhold, 1967.

Cayless, R.B.C. "Alloy and Temper Designation Systems for Aluminum and Aluminum Alloys." pp. 15–28 in *Metals Handbook. Vol. 2. Properties and Selection: Nonferrous Alloys and Special-purpose Materials.* Materials Park, OH: ASM International, 1990.

Child, R. "Modern Electroplating and Electrofinishing Techniques." pp. 291–300 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Corbeil, M.-C., K. Helwig, and L. Selwyn. *Analysis of a Metal Part from a Halifax Bomber.* CCI Analytical Report ARS 3444. Ottawa, ON: Canadian Conservation Institute, 1995.

Degrigny, C. "Stabilisation de Moteurs d'Avions Immerges." *Studies in Conservation* 40 (1995), pp. 10–18.

Degrigny, C. "La mise au point d'un traitement cathodique de stabilisation de vestiges aéronautiques immergés en alliages d'aluminium." pp. 373–380 in *Saving the Twentieth Century: The Conservation of Modern Materials* (edited by D.W. Grattan). Ottawa, ON: Canadian Conservation Institute, 1993.

Doyle, W. "Aluminium 2: Hiduminium and RR Aluminium Alloys up to 1950." *Historical Metallurgy* 19 (1985), pp. 44–47.

Duncan, S. "Aluminium: Its Alloys, Coatings and Corrosion." pp. 27–32 in *Modern Metals in Museums* (edited by R.E. Child and J.M. Townsend). London, UK: Institute of Archaeology, 1988.

Gayle, M., and D.W. Look. "Aluminum." pp. 84–87 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite). Washington, DC: National Park Service, 1992.

Ghali, E. "Aluminum and Aluminum Alloys." pp. 677–716 in *Uhlig's Corrosion Handbook, 2nd ed.* (edited by R.W. Revie). New York, NY: John Wiley & Sons, 2000.

Graedel, T.E. "Corrosion Mechanisms for Aluminum exposed to the Atmosphere." *Journal of the Electrochemical Society* 136 (1989), pp. 204C–212C.

Green, L.R., and D. Thickett. "Modern Metals in Museum Collections." pp. 261–272 in *Saving the Twentieth Century: The Conservation of Modern Materials* (edited by D.W. Grattan). Ottawa, ON: Canadian Conservation Institute, 1993.

Hallam, D.L., C.D. Adams, G. Bailey, and G.A. Heath. "Redefining the Electrochemical Treatment of Historic Aluminium Objects." pp. 220–222 in *Metal 95* (edited by I.D. MacLeod, S.L. Pennec, and L. Robbiola). London, UK: James & James Science Publishers, 1997.

Hammond, C.R. "The Elements — Aluminum." p. 4-3 in *CRC Handbook of Chemistry and Physics, 79th ed.* Boca Raton, FL: CRC Press, 1998.

Hollingsworth, E.H., H.Y. Hunsicker, and P.A. Schweitzer. "Aluminum Alloys." pp. 153–186 in *Corrosion and Corrosion Protection Handbook, 2nd ed.* (edited by P.A. Schweitzer). New York, NY: Marcel Dekker, 1989.

Holroyd, N.J.H. "Aluminum Alloys." pp. 173–251 in *Environmental Effects on Engineered Materials* (edited by R.H. Jones). New York, NY: Marcel Dekker, 2001.

Kelley, S. "Aluminum." pp. 47–51 in *Twentieth-century Building Materials* (edited by T.C. Jester). Toronto, ON: McGraw-Hill, 1995.

King, F. "Aluminium 1: 1900–1950." *Historical Metallurgy* 19 (1985), pp. 39–43.

Krause, C.L., and C. Mishler. *Standard Catalogue of World Coins* (edited by C.R. Bruce II). Iola, WI: Krause Publications, 1991.

Leth-Olsen, H., and K. Nisancioglu. "Filiform Corrosion of Aluminium Sheet. I. Corrosion Behaviour of Painted Material." *Corrosion Science* 40 (1998), pp. 1179–1194.

MacLeod, I.D. "Stabilization of Corroded Aluminium." *Studies in Conservation* 28 (1983), pp. 1–7.

Ruggeri, R.T., and T.R. Beck. "An Analysis of Mass Transfer in Filiform Corrosion." *Corrosion* 39 (1983), pp. 452–465.

Sirois, J., E. Moffatt, L. Selwyn, and C. Bigras. *Analysis of Corrosion and Accretion on a Gemini Space Glove.* CCI Analytical Report ARL 4033. Ottawa, ON: Canadian Conservation Institute, 2002.

Staley, J.T. "History of Wrought-aluminum-alloy Development." pp. 3–31 in *Aluminum Alloys — Contemporary Research and Applications. Vol. 31* (edited by A.K. Vasudevan and R.D. Doherty). San Diego, CA: Academic Press, 1989.

Staley, J.T., and W. Haupin. "Aluminum and Alloys." pp. 184–251 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 2.* New York, NY: John Wiley & Sons, 1992.

Steele, G.D. "Filiform Corrosion on Architectural Aluminum — A Review." *Aluminum Industry* 13 (1994), pp. 3–7.

Waite, J.G. "Aluminum; Preservation and Repair." pp. 149–153 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite). Washington, DC: National Park Service, 1992.

Young, M. "Aluminium 3: The Early History of Alloys." *Historical Metallurgy* 19 (1985), pp. 48–56.

Zahner, L.W. "Aluminum." pp. 29–91 in *Architectural Metals: A Guide to Selection, Specification, and Performance*. New York, NY: John Wiley & Sons, 1995a.

Zahner, L.W. "Metallic Coatings on Metals." pp. 299–334 in *Architectural Metals: A Guide to Selection, Specification, and Performance*. New York, NY: John Wiley & Sons, 1995b.

CHAPTER 6. COPPER

Alunno-Rossetti, V., and M. Marabelli. "Analyses of the Patinas of a Gilded Horse of St. Mark's Basilica in Venice: Corrosion Mechanisms and Conservation Problems." *Studies in Conservation* 21 (1976), pp. 161–170.

Ashurst, J., and N. Ashurst. "Traditional Copper Roofing." pp. 42–79 in *Practical Building Conservation: English Heritage Technical Handbook. Vol. 4. Metals.* Aldershot, UK: Gower Technical Press, 1988.

ASM International. *ASM Handbook. Vol. 3. Alloy Phase Diagrams.* Materials Park, OH: ASM International, 1992.

Baboian, R. "Galvanic Corrosion on the Statue of Liberty." pp. 93–99 in *The Statue of Liberty Restoration* (edited by R. Baboian, E. Cliver, and E.L. Bellante). Houston, TX: National Association of Corrosion Engineers, 1990.

Baboian, R., E.B. Cliver, and E.L. Bellante (editors). *The Statue of Liberty Restoration.* Houston, TX: National Association of Corrosion Engineers, 1990.

Bacon, L. "The Deterioration of Four Giorgi Flutes made of Ebonite and a Possible Method for their Conservation." pp. 96–100 in *Conservation Today: Papers presented at the UKIC 30th Anniversary Conference, 1988* (edited by V. Todd). London, UK: United Kingdom Institute for Conservation of Historic and Artistic Works, 1988.

Bailey, R.A., and J.A. Zaccardi. "Corrosion of Copper and Other Metals by Perspiration." *Journal of Electroanalytical Chemistry* 144 (1983), pp. 443–448.

Barclay, R.L. "The Metal." pp. 33–66 in *The Art of the Trumpet-maker: The Materials, Tools, and Techniques of the Seventeenth and Eighteenth Centuries in Nuremberg*. Early Music Series, No. 14. Oxford, UK: Oxford University Press, 1992.

Barclay, R.L. "The Metals of the Scientific Instrument Maker: Part I: Brass." *Bulletin of the Scientific Instrument Society* 39 (1993), pp. 32–36.

Bayley, J. "The Production of Brass in Antiquity with Particular Reference to Roman Britain." pp. 7–26 in *2000 Years of Zinc and Brass*. British Museum Occasional Paper, No. 50. London, UK: British Museum Publications Ltd., 1998.

Birnie, L. "Special Finishes on Non-ferrous Metals at the National Maritime Museum." pp. 148–154 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Bradley, S., and D. Thickett. "The Pollution Problem in Perspective." pp. 8–13 in *ICOM Committee for Conservation, 12th Triennial Meeting, Lyon, France* (edited by J. Bridgland). London, UK: James & James Science Publishers, 1999.

Breedis, J.F., and R.N. Caron. "Wrought Copper and Wrought Copper Alloys." pp. 429–473 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 7.* New York, NY: John Wiley & Sons, 1993.

Brock, A.J. "Corrosion of Copper and its Alloys." pp. 115–150 in *Environmental Effects on Engineered Materials* (edited by R.H. Jones). New York, NY: Marcel Dekker, 2001.

Bullard, S.J., S.D. Cramer, B.S. Covino, and G.R. Holcomb. "Copper Corrosion in Coastal Oregon." pp. 700/1–700/10 in *Corrosion 98*. Paper No. 700. Houston, TX: National Association of Corrosion Engineers, 1998.

Burmester, A., and J. Koller. "Known and New Corrosion Products on Bronzes: Their Identification and Assessment, particularly in relation to Organic Protective Coatings." pp. 97–103 in *Recent Advances in the Conservation and Analysis of Artifacts*. London, UK: Summer Schools Press, 1987.

Chase, W.T. "Chinese Bronzes: Casting, Finishing, Patination, and Corrosion." pp. 85–117 in *Ancient & Historic Metals, Conservation and Scientific Research* (edited by D.A. Scott, J. Podany, and B. Considine). Marina del Rey, CA: Getty Conservation Institute, 1994.

Child, R. "The Identification of Post-Industrial Revolution Metals." pp. 7–14 in *Modern Metals in Museums* (edited by R.E. Child and J.M. Townsend). London, UK: Institute of Archaeology, 1988.

Child, R. "Modern Electroplating and Electrofinishing Techniques." pp. 291–300 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Clydesdale, A. "The Buiston Bowl: Cleaning Trials for Chalcopyrite Removal." *SSCR Journal* 4 (1993), pp. 12–14.

Copper Development Association. "Standard Designations for Wrought and Cast Copper and Copper Alloys." pp. 865–893 in *Annual Book of ASTM Standards 2001. Vol. 02.01.* West Conshohocken, PA: American Society for Testing and Materials, 2001.

Corfield, M. "Copper Plating on Iron." pp. 276–283 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Cowden, A.B. "Nickel Silver." pp. 59–63 in *Twentieth-century Building Materials* (edited by T.C. Jester). Toronto, ON: McGraw-Hill, 1995.

Craddock, P.T. (editor). *2000 Years of Zinc and Brass.* British Museum Occasional Paper, No. 50. London, UK: British Museum Publications Ltd., 1998.

Craddock, P., and A. Giumlia-Mair. "*Hśmn-Km*, Corinthian Bronze, *Shakudo*: Black-patinated Bronze in the Ancient World." pp. 101–127 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Cser, L., J. Sirois, E. Moffatt, K. Helwig, and S. Stock. "The Examination and Analysis of the Interior and Exterior Decorative Elements of the Library of Parliament." pp. 17–24 in *The Conservation of Heritage Interiors*. Ottawa, ON: Canadian Conservation Institute, 2000.

Day, J. "Copper, Zinc and Brass Production." pp. 131–199 in *The Industrial Revolution in Metals* (edited by J. Day and R.F. Tylecote). London, UK: The Institute of Metals, 1991.

Duncan, S.J., and H. Ganiaris. "Some Sulphide Corrosion Products on Copper Alloys and Lead Alloys from London Waterfront Sites." pp. 109–118 in *Recent Advances in the Conservation and Analysis of Artifacts*. London, UK: Summer Schools Press, 1987.

Dutrizac, J.E., and J.B. O'Reilly. "The Origins of Zinc and Brass." *CIM Bulletin* 77 (1984), pp. 69–73.

Eggert, G., and H. Kutzke. "All that Glitters is not Pseudogold: A Study in Pseudo-pseudogilding." pp. 860–864 in *ICOM Committee for Conservation, 13th Triennial Meeting, Rio de Janeiro, Brazil* (edited by R. Vontobel). London, UK: James & James Science Publishers, 2002.

Eggert, G., and U. Sobottka-Braun. "Black Spots on Bronzes and Elemental Sulphur." pp. 823–827 in *ICOM Committee for Conservation, 12th Triennial Meeting, Lyon, France* (edited by J. Bridgland). London, UK: James & James Science Publishers, 1999.

Fabrizi, M., H. Ganiaris, S. Tarling, and D.A. Scott. "The Occurrence of Sampleite, a Complex Copper Phosphate, as a Corrosion Product on Copper Alloy Objects from Memphis, Egypt." *Studies in Conservation* 34 (1989), pp. 45–51.

Fabrizi, M., and D. Scott. "Unusual Copper Corrosion Products and Problems of Identity." pp. 131–133 in *Recent Advances in the Conservation and Analysis of Artifacts.* London, UK: Summer Schools Press, 1987.

Fjaestad, M., A.G. Nord, K. Tronner, I. Ullén, and A. Lagerlöf. "Environmental Threats to Archaeological Artefacts." pp. 870–875 in *ICOM Committee for Conservation, 11th Triennial Meeting, Edinburgh, Scotland* (edited by J. Bridgland). London, UK: James & James Science Publishers, 1996.

Fjaestad, M., I. Ullén, A.G. Nord, K. Tronner, G.C. Borg, and M. Sandberg. "Are Recently Excavated Bronze Artifacts More Deteriorated than Earlier Finds?" pp. 71–79 in *Metal 98* (edited by W. Mourey and L. Robbiola). London, UK: James & James Science Publishers, 1998.

Flotte, J., and J. Dommermuth. "Richard Lippold's *The Sun* — Investigation and Treatment Considerations." pp. 329–336 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Franzon, M. *Deterioration and Conservation of Enamelled Objects.* Graduation Thesis. Göteborg, Sweden: Göteborg University, 2000.

Gayle, M., and D.W. Look. "Copper and Copper Alloys." pp. 22–34 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite). Washington, DC: National Park Service, 1992a.

Gayle, M., and D.W. Look. "Nickel and Nickel Alloys." pp. 35–41 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite). Washington, DC: National Park Service, 1992b.

Gayle, M., and D.W. Look. "Lead." pp. 8–11 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite). Washington, DC: National Park Service, 1992c.

George, D.B. "Copper." pp. 381–428 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 7.* New York, NY: John Wiley & Sons, 1993.

Gettens, R.J. "Patina: Noble and Vile." pp. 57–72 in *Art and Technology: A Symposium on Classical Bronzes* (edited by S. Doeringer, D.G. Mitten, and A. Steinberg). Cambridge, MA: MIT Press, 1970.

Gettens, R.J., and C. Frondel. "Chalconatronite: An Alteration Product on Some Ancient Egyptian Bronzes." *Studies in Conservation* 2 (1955), pp. 64–75.

Gettens, R.J., and E.W. Fitzhugh. "Azurite and Blue Verditer." pp. 23–35 in *Artists' Pigments: A Handbook of their History and Characteristics. Vol. 2* (edited by A. Roy). Washington, DC: National Gallery of Art, 1993a.

Gettens, R.J., and E.W. Fitzhugh. "Malachite and Green Verditer." pp. 183–202 in *Artists' Pigments: A Handbook of their History and Characteristics. Vol. 2* (edited by A. Roy). Washington, DC: National Gallery of Art, 1993b.

Gilberg, M. "History of Bronze Disease and its Treatment." pp. 59–70 in *Recent Advances in Conservation* (edited by V. Daniels). British Museum Occasional Paper, No. 65. London, UK: British Museum Publications Ltd., 1988.

Gohard, F. "Addendum: Gilding the Flame." p. 146 in *The Statue of Liberty Restoration* (edited by R. Baboian, E.B. Cliver, and E.L. Bellante). Houston, TX: National Association of Corrosion Engineers, 1990.

Graedel, T.E. "Copper Patinas formed in the Atmosphere — II. A Qualitative Assessment of Mechanisms. *Corrosion Science* 27 (1987a), pp. 721–740.

Graedel, T.E. "Copper Patinas formed in the Atmosphere — III. A Semi-quantitative Assessment of Rates and Constraints in the Greater New York Metropolitan Area." *Corrosion Science* 27 (1987b), pp. 741–769.

Graedel, T.E., J.P. Franey, G.W. Kammlott, and J.M. Vandenberg. "The Atmospheric Sulfidation of Copper Single Crystals." *Journal of the Electrochemical Society* 134 (1987a), pp. 1632–1635.

Graedel, T.E., K. Nassau, and J.P. Franey. "Copper Patinas formed in the Atmosphere — I. Introduction." *Corrosion Science* 27 (1987b), pp. 639–657.

Grice, J.D., and E. Gasparrini. "Spertiniite, $Cu(OH)_2$, a New Mineral from the Jeffrey Mine, Quebec." *Canadian Mineralogist* 19 (1981), pp. 337–340.

Griffin, P.S. "The Selective Use of Gilding on Egyptian Polychromed Bronzes." pp. 49–72 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Grissom, C.A. "The Conservation of Outdoor Zinc Sculpture." pp. 279–304 in *Ancient & Historic Metals, Conservation and Scientific Research* (edited by D.A. Scott, J. Podany, and B.B. Considine). Marina del Rey, CA: Getty Conservation Institute, 1994.

Habashi, F. "Mirrors through the Ages." *CIM Bulletin* 91 (1998), pp. 87–90.

Hayden, R.S., and T.W. Despont. *Restoring the Statue of Liberty.* New York, NY: McGraw-Hill, 1986.

Helwig, K., G. Sansoucy, and J. Sirois. *Analysis of Corrosion on a Set of Pastel Crayons.* CCI Analytical Report ARL 3899. Ottawa, ON: Canadian Conservation Institute, 2001.

Hjelm-Hansen, N. "Cleaning and Stabilization of Sulphide-corroded Bronzes." *Studies in Conservation* 29 (1984), pp. 17–20.

Horie, C.V., and J.A. Vint. "Chalconatronite: A By-product of Conservation?" *Studies in Conservation* 27 (1982), pp. 185–186.

Howie, F.M. "Sulphides and Allied Minerals in Collections." pp. 56–69 in *The Care and Conservation of Geological Material: Minerals, Rocks, Meteorites and Lunar Finds* (edited by F.M. Howie). Oxford, UK: Butterworth-Heinemann, 1992.

Hughes, R. "Artificial Patination." pp. 231–243 in *Dialogue 89 — The Conservation of Bronze Sculpture in the Outdoor Environment* (edited by T. Drayman-Weisser). Houston, TX: National Association of Corrosion Engineers, 1992.

Hughes, R. "Artificial Patination." pp. 1–18 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Hughes, R., and M. Rowe. *The Colouring, Bronzing and Patination of Metals.* London, UK: Crafts Council, 1982.

Jambor, J.L., J.E. Dutrizac, A.C. Roberts, J.D. Grice, and J.T. Szymanski. "Clinoatacamite, a New Polymorph of $Cu_2(OH)_3Cl$, and its Relationship to Paratacamite and "Anarakite"." *Canadian Mineralogist* 34 (1996), pp. 61–72.

Kammlott, G.W., J.P. Franey, and T.E. Graedel. "Atmospheric Sulfidation of Copper Alloys." *Journal of the Electrochemical Society* 131 (1984), pp. 505–511.

Kühn, H. "Verdigris and Copper Resinate." pp. 131–158 in *Artists' Pigments: A Handbook of their History and Characteristics. Vol. 2* (edited by A. Roy). Washington, DC: National Gallery of Art, 1993.

Lambert, J.B. "Metals." pp. 168–213 in *Traces of the Past; Unraveling the Secrets of Archaeology through Chemistry.* Reading, MA: Perseus Books, 1997.

Lang, R. "Corrosion of Copper-alloy Antiquities in Wooden Storage Boxes." *Conservation News* 61 (1996), pp. 57–58.

La Niece, S. "Silver Plating on Copper, Bronze and Brass." *The Antiquaries Journal* 70 (1990), pp. 102–114.

La Niece, S. "Japanese Polychrome Metalwork." pp. 87–94 in *Archaeometry '90* (edited by E. Pernicka and G.A. Wagner). Berlin, Germany: Birkhäuser Verlag, 1991.

La Niece, S. "Silvering." pp. 201–210 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Larsen, E.B. *Electrotyping*. Copenhagen, Denmark: School of Conservation, 1984.

Lee, L.R., and D. Thickett. "Why is Testing Necessary?" pp. 1–10 in *Selection of Materials for the Storage or Display of Museum Objects*. British Museum Occasional Paper, No. 111. London, UK: British Museum Publications Ltd., 1996.

Lins, A. "Outdoor Bronzes: Some Basic Metallurgical Considerations." pp. 8–20 in *Sculptural Monuments in an Outdoor Environment* (edited by V.N. Naudé). Philadelphia, PA: Pennsylvania Academy of the Fine Arts, 1985.

Lins, A., and T. Power. "The Corrosion of Bronze Monuments in Polluted Urban Sites: A Report on the Stability of Copper Mineral Species at Different pH Levels." pp. 119–151 in *Ancient & Historic Metals, Conservation and Scientific Research* (edited by D.A. Scott, J. Podany, and B.B. Considine). Marina del Rey, CA: Getty Conservation Institute, 1994.

Lobnig, R., J.D. Sinclair, M. Unger, and M. Stratmann. "Mechanism of Atmospheric Corrosion of Copper in the presence of Ammonium Sulfate Particles." *Journal of the Electrochemical Society* 150 (2003), pp. A835–A849.

MacLeod, I.D. "Conservation of Corroded Copper Alloys: A Comparison of New and Traditional Methods for Removing Chloride Ions." *Studies in Conservation* 32 (1987a), pp. 25–40.

MacLeod, I.D. "Stabilization of Corroded Copper Alloys: A Study of Corrosion and Desalination Mechanisms." pp. 1079–1085 in *ICOM Committee for Conservation, 8th Triennial Meeting, Sydney, Australia* (edited by K. Grimstad). Marina del Rey, CA: Getty Conservation Institute, 1987b.

MacLeod, I.D. "Identification of Corrosion Products on Non-ferrous Metal Artifacts recovered from Shipwrecks." *Studies in Conservation* 36 (1991), pp. 222–234.

Massey, A.G. "Copper." pp. 1–78 in *The Chemistry of Copper, Silver and Gold*. New York, NY: Pergamon Press, 1973.

Mattsson, E., and R. Holm. "Atmospheric Corrosion of Copper and its Alloys." pp. 365–381 in *Atmospheric Corrosion* (edited by W.H. Ailor). New York, NY: John Wiley & Sons, 1982.

McDonnell, J.G. "Pyrotechnology." pp. 493–505 in *Handbook of Archaeological Sciences* (edited by D.R. Brothwell and A.M. Pollard). Chichester, UK: John Wiley & Sons, 2001.

McNeil, M.B., J.M. Jones, and B.J. Little. "Production of Sulfide Minerals by Sulfate-reducing Bacteria during Microbiologically Influenced Corrosion of Copper." *Corrosion* 47 (1991), pp. 674–677.

McNeil, M.B., and B.J. Little. "Corrosion Products and Mechanisms in Long Term Corrosion of Copper." pp. 311–316 in *Scientific Basis for Nuclear Waste Management. XIV*. Materials Research Society Symposium Proceedings. Vol. 212. Warrendale, PA: Materials Research Society, 1991.

McNeil, M.B., and B.J. Little. "The Use of Mineralogical Data in Interpretation of Long-term Microbiological Corrosion Processes: Sulfiding Reactions." *Journal of the American Institute for Conservation* 38 (1999), pp. 186–199.

McNeil, M.B., and D.W. Mohr. "Interpretation of Bronze Disease and Related Copper Corrosion Mechanisms in Terms of Log-Activity Diagrams." pp. 1055–1063 in *Materials Issues in Art and Archaeology. III* (edited by P.B. Vandiver, J.R. Druzik, G.S. Wheeler, and I.C. Freestone). Materials Research Society Symposium Proceedings. Vol. 267. Warrendale, PA: Materials Research Society, 1992a.

McNeil, M.B., and D.W. Mohr. "Sulfate Formation during Corrosion of Copper Alloy Objects." pp. 1047–1053 in *Materials Issues in Art and Archaeology. III* (edited by P.B. Vandiver, J.R. Druzik, G.S. Wheeler, and I.C. Freestone). Materials Research Society Symposium Proceedings. Vol. 267. Warrendale, PA: Materials Research Society, 1992b.

McNeil, M.B., and D.W. Mohr. "Formation of Copper–Iron Sulfide Minerals during Corrosion of Artifacts and Possible Implications for Pseudogilding." *Geoarchaeology* 8 (1993), pp. 23–33.

McNeil, M., and L.S. Selwyn. "Electrochemical Processes in Metallic Corrosion." pp. 605–614 in *Handbook of Archaeological Sciences* (edited by D.R. Brothwell and A.M. Pollard). Chichester, UK: John Wiley & Sons, 2001.

Meakin, J.D., D.L. Ames, and D.A. Dolske. "Degradation of Monumental Bronzes." *Atmospheric Environment* 26B (1992), pp. 207–215.

Meeks, N. "Tin-rich Surfaces on Bronze — Some Experimental and Archaeological Considerations." *Archaeometry* 28 (1986), pp. 133–162.

Meeks, N. "Patination Phenomena on Roman and Chinese High-tin Bronze Mirrors and Other Artefacts." pp. 63–84 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993a.

Meeks, N. "Surface Characterization of Tinned Bronze, High-tin Bronze, Tinned Iron and Arsenical Bronze." pp. 247–275 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993b.

Merk, L.E. "A Study of Reagents used in the Stripping of Bronzes." *Studies in Conservation* 23 (1978), pp. 15–22.

Murakami, R. "Japanese Traditional Alloys." pp. 85–94 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Nagy, E. "Corrosion Intercept Tent Packing and Handling System for Donald Judd's Brass and Copper Sculptures: Experiences with Packing and Handling Methods." *AIC Objects Specialty Group Postprints* 6 (1999), pp. 11–35.

Newton, R., and S. Davison. "Deterioration of Glass." pp. 135–287 in *Conservation of Glass*. Oxford, UK: Butterworth-Heinemann, 1989.

Notis, M.R. "The Japanese Alloy *Shakudo*: Its History and its Patination." pp. 315–327 in *The Beginning of the Use of Metals and Alloys* (edited by R. Maddin). Cambridge, MA: MIT Press, 1988.

Oddy, A., and S.M. Bradley. "The Corrosion of Metal Objects in Storage and on Display." pp. 225–243 in *Current Problems in the Conservation of Metal Antiquities* (edited by S. Aoki). Tokyo, Japan: Tokyo National Research Institute of Cultural Properties, 1993.

Oddy, A., and M.J. Hughes. "The Stabilization of 'Active' Bronze and Iron Antiquities by the Use of Sodium Sesquicarbonate." *Studies in Conservation* 15 (1970), pp. 183–189.

Organ, R.M. "The Examination and Treatment of Bronze Antiquities." pp. 104–110 in *Recent Advances in Conservation* (edited by G. Thomson). London, UK: Butterworths, 1963.

Organ, R.M. "The Conservation of Bronze Objects." pp. 73–84 in *Art and Technology: A Symposium on Classical Bronzes* (edited by S. Doeringer, D.G. Mitten, and A. Steinberg). Cambridge, MA: MIT Press, 1970.

Otieno-Alego, V., D. Hallam, A. Viduka, G. Heath, and D. Creagh. "Electrochemical Impedance Studies of the Corrosion Resistance of Wax Coatings on Artificially Patinated Bronze." pp. 315–319 in *Metal 98* (edited by W. Mourey and L. Robbiola). London, UK: James & James Science Publishers, 1998.

Paterakis, A.B. "Archaeological Metals in the Ancient Athenian Agora." pp. 253–259 in *Metal 98* (edited by W. Mourey and L. Robbiola). London, UK: James & James Science Publishers, 1998.

Paterakis, A.B. "The Hidden Secrets of Copper Alloy Artifacts in the Athenian Agora." *AIC Objects Specialty Group Postprints* 6 (1999), pp. 70–76.

Paterakis, A.B. "Athenian Gilded Bronzes from a Conservation Perspective." pp. 173–177 in *From the Parts to the Whole* (edited by C.C. Mattusch, A. Brauer, and S.E. Knudsen). Portsmouth, RI: Journal of Roman Archaeology, 2000.

Paterakis, A.B. "The Influence of Conservation Treatments and Environmental Storage Factors on Corrosion of Copper Alloys in the Ancient Athenian Agora." *Journal of the American Institute for Conservation* 42 (2003), pp. 313–339.

Pollard, A.M., R.G. Thomas, and P.A. Williams. "Synthesis and Stabilities of the Basic Copper(II) Chlorides Atacamite, Paratacamite and Botallackite." *Mineralogical Magazine* 53 (1989), pp. 557–563.

Pollard, A.M., R.G. Thomas, and P.A. Williams. "Mineralogical Changes Arising from the Use of Aqueous Sodium Carbonate Solutions for the Treatment of Archaeological Copper Objects." *Studies in Conservation* 35 (1990), pp. 148–152.

Pollard, A.M., R.G. Thomas, and P.A. Williams. "The Copper Chloride System and Corrosion: A Complex Interplay of Kinetic and Thermodynamic Factors." pp. 123–133 in *Dialogue 89 —The Conservation of Bronze Sculpture in the Outdoor Environment* (edited by T. Drayman-Weisser). Houston, TX: National Association of Corrosion Engineers, 1992.

Pollard, A.M., R.G. Thomas, P.A. Williams, J. Just, and P.J. Bridge. "The Synthesis and Composition of Georgeite and its Reactions to form Other Secondary Copper(II) Carbonates." *Mineralogical Magazine* 55 (1991), pp. 163–166.

Richardson, H.W. "Copper Compounds." pp. 505–520 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 7.* New York, NY: John Wiley & Sons, 1993.

Robbiola, L., J.-M. Blengino, and C. Fiaud. "Morphology and Mechanisms of Formation of Natural Patinas on Archaeological Cu–Sn Alloys." *Corrosion Science* 40 (1998a), pp. 2083–2111.

Robbiola, L., C. Fiaud, and S. Pennec. "New Model of Outdoor Bronze Corrosion and its Implications for Conservation." pp. 796–802 in *ICOM Committee for Conservation, 10th Triennial Meeting, Washington, DC* (edited by J. Bridgland). Paris, France: International Council of Museums Committee for Conservation, 1993.

Robbiola, L., N. Pereira, K. Thaury, C. Fiaud, and J.-P. Labbé. "Decuprification Phenomenon of Cu–Sn Alloys in Aqueous Solution in Nearly Neutral pH Conditions." pp. 136–144 in *Metal 98* (edited by W. Mourey and L. Robbiola). London, UK: James & James Science Publishers, 1998b.

Robinet, L., and M.-C. Corbeil. "The Characterization of Metal Soaps." *Studies in Conservation* 48 (2003), pp. 23–40.

Römich, H. *New Conservation Methods for Outdoor Bronze Sculptures*. Project EV5V-CT92-0107. Brussels, Belgium: European Commission, 1996.

Schrenk, J.L. "Corrosion and Past "Protective" Treatments of the Benin "Bronzes" in the National Museum of African Art." pp. 805–812 in *Materials Issues in Art and Archaeology. II* (edited by P.B. Vandiver, J. Druzik, and G.S. Wheeler). Materials Research Society Symposium Proceedings. Vol. 185. Warrendale, PA: Materials Research Society, 1991.

Schrenk, J.L. "The Royal Art of Benin: Surfaces, Past and Present." pp. 51–62 in *Ancient & Historic Metals, Conservation and Scientific Research* (edited by D.A. Scott, J. Podany, and B. Considine). Marina del Rey, CA: Getty Conservation Institute, 1994.

Schweizer, F. "Bronze Objects from Lake Sites: From Patina to "Biography"." pp. 33–50 in *Ancient & Historic Metals, Conservation and Scientific Research* (edited by D.A. Scott, J. Podany, and B. Considine). Marina del Rey, CA: Getty Conservation Institute, 1994.

Scott, D.A. "Bronze Disease: A Review of Some Chemical Problems and the Role of Relative Humidity." *Journal of the American Institute for Conservation* 29 (1990), pp. 193–206.

Scott, D.A. "Copper Compounds in Metals and Colorants: Oxides and Hydroxides." *Studies in Conservation* 42 (1997), pp. 93–100.

Scott, D.A. "A Review of Copper Chlorides and Related Salts in Bronze Corrosion and as Painting Pigments." *Studies in Conservation* 45 (2000a), pp. 39–53.

Scott, D.A. "A Review of Gilding Techniques in Ancient South America." pp. 203–222 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000b.

Scott, D.A. *Copper and Bronze in Art: Corrosion, Colorants, Conservation.* Marina del Rey, CA: Getty Conservation Institute, 2002.

Scott, D.A., Y. Taniguchi, and E. Koseto. "The Verisimilitude of Verdigris: A Review of the Copper Carboxylates." *Reviews in Conservation* 2 (2001), pp. 73–91.

Selwyn, L. "Corrosion Chemistry of Gilded Silver and Copper." pp. 21–47 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Selwyn, L.S., N.E. Binnie, J. Poitras, M.E. Laver, and D.A. Downham. "Outdoor Bronze Statues: Analysis of Metal and Surface Samples." *Studies in Conservation* 41 (1996), pp. 205–228.

Sequeira, C.A.C. "Corrosion of Copper and Copper Alloys." pp. 729–765 in *Uhlig's Corrosion Handbook, 2nd ed.* (edited by R.W. Revie). New York, NY: John Wiley & Sons, 2000.

Shashoua, Y.R. *Inhibiting the Deterioration of Plasticized Poly(vinyl chloride)— A Museum Perspective.* Ph.D. Thesis. Copenhagen, Denmark: The National Museum of Denmark, 2001.

Shearman, W.M. *Metal Alloys and Patinas for Castings.* Ashland, OH: Kent State University Press, 1976.

Sirois, J. *Identification of Blue Corrosion on Egyptian Situla 976.151.45.* CCI Analytical Report ARL 4176. Ottawa, ON: Canadian Conservation Institute, 2003.

Sirois, J., E. Moffatt, and L. Selwyn. *Analysis of Corrosion Products on Bronze Sculptures (Phase III).* CCI Analytical Report ARL 3864. Ottawa, ON: Canadian Conservation Institute, 2002.

Sirois, J., E. Moffatt, and L. Selwyn. *Analysis of Corrosion Products on Bronze Sculptures (Phase IV).* CCI Analytical Report ARL 4153. Ottawa, ON: Canadian Conservation Institute, 2003a.

Sirois, J., E. Moffatt, and M. Singer. "The Analysis of Outdoor Bronze Sculptures from the Assemblée nationale in Québec City, Canada." Presented at the Northern Area Eastern Conference (of the National Association of Corrosion Engineers), 15–17 September, 2003b. (A CD of the conference proceedings is available for CAN$50 from Bruce Baldock, National Research Council Canada, Institute for Research in Construction, Building M-20, 1200 Montreal Road, Ottawa ON K1A 0R6, Canada; e-mail bruce.baldock@nrc.ca for more information.)

Strahan, D.K. "Treatment of a Silver Dragon for the Removal of Silver Cyanide and Chalconatronite." *Journal of the American Institute for Conservation* 25 (1986), pp. 73–81.

Strandberg, H. "Reactions of Copper Patina Compounds — I. Influence of Some Air Pollutants." *Atmospheric Environment* 32 (1998a), pp. 3511–3520.

Strandberg, H. "Reactions of Copper Patina Compounds — II. Influence of Sodium Chloride in the presence of Some Air Pollutants." *Atmospheric Environment* 32 (1998b), pp. 3521–3526.

Strandberg, H. "Perspectives on Bronze Sculpture Conservation Modelling Corrosion." pp. 297–302 in *Metal 98* (edited by W. Mourey and L. Robbiola). London, UK: James & James Science Publishers, 1998c.

Strandberg, H., and L.-G. Johansson. "Role of O_3 in the Atmospheric Corrosion of Copper in the presence of SO_2." *Journal of the Electrochemical Society* 144 (1997), pp. 2334–2342.

Strandberg, H., and L.-G. Johansson. "Some Aspects of the Atmospheric Corrosion of Copper in the presence of Sodium Chloride." *Journal of the Electrochemical Society* 145 (1998), pp. 1093–1100.

Strandberg, H., L.-G. Johansson, and O. Lindqvist. "The Atmospheric Corrosion of Statue Bronzes exposed to SO_2 and NO_2." *Materials and Corrosion* 48 (1997), pp. 721–730.

Strandberg, H., L.-G. Johansson, and J. Rosvall. "Outdoor Bronze Sculptures — A Conservation View on the Examination of the State of Preservation." pp. 894–900 in *ICOM Committee for Conservation, 11th Triennial Meeting, Edinburgh, Scotland* (edited by J. Bridgland). London, UK: James & James Science Publishers, 1996.

Temple, S. "Copper 2: Brasses, Bronzes and Nickel Silvers." *Historical Metallurgy* 19 (1985), pp. 12–16.

Tennent, N.H., and T. Baird. "The Identification of Acetate Efflorescence on Bronze Antiquities stored in Wooden Cabinets." *The Conservator* 16 (1992), pp. 39–47.

Thickett, D., S. Bradley, and L. Lee. "Assessment of the Risks to Metal Artifacts posed by Volatile Carbonyl Pollutants." pp. 260–264 in *Metal 98* (edited by W. Mourey and L. Robbiola). London, UK: James & James Science Publishers, 1998.

Thickett, D., and M. Odlyha. "Note on the Identification of an Unusual Pale Blue Corrosion Product from Egyptian Copper Alloy Artifacts." *Studies in Conservation* 45 (2000), pp. 63–67.

Thornton, J. "All that Glitters is not Gold: Other Surfaces that Appear to be Gilded." pp. 307–317 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Tilbrooke, D. "The Fatty Acid Corrosion of Copper Alloys and its Treatment." *ICCM Bulletin* 6 (1980), pp. 46–52.

Trentelman, K., L. Stodulski, D. Scott, M. Back, S. Stock, D. Strahan, A.R. Drews, A. O'Neill, W.H. Weber, A.E. Chen, and S.J. Garrett. "The Characterization of a New Pale Blue Corrosion Product found on Copper Alloy Artifacts." *Studies in Conservation* 47 (2002), pp. 217–227.

Tundermann, J.H., J.K. Tien, and T.E. Howson. "Nickel and Nickel Alloys." pp. 1–17 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 17.* New York, NY: John Wiley & Sons, 1996.

Twarog, D.L. "Cast Copper Alloys." pp. 474–505 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 7.* New York, NY: John Wiley & Sons, 1993.

Vaccaro, A.M. "The Equestrian Statue of Marcus Aurelius." pp. 108–121 in *The Art of the Conservator* (edited by A. Oddy). Washington, DC: Smithsonian Institution Press, 1992.

Van Zelst, L., and J.-L. Lachevre. "Outdoor Bronze Sculpture: Problems & Procedures of Protective Treatment." *Technology & Conservation* 8 (1983), pp. 18–24.

Waite, J.G. "Copper and Copper Alloys; Preservation and Repair." pp. 118–127 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite). Washington, DC: National Park Service, 1992.

Waller, R. "Temperature- and Humidity-sensitive Mineralogical and Petrological Specimens." pp. 25–50 in *The Care and Conservation of Geological Material: Minerals, Rocks, Meteorites and Lunar Finds* (edited by F.M. Howie). Oxford, UK: Butterworth-Heinemann, 1992.

Wayman, M., and P. Craddock. "*Wu tong*, a Neglected Chinese Decorative Technology." pp. 128–134 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Weaver, M.E. "Architectural Metalwork." pp. 175–215 in *Conserving Buildings; Guide to Techniques and Materials*. New York, NY: John Wiley & Sons, 1993.

Weisser, T.D. "The Use of Sodium Carbonate as a Pre-treatment for Difficult-to-stabilise Bronzes." pp. 105–108 in *Recent Advances in the Conservation and Analysis of Artifacts*. London, UK: Summer Schools Press, 1987.

Weisser, T.D. "Some Practical Considerations and Solutions for Preservation in the Museum Environment." pp. 81–96 in *Cultural Property and its Environment*. Tokyo, Japan: Tokyo National Research Institute of Cultural Properties, 1990.

Weisser, T.S. "The De-alloying of Copper Alloys." pp. 207–214 in *Conservation in Archaeology and the Applied Arts*. London, UK: International Institute for Conservation, 1975.

Wilthew, P. "Bronze and Silver Corrosion in Display Galleries in the National Museums of Scotland." pp. 67–70 in *Conservation Science in the U.K.* (edited by N.H. Tennent). London, UK: James & James Science Publishers, 1993.

Woods, T.L., and R.M. Garrels. "Use of Oxidized Copper Minerals as Environmental Indicators." *Applied Geochemistry* 1 (1986a), pp. 181–187.

Woods, T.L., and R.M. Garrels. "Phase Relations of Some Cupric Hydroxy Minerals." *Economic Geology* 81 (1986b), pp. 1989–2007.

Young, R.D. *Contemporary Patination, 5th ed.* Escondido, CA: Sculpt Nouveau, 2000.

Young, R.D., and R.A. Fennell. *Methods for Modern Sculptors*. Escondido, CA: Sculpt Nouveau, 1980.

Zahner, L.W. "Copper." pp. 92–129 in *Architectural Metals: A Guide to Selection, Specification, and Performance*. New York, NY: John Wiley & Sons, 1995a.

Zahner, L.W. "The Major Copper Alloys — Brasses, Bronzes, and Nickel Silver." pp. 130–182 in *Architectural Metals: A Guide to Selection, Specification, and Performance*. New York, NY: John Wiley & Sons, 1995b.

CHAPTER 7. GOLD

Alunno-Rossetti, V., and M. Marabelli. "Analyses of the Patinas of a Gilded Horse of St. Mark's Basilica in Venice: Corrosion Mechanisms and Conservation Problems." *Studies in Conservation* 21 (1976), pp. 161–170.

ASM International. *ASM Handbook. Vol. 3. Alloy Phase Diagrams*. Materials Park, OH: ASM International, 1992.

Child, R. "Modern Electroplating and Electrofinishing Techniques." pp. 291–300 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Cohn, J.G., and E.W. Stern. "Gold and Gold Compounds." pp. 738–767 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 12*. New York, NY: John Wiley & Sons, 1994.

Courty, C., H.J. Mathieu, and D. Landolt. "Tarnishing of Au–Ag–Cu Alloy Studies by Auger Electron Spectroscopy and Coulometry." *Werkstoffe und Korrosion* 42 (1991), pp. 288–295.

Cretu, C., and E. van der Lingen. "Coloured Gold Alloys." *Gold Bulletin* 32 (1999), pp. 115–126.

Dick, L.F.P., H. Kaiser, and H. Kaesche. "The Tarnishing of Ag and Ag–Au Alloys in Aqueous Sulfide Solutions and in H_2S Atmospheres." pp. 406–414 in *Corrosion and Reliability of Electronic Materials and Devices*. Pennington, NJ: The Electrochemical Society, 1993.

Drost, E., and J. Haußelt. "Uses of Gold in Jewellery." *Interdisciplinary Science Reviews* 17 (1992), pp. 271–292.

Edwards, G. "The Conservation of Gilded Archaeological Artefacts: Its Effects and Implications." pp. 7–12 in *Gilding: Approaches to Treatment*. London, UK: James & James Science Publishers, 2001.

Egan, T.F., and A. Mendizza. "Creeping Silver Sulfide." *Journal of the Electrochemical Society* 107 (1960), pp. 353–354.

Fioravanti, K.J., and R.M. German. "Corrosion and Tarnishing Characteristics of Low Gold Content Dental Casting Alloys." *Gold Bulletin* 21 (1988), pp. 99–110.

Forty, A.J. "Micromorphological Studies of the Corrosion of Gold Alloys." *Gold Bulletin* 14 (1981), pp. 25–35.

Frant, M.S. "Copper Sulfide Creep on Porous Electroplate." *Journal of the Electrochemical Society* 107 (1960), pp. 1009–1011.

Frantz, J.H., and D. Schorsch. "Egyptian Red Gold." *Archeomaterials* 4 (1990), pp. 133–152.

German, R.M. "The Role of Microstructure in the Tarnish of Low-gold Alloys." *Metallography* 14 (1981), pp. 253–266.

Gohard, F. "Addendum: Gilding the Flame." p. 146 in *The Statue of Liberty Restoration* (edited by R. Baboian, E.B. Cliver, and E.L. Bellant). Houston, TX: National Association of Corrosion Engineers, 1990.

Grimwade, M. *Introduction to Precious Metals.* London, UK: Newnes Technical Books, 1985.

Halahan, F. "Care of Gilded Objects." p. 25 in *Gilding and Surface Decoration* (edited by S. Budden). London, UK: United Kingdom Institute for Conservation of Historic and Artistic Works, 1991.

Johnson, B.F.G., and R. Davis. "Gold." pp. 129–186 in *The Chemistry of Copper, Silver and Gold*. New York, NY: Pergamon Press, 1973.

Kramer, M.W. "Architectural Gilding on Exterior Metal: An Overview of Materials and Methodology." pp. 351–361 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Lechtman, H.N. "Ancient Methods of Gilding Silver: Examples from the Old and New Worlds." pp. 2–30 in *Science and Archaeology* (edited by R.H. Brill). Cambridge, MA: MIT Press, 1971.

Lewis, L. "Properties and Applications of Electro-plated Coatings." pp. 39–40 in *Modern Metals in Museums* (edited by R.E. Child and J.M. Townsend). London, UK: Institute of Archaeology, 1988.

Lins, A. "Basic Properties of Gold Leaf." pp. 17–23 in *Gilded Wood: Conservation and History* (edited by D. Bigelow). Madison, CT: Sound View Press, 1991.

Lins, A. "Gilding Techniques of the Renaissance and After." pp. 241–265 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Lins, A., and S. Malenka. "The Use of Mercury Salts in Gold Electroplating." pp. 267–282 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Lins, P.A., and W.A. Oddy. "The Origins of Mercury Gilding." *Journal of Archaeological Science* 2 (1975), pp. 365–373.

Merk-Gould, L. "Preservation of a Gilded Monumental Sculpture: Research and Treatment of Daniel Chester French's *Quadriga*." pp. 337–349 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Murakami, R. "Archaeological Gilded Metals excavated in Japan." pp. 157–168 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Northover, P., and K. Anheuser. "Gilding in Britain: Celtic, Roman and Saxon." pp. 109–121 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Oddy, A. "Gilding: An Outline of the Technological History of the Plating of Gold on to Silver or Copper in the Old World." *Endeavour* 15 (1991), pp. 29–33.

Oddy, A. "Gilding of Metals in the Old World." pp. 171–181 in *Metal Plating and Patination: Cultural, Technical and Historical Developments* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Oddy, A. "A History of Gilding with Particular Reference to Statuary." pp. 1–19 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Oddy, A., M.R. Cowell, P.T. Craddock, and D.R. Hook. "The Gilding of Bronze Sculpture in the Classical World." pp. 103–124 in *Small Bronze Sculpture from the Ancient World*. Malibu, CA: J. Paul Getty Museum, 1990.

Oddy, A., S. La Niece, J.E. Curtis, and N.D. Meeks. "Diffusion-bonding as a Method of Gilding in Antiquity." *MASCA Journal* 1 (1981), pp. 239–241.

Oddy, A., P. Pearce, and L. Green. "An Unusual Gilding Technique on Some Egyptian Bronzes." pp. 35–39 in *Conservation of Ancient Egyptian Materials* (edited by S.C. Watkins and C.E. Brown). London, UK: United Kingdom Institute for Conservation of Historic and Artistic Works, 1988.

Randin, J.P., P. Ramoni, and J.P. Renaud. "Tarnishing of AuAgCu Alloys — Effect of the Composition." *Werkstoffe und Korrosion* 43 (1992), pp. 48–55.

Rapson, W.S., and T. Groenewald. *Gold Usage.* London, UK: Academic Press, 1978.

Scott, D.A. "The Deterioration of Gold Alloys and Some Aspects of their Conservation." *Studies in Conservation* 28 (1983), pp. 194–203.

Scott, D.A. "A Review of Gilding Techniques in Ancient South America." pp. 203–222 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Selwyn, L. "Corrosion Chemistry of Gilded Silver and Copper." pp. 21–47 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Sembrat, J. "Reliable Methods for the Measurement and Inspection of Protective Barrier Coatings for Outdoor Monuments." pp. 286–290 in *Metal 98* (edited by W. Mourey and L. Robbiola). London, UK: James & James Science Publishers, 1998.

Strahan, D.K., and C.A. Maines. "Lacquer as an Adhesive for Gilding on Copper Alloy Sculpture in Southeast Asia." pp. 185–201 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Tear, P. "The Treatment of Gilt-bronze in the Wallace Collection: The Cleaning and Conservation of the F68 Balustrade." pp. 19–26 in *Gilding: Approaches to Treatment.* London, UK: James & James Science Publishers, 2001.

Thornton, J. "All that Glitters is not Gold: Other Surfaces that Appear to be Gilded." pp. 307–317 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Vaccaro, A.M. "The Equestrian Statue of Marcus Aurelius." pp. 108–121 in *The Art of the Conservator* (edited by A. Oddy). Washington, DC: Smithsonian Institution Press, 1992.

van Langh, R. "The Delamination of Mercury-gilded Silver." *Met Objectives* 1 (2000), pp. 6 and 9.

Wise, E.M. (editor). *Gold: Recovery, Properties, and Applications*. Princeton, NJ: Van Nostrand, 1964.

CHAPTER 8. IRON

American Concrete Institute, Committee 222. *Corrosion of Metals in Concrete.* Farmington Hills, MI: American Concrete Institute, 1997.

Ashurst, J., and N. Ashurst. "The Repair and Maintenance of Cast Iron and Wrought Iron." pp. 13–41 in *Practical Building Conservation: English Heritage Technical Handbook. Vol. 4. Metals.* Aldershot, UK: Gower Technical Press, 1988.

Askey, A., S.B. Lyon, G.E. Thompson, J.B. Johnson, G.C. Wood, M. Cooke, and P. Sage. "The Corrosion of Iron and Zinc by Atmospheric Hydrogen Chloride." *Corrosion Science* 34 (1993), pp. 233–247.

ASM International. "Classification and Designation of Carbon and Low-alloy Steels." pp. 140–194 in *ASM Handbook. Vol. 1. Properties and Selection: Iron, Steels, and High-performance Alloys*. Materials Park, OH: ASM International, 1990a.

ASM International. "High-strength Structural and High-strength Low-alloy Steels." pp. 389–423 in *ASM Handbook. Vol. 1. Properties and Selection: Iron, Steels, and High-performance Alloys*. Materials Park, OH: ASM International, 1990b.

ASM International. *ASM Handbook. Vol. 3. Alloy Phase Diagrams.* Materials Park, OH: ASM International, 1992.

ASM International. "Phosphate Coatings." pp. 379–404 in *ASM Handbook. Vol. 5. Surface Engineering*. Materials Park, OH: ASM International, 1994.

ASTM. "E527-83 (Reapproved 1997). Standard Practice for Numbering Metals and Alloys (UNS)." pp. 764–768 in *Annual Book of ASTM Standards 2001. Vol. 01.01. Steel — Piping, Tubing, Fittings.* West Conshohocken, PA: American Society for Testing and Materials, 2001a.

ASTM. "A242/A 242M. Standard Specification for High-strength Low-alloy Structural Steel." pp. 152–153 in *Annual Book of ASTM Standards 2001. Vol. 01.04. Steel — Structural, Reinforcing, Pressure Vessel, Railway.* West Conshohocken, PA: American Society for Testing and Materials, 2001b.

ASTM. "A588/A 588M. Standard Specification for High-strength Low-alloy Structural Steel with 50 ksi [345MPa] Minimum Yield Point to 4 in. [100mm] Thick." pp. 292–293 in *Annual Book of ASTM Standards 2001. Vol. 01.04. Steel — Structural, Reinforcing, Pressure Vessel, Railway.* West Conshohocken, PA: American Society for Testing and Materials, 2001c.

Baboian, R. "Galvanic Corrosion on the Statue of Liberty." pp. 93–99 in *The Statue of Liberty Restoration* (edited by R. Baboian, E.B. Cliver, and E.L. Bellante). Houston, TX: National Association of Corrosion Engineers, 1990.

Barraclough, K.C. "The Chemistry of Metal Extraction." pp. 307–311 in *The Industrial Revolution in Metals* (edited by J. Day and R.F. Tylecote). London, UK: The Institute of Metals, 1991a.

Barraclough, K.C. "Steel in The Industrial Revolution." pp. 261–306 in *The Industrial Revolution in Metals* (edited by J. Day and R.F. Tylecote). London, UK: The Institute of Metals, 1991b.

Bayer, A.M., and L.R. Walton. "Wrought Tool Steels." pp. 757–779 in *ASM Handbook. Vol. 1. Properties and Selection: Iron, Steels, and High-performance Alloys.* Materials Park, OH: ASM International, 1990.

Bevan, A.W.R. "Meteorites." pp. 85–101 in *The Care and Conservation of Geological Material: Minerals, Rocks, Meteorites and Lunar Finds* (edited by F.M. Howie). Oxford, UK: Butterworth-Heinemann, 1992.

Binnie, N.E., L.S. Selwyn, C. Schlichting, and D.A. Rennie-Bisaillion. "Corrosion Protection of Outdoor Iron Artifacts using Commercial Rust Converters." *Journal of the International Institute for Conservation - Canadian Group* 20 (1995), pp. 26–40.

Broomfield, J.P. *Corrosion of Steel in Concrete: Understanding, Investigation and Repair.* London, UK: E&FN SPON, 1997.

Broomfield, J.P. "Corrosion of Steel in Concrete." pp. 581–600 in *Uhlig's Corrosion Handbook, 2nd ed.* (edited by R.W. Revie). New York, NY: John Wiley & Sons, 2000.

Buchwald, V.F. "The Mineralogy of Iron Meteorites." *Philosophical Transactions of the Royal Society of London* A286 (1977), pp. 453–491.

Buchwald, V.F., and R.S. Clarke. "Corrosion of Fe–Ni Alloys by Cl-containing Akaganéite (β-FeOOH): The Antarctic Meteorite Case." *American Mineralogist* 74 (1989), pp. 656–667.

Budavari, S. (editor). *The Merck Index, 12th ed.* Whitehouse Station, NJ: Merck & Co., 1996.

Budka, P.Z., J.R.M. Viertl, and S.V. Thamboo. "Meteorites and the Iron–Nickel Phase Diagram." *Advanced Materials & Processes* 7 (1996), pp. 27–30.

Burgess, H. "The Use of Chelating Agents in Conservation Treatments." *The Paper Conservator* 15 (1991), pp. 36–44.

Canadian Conservation Institute. *Tannic Acid Treatment.* CCI Notes, No. 9/5. Ottawa, ON: Canadian Conservation Institute, 1997.

Child, R. "Modern Electroplating and Electrofinishing Techniques." pp. 291–300 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Corbeil, M.-C., and E. Moffatt. *Analysis of a Corrosion Sample.* CCI Analytical Report ARS 3513. Ottawa, ON: Canadian Conservation Institute, 1996.

Corfield, M. "Copper Plating on Iron." pp. 276–283 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Cornell, R.M., and U. Schwertmann. *The Iron Oxides.* Weinheim, Germany: VCH Publishers, 1996.

Craig, B. "Ferrous Alloys (Ferritic and Martensetic)." pp. 1–30 in *Environmental Effects on Engineered Materials* (edited by R.H. Jones). New York, NY: Marcel Dekker, 2001.

Cser, L., J. Sirois, E. Moffatt, K. Helwig, and S. Stock. "The Examination and Analysis of the Interior and Exterior Decorative Elements of the Library of Parliament." pp. 17–24 in *The Conservation of Heritage Interiors*. Ottawa, ON: Canadian Conservation Institute, 2000.

Day, C. "A Technical Note on the Treatment of Tin Plate: The Five Percent Solution." *Journal of the Canadian Association for Conservation* 22 (1997), pp. 77–80.

Dulieu, D. "A History of Alloy Steels 1900–1950." *Historical Metallurgy* 19 (1985), pp. 104–115.

Duncan, S.J., and H. Ganiaris. "Some Sulphide Corrosion Products on Copper Alloys and Lead Alloys from London Waterfront Sites." pp. 109–118 in *Recent Advances in the Conservation and Analysis of Artifacts*. London, UK: Summer Schools Press, 1987.

Dunlap, R.F. "Browning, Blueing and Blacking of Metal." pp. 366–403 in *Gunsmithing, 2nd ed.* Harrisburg, PA: Stackpole Books, 1963.

Einbinder, M. "Armature Replacement on the Statue." pp. 129–130 in *The Statue of Liberty Restoration* (edited by R. Baboian, E.B. Cliver, and E.L. Bellante). Houston, TX: National Association of Corrosion Engineers, 1990.

Favre, M., and D. Landolt. "The Influence of Gallic Acid on the Reduction of Rust on Painted Steel Surfaces." *Corrosion Science* 34 (1993), pp. 1481–1494.

Favre, M., D. Landolt, K. Hoffman, and M. Stratmann. "Influence of Gallic Acid on the Phase Transformation in Iron Oxide Layers below Organic Coatings studied with Moessbauer Spectroscopy." *Corrosion Science* 40 (1998), pp. 793–803.

Fell, V., and M. Ward. "Iron Sulphides: Corrosion Products on Artifacts from Waterlogged Deposits." pp. 111–115 in *Metal 98* (edited by W. Mourey and L. Robbiola). London, UK: James & James Science Publishers, 1998.

Fellowes, D., and P. Hagan. "Pyrite Oxidation: The Conservation of Historic Shipwrecks and Geological and Palaeontological Specimens." *Reviews in Conservation* 4 (2003), pp. 26–38.

Fishlock, D. *Metal Colouring*. Teddington, UK: Robert Draper, 1962.

Fontana, M.G. *Corrosion Engineering, 3rd ed.* New York, NY: McGraw-Hill, 1986.

Gayle, M., and D.W. Look. "Iron and Iron Alloys." pp. 42–83 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite). Washington, DC: National Park Service, 1992.

Gent, M., and J. Rees. "A Conservation Treatment to Remove Residual Iron from Platinum Prints." *The Paper Conservator* 18 (1994), pp. 90–95.

Goodway, M. "Materials Choices for the Statue of Liberty." pp. 37–42 in *The Statue of Liberty Restoration* (edited by R. Baboian, E.B. Cliver, and E.L. Bellante). Houston, TX: National Association of Corrosion Engineers, 1990.

Goodway, M. "The Patination of Iron by Bower-Barffing." pp. 155–160 in *Metal Plating and Patination* (edited by S. La Niece and P. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Gordon, J.E. "Iron and Steel." pp. 231–253 in *The New Science of Strong Materials, 2nd ed.* London, UK: Penguin Books, 1976.

Gottlieb, A. "Chemistry and Conservation of Platinum and Palladium Photographs." *Journal of the American Institute for Conservation* 34 (1995), pp. 11–31.

Graedel, T.E., and R.P. Frankenthal. "Corrosion Mechanisms for Iron and Low Alloy Steels exposed to the Atmosphere." *Journal of the Electrochemical Society* 137 (1990), pp. 2385–2394.

Grattan, D. *The Stability of Photocopied and Laser-printed Documents and Images: General Guidelines*. CCI Technical Bulletin, No. 22. Ottawa, ON: Canadian Conservation Institute, 2000.

Habashi, F. "History of Alloys: Part I." *CIM Bulletin* 92 (1999), pp. 67–71.

Hendriks, K.B., B. Thurgood, J. Iraci, B. Lesser, and G. Hill. *Fundamentals of Photograph Conservation: A Study Guide*. Toronto, ON: Lugus, 1991.

Hawley, J.K., E.A. Kawai, and C. Sergeant. "The Removal of Rust Stains from Arctic Tin Can Labels using Sodium Hydrosulfite." *Journal of the International Institute for Conservation - Canadian Group* 6 (1981), pp. 17–24.

Helwig, K. "A Note on Burnt Yellow Earth Pigments: Documentary Sources and Scientific Analysis." *Studies in Conservation* 42 (1997), pp. 181–188.

Helwig, K. "Iron Oxide Pigments: Natural and Synthetic." in *Artists' Pigments: A Handbook of their History and Characteristics. Vol. 4* (edited by B.H. Berrie). Washington, DC: National Gallery of Art. Forthcoming.

Hodges, H. *Artifacts; An Introduction to Early Materials and Technology*. London, UK: John Baker, 1964.

Howie, F.M. "Pyrite and Marcasite." pp. 70–84 in *The Care and Conservation of Geological Material: Minerals, Rocks, Meteorites and Lunar Finds* (edited by F.M. Howie). Oxford, UK: Butterworth-Heinemann, 1992.

Jespersen, K. "Precipitation of Iron-corrosion Products on PEG-treated Wood." pp. 141–152 in *Conservation of Wet Wood and Metal* (edited by I.D. MacLeod). Perth, Australia: Western Australian Museum, 1989.

Jones, R.H., S.M. Bruemmer, M.J. Danielson, and B. Craig. "Austenitic Stainless Steels." pp. 31–53 in *Environmental Effects on Engineered Materials* (edited by R.H. Jones). New York, NY: Marcel Dekker, 2001.

Keown, S. "Tool Steels and High Speed Steels 1900–1950." *Historical Metallurgy* 19 (1985a), pp. 97–103.

Keown, S. "A History of Alloy Steels with Particular Reference to Sheffield Contributions." *Historical Metallurgy* 19 (1985b), pp. 126–133.

Knight, B. "A Review of the Corrosion of Iron from Terrestrial Sites and the Problem of Post-excavation Corrosion." *The Conservator* 14 (1990), pp. 37–43.

Lambert, J.B. "Metals." pp. 168–213 in *Traces of the Past; Unraveling the Secrets of Archaeology through Chemistry*. Reading, MA: Perseus Books, 1997.

Lee, L.R., and D. Thickett. *Selection of Materials for the Storage or Display of Museum Objects*. British Museum Occasional Paper, No. 111. London, UK: British Museum Publications Ltd., 1996.

Lepinski, J.A., and J.C. Myers. "Iron." pp. 829–855 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 14*. New York, NY: John Wiley & Sons, 1995.

Lewis, L. "Properties and Applications of Electro-plated Coatings." pp. 39–40 in *Modern Metals in Museums* (edited by R.E. Child and J.M. Townsend). London, UK: Institute of Archaeology, 1988.

Lobnig, R.E., R.P. Frankenthal, D.J. Siconolfi, and J.D. Sinclair. "The Effect of Submicron Ammonium Sulfate Particles on the Corrosion of Copper." pp. 336–356 in *Corrosion and Reliability of Electronic Materials and Devices*. Pennington, NJ: The Electrochemical Society, 1993.

Lowson, R.T. "Aqueous Oxidation of Pyrite by Molecular Oxygen." *Chemical Reviews* 82 (1982), pp. 461–497.

MacDonald, D.D., B. Roberts, and J.B. Hyne. "The Corrosion of Carbon Steel by Wet Elemental Sulphur." *Corrosion Science* 18 (1978), pp. 411–425.

MacLeod, I.D., and C. Kenna. "Degradation of Archaeological Timbers by Pyrite: Oxidation of Iron and Sulphur Species." pp. 133–142 in *Proceedings of the 4th ICOM-Group on Wet Organic Archaeological Materials* (edited by P. Hoffmann). Bremerhaven, Germany: International Council of Museums, 1991.

Maddin, R., J.D. Muhly, and T.S. Wheeler. "How the Iron Age Began." *Scientific American* 237 (1977), pp. 122–131.

Matero, F.G. "Conservation of Architectural Metalwork: Historical Approaches to the Surface Treatment of Iron." pp. 197–228 in *Ancient & Historic Metals, Conservation and Scientific Research* (edited by D.A. Scott, J. Podany, and B.B. Considine). Marina del Rey, CA: Getty Conservation Institute, 1994.

Matero, F.G., and A.A. Tagle. "Cleaning, Iron Stain Removal, and Surface Repair of Architectural Marble and Crystalline Limestone: The Metropolitan Club." *Journal of the American Institute for Conservation* 34 (1995), pp. 49–68.

Matthiesen, H., L.R. Hilbert, and D.J. Gregory. "Siderite as a Corrosion Product on Archaeological Iron from a Waterlogged Environment." *Studies in Conservation* 48 (2003), pp. 183–194.

McNeil, M.B., and B.J. Little. "The Use of Mineralogical Data in Interpretation of Long-term Microbiological Corrosion Processes: Sulfiding Reactions." *Journal of the American Institute for Conservation* 38 (1999), pp. 186–199.

McNeil, M.B., and D.W. Mohr. "Formation of Copper–Iron Sulfide Minerals during Corrosion of Artifacts and Possible Implications for Pseudogilding." *Geoarchaeology* 8 (1993), pp. 23–33.

McNeil, M., and L.S. Selwyn. "Electrochemical Processes in Metallic Corrosion." pp. 605–614 in *Handbook of Archaeological Sciences* (edited by D.R. Brothwell and A.M. Pollard). Chichester, UK: John Wiley & Sons, 2001.

Misawa, T. "The Thermodynamic Consideration for Fe–H_2O System at 25°C." *Corrosion Science* 13 (1973), pp. 659–676.

Murata, T. "Weathering Steel." pp. 569–580 in *Uhlig's Corrosion Handbook, 2nd ed.* (edited by R.W. Revie). New York, NY: John Wiley & Sons, 2000.

Narayanan, T.S.N.S. "Phosphate Conversion Coatings — A Metal Pretreatment Process." *Corrosion Reviews* 12 (1994), pp. 201–238.

Nassau, K. *The Physics and Chemistry of Color: The Fifteen Causes of Color*. New York, NY: John Wiley & Sons, 1983.

Paxton, H. "Steel." pp. 765–832 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 22*. New York, NY: John Wiley & Sons, 1997.

Post, J.E., and V.F. Buchwald. "Crystal Structure Refinement of Akaganéite." *American Mineralogist* 76 (1991), pp. 272–277.

Post, J.E., P.J. Heaney, R.B. Von Dreele, and J.C. Hanson. "Neutron and Temperature-resolved Synchrotron X-ray Powder Diffraction Study of Akaganéite." *American Mineralogist* 88 (2003), pp. 782–788.

Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd ed.* Houston, TX: National Association of Corrosion Engineers, 1974.

Prytulak, G. "Rust and the Working Surfaces of Industrial Artefacts." pp. 59–64 in *Industial Collections: Care and Conservation* (edited by D. Dollery and J. Henderson). London, UK: United Kingdom Institute for Conservation of Historic and Artistic Works, 1999.

Raymond, R. *Out of the Fiery Furnace; The Impact of Metals on the History of Mankind*. University Park, PA: Pennsylvania State University Press, 1984.

Refait, P., and J.-M.R. Génin. "The Oxidation of Ferrous Hydroxide in Chloride-containing Aqueous Media and Pourbaix Diagrams of Green Rust One." *Corrosion Science* 34 (1993), pp. 797–819.

Refait, P., and J.-M.R. Génin. "The Mechanisms of Oxidation of Ferrous Hydroxychloride β-$Fe_2(OH)_3Cl$ in Aqueous Solution: The Formation of Akaganeite vs Goethite." *Corrosion Science* 39 (1997), pp. 539–553.

Ruggeri, R.T., and T.R. Beck. "An Analysis of Mass Transfer in Filiform Corrosion." *Corrosion* 39 (1983), pp. 452–465.

Ryan, M.P., D.E. Williams, R.J. Chater, B.M. Hutton, and D.S. McPhail. "Why Stainless Steel Corrodes." *Nature* 415 (2002), pp. 770–774.

Samson, R. *The Forges du Saint-Maurice; Beginnings of the Iron and Steel Industry in Canada, 1730–1883*. Saint-Foy, QC: Presses de l'Université Laval, 1998.

Sandström, M., F. Jalilehvand, I. Persson, U. Gelius, P. Frank, and I. Hall-Roth. "Deterioration of the Seventeenth-century Warship *Vasa* by Internal Formation of Sulphuric Acid." *Nature* 415 (2002), pp. 893–897.

Schubert, H.R. "Extraction and Production of Metals: Iron and Steel." pp. 99–117 in *A History of Technology. Vol. IV. The Industrial Revolution, c1750 to c1850* (edited by C. Singer, E.J. Holmyard, A.R. Hall, and T.I. Williams). Oxford, UK: Clarendon Press, 1958.

Schwertmann, U., and R.M. Cornell. *Iron Oxides in the Laboratory*. Weinheim, Germany: VCH Publishers, 1991.

Score, R., and I.J. Cohen. "Stainless Steel." pp. 64–71 in *Twentieth-century Building Materials* (edited by T.C. Jester). Toronto, ON: McGraw-Hill, 1995.

Scott, J. "Conservation of Weathering Steel Sculpture." pp. 307–322 in *Saving the Twentieth Century: The Conservation of Modern Materials* (edited by D.W. Grattan). Ottawa, ON: Canadian Conservation Institute, 1993.

Scott, J.C., and C.L. Searls. "Weathering Steel." pp. 73–77 in *Twentieth-century Building Materials* (edited by T.C. Jester). Toronto, ON: McGraw-Hill, 1995.

Selwyn, L.S. "Corrosion of Archaeological Iron Before and After Excavation." pp. 1–8 in *Corrosion and its Control in the New Millennium*. Houston, TX: NACE International, 1999.

Selwyn, L.S., P.J. Sirois, and V. Argyropoulos. "The Corrosion of Excavated Archaeological Iron with Details on Weeping and Akaganéite." *Studies in Conservation* 44 (1999), pp. 217–232.

Selwyn, L.S., W.R. McKinnon, and V. Argyropoulos. "Models for Chloride Ion Diffusion in Archaeological Iron." *Studies in Conservation* 46 (2001), pp. 109–120.

Severson, D.G. "Alfred Stieglitz's Palladium Photographs and their Treatment by Edward Steichen." *Journal of the American Institute for Conservation* 34 (1995), pp. 1–10.

Society of Automotive Engineers (SAE) and American Society for Testing and Materials (ASTM). *Metals & Alloys in the Unified Numbering System, 5th ed.* Warrendale, PA: Society of Automotive Engineers, 1989.

Ståhl, K., K. Nielsen, J. Jiang, B. Lebech, J.C. Hanson, P. Norby, and J. Van Lanschot. "On the Akaganéite Crystal Structure, Phase Transformations and Possible Role in Post-excavational Corrosion of Iron Artifacts." *Corrosion Science* 45 (2003), pp. 2563–2575.

Stefanescu, D.M. "Classification and Basic Metallurgy of Cast Iron." pp. 3–11 in *ASM Handbook. Vol. 1. Properties and Selection: Irons, Steels, and High-performance Alloys.* Materials Park, OH: ASM International, 1990.

Stolzenberg, A.M. "Iron Compounds." pp. 873–902 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 14.* New York, NY: John Wiley & Sons, 1995.

Stratmann, M. "The Atmospheric Corrosion of Iron — A Discussion of the Physico-chemical Fundamentals of this Omnipresent Corrosion Process; Invited Review." *Berichte der Bunsengesellschaft für Physikalische Chemie* 94 (1990), pp. 626–639.

Stratmann, M., and J. Müller. "The Mechanism of the Oxygen Reduction on Rust-covered Metal Substrates." *Corrosion Science* 36 (1994), pp. 327–359.

Street, A., and W. Alexander. *Metals in the Service of Man, 10th ed.* London, UK: Penguin Books, 1995.

Tennent, N.H., B.G. Cooksey, D. Littlejohn, B.J. Ottaway, S.E. Tarling, and M. Vickers. "Unusual Corrosion and Efflorescence Products on Bronze and Iron Antiquities stored in Wooden Cabinets." pp. 60–66 in *Conservation Sceince in the U.K.* (edited by N.H. Tennent). London, UK: James & James Science Publishers, 1993.

Tullmin, M., and P.R. Roberge. "Atmospheric Corrosion." pp. 305–321 in *Uhlig's Corrosion Handbook, 2nd ed.* (edited by R.W. Revie). New York, NY: John Wiley & Sons, 2000.

Truman, J. "The Initiation and Growth of High Alloy (Stainless) Steel Production." *Historical Metallurgy* 19 (1985), pp. 116–125.

Turgoose, S. "Post-excavation Changes in Iron Antiquities." *Studies in Conservation* 27 (1982a), pp. 97–101.

Turgoose, S. "The Nature of Surviving Iron Objects." pp. 1–7 in *Conservation of Iron* (edited by R.W. Clarke and S.M. Blackshaw). Maritime Monographs and Reports, No. 53. Greenwich, UK: National Maritime Museum, 1982b.

Turgoose, S. "The Corrosion of Archaeological Iron during Burial and Treatment." *Studies in Conservation* 30 (1985), pp. 13–18.

Turgoose, S. "Structure, Composition and Deterioration of Unearthed Iron Objects." pp. 35–52 in *Current Problems in the Conservation of Metal Antiquities* (edited by S. Aoki). Tokyo, Japan: Tokyo National Research Institute of Cultural Properties, 1993.

Tylecote, R.F. "Iron in The Industrial Revolution." pp. 200–260 in *The Industrial Revolution in Metals* (edited by J. Day and R.F. Tylecote). London, UK: The Institute of Metals, 1991.

Vander Voort, G.F. "A Note on Metallographic Techniques for Iron Meteorites." *Materials Characterization* 29 (1992), pp. 223–241.

Verhoeven, J.D., and A.H. Pendray. "Experiments to Reproduce the Pattern of Damascus Steel Blades." *Materials Characterization* 29 (1992), pp. 195–212.

Waite, J.G. "Iron and Iron Alloys; Preservation and Repair." pp. 130–148 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite). Washington, DC: National Park Service, 1992.

Walker, R. "Instability of Iron Sulfides on Recently Excavated Artifacts." *Studies in Conservation* 46 (2001), pp. 141–152.

Ware, M. *Cyanotype: The History, Science and Art of Photographic Printing in Prussian Blue.* London, UK: Science Museum, 1998.

Washko, S.D., and G. Aggen. "Wrought Stainless Steels." pp. 841–907 in *ASM Handbook. Vol. 1. Properties and Selection: Iron, Steels, and High-performance Alloys.* Materials Park, OH: ASM International, 1990.

Wayman, M.L. "On the Early Use of Iron in the Arctic, Part I: Meteoritic Iron." *CIM Bulletin* 80 (1987a), pp. 147–150.

Wayman, M.L. "On the Early Use of Iron in the Arctic, Part II: Telluric Iron." *CIM Bulletin* 80 (1987b), pp. 64–66.

Weaver, M.E. "Architectural Metalwork." pp. 175–215 in *Conserving Buildings; Guide to Techniques and Materials.* New York, NY: John Wiley & Sons, 1993.

Wernick, J. "Magnetic Materials: Thin Films and Particles." pp. 769–788 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 15.* New York, NY: John Wiley & Sons, 1995.

Williams, R.S. *Display and Storage of Museum Objects Containing Cellulose Nitrate.* CCI Notes, No. 15/3. Ottawa, ON: Canadian Conservation Institute, 1994.

Young, R.D., and R.A. Fennell. *Methods for Modern Sculptors.* Escondido, CA: Sculpt Nouveau, 1980.

Zahner, L.W. "Iron, Steel, and the Stainless Steels." pp. 183–261 in *Architectural Metals: A Guide to Selection, Specification, and Performance.* New York, NY: John Wiley & Sons, 1995a.

Zahner, L.W. "Metallic Coatings on Metals." pp. 299–334 in *Architectural Metals: A Guide to Selection, Specification, and Performance.* New York, NY: John Wiley & Sons, 1995b.

CHAPTER 9. LEAD

Abel, E.W. "Lead." pp. 105–146 in *The Chemistry of Germanium, Tin and Lead.* Oxford, UK: Pergamon Press, 1973.

Allen, G.C., L. Black, P.D. Forshaw, and N.J. Seeley. "Raindrops Keep Falling on My Lead." *Journal of Architectural Conservation* 9 (2003), pp. 23–44.

Ashurst, J., and N. Ashurst. "The Repair and Maintenance of Lead Sheet Roofing." pp. 93–110 in *Practical Building Conservation: English Heritage Technical Handbook. Vol. 4. Metals.* Aldershot, UK: Gower Technical Press, 1988a.

Ashurst, J., and N. Ashurst. "Lead Sculpture and its Conservation." pp. 111–118 in *Practical Building Conservation: English Heritage Technical Handbook. Vol. 4. Metals.* Aldershot, UK: Gower Technical Press, 1988b.

ASM International. *ASM Handbook. Vol. 3. Alloy Phase Diagrams.* Materials Park, OH: ASM International, 1992.

ASTM. "B744-00. Standard Specification for Low Melting Point Alloys." pp. 857–860 in *Annual Book of ASTM Standards 2001. Vol. 02.04. Nonferrous Metals.* West Conshohocken, PA: American Society for Testing and Materials, 2001.

Avery, R. "Techniques used in the Fabrication and Joining of Metals." pp. 23–26 in *Modern Metals in Museums* (edited by R.E. Child and J.M. Townsend). London, UK: Institute of Archaeology, 1988.

Black, L., and G.C. Allen. "Nature of Lead Patination." *British Corrosion Journal* 34 (1999), pp. 192–197.

Boon, J.J., J. van der Weerd, K. Keune, P. Noble, and J. Wadum. "Mechanical and Chemical Changes in Old Master Paintings: Dissolution, Metal Soap Formation and Remineralization Processes in Lead Pigmented Ground/Intermediate Paint Layers of 17th Century Paintings." pp. 401–406 in *ICOM Committee for Conservation, 13th Triennial Meeting, Rio de Janeiro, Brazil* (edited by R. Vontobel). London, UK: James & James Science Publishers, 2002.

Bradley, S., and D. Thickett. "The Pollution Problem in Perspective." pp. 8–13 in *ICOM Committee for Conservation, 12th Triennial Meeting, Lyon, France* (edited by J. Bridgland). London, UK: James & James Science Publishers, 1999.

Carr, D.S., W.C. Spangenberg, and K. Chronley. "Lead Compounds (Salts)." pp. 132–152 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 15.* New York, NY: John Wiley & Sons, 1995.

Cser, L., J. Sirois, E. Moffatt, K. Helwig, and S. Stock. "The Examination and Analysis of the Interior and Exterior Decorative Elements of the Library of Parliament." pp. 17–24 in *The Conservation of Heritage Interiors*. Ottawa, ON: Canadian Conservation Institute, 2000.

Davis, M., F. Hunter, and A. Livingstone. "The Corrosion, Conservation and Analysis of a Lead and Cannel Coal Necklace from the Early Bronze Age." *Studies in Conservation* 40 (1995), pp. 257–264.

Dunn, E.J. "Lead Pigments." pp. 333–427 in *Treatise On Coatings. Vol. 3. Pigments. Part 1* (edited by R.R. Myers and J.S. Long). New York, NY: Marcel Dekker, 1975.

Fischbein, A., K.E. Anderson, S. Sassa, R. Lilis, S. Kon, L. Sarkozi, and A. Kappas. "Lead Poisoning from "Do-it-yourself" Heat Guns for Removing Lead-based Paint: Report of Two Cases." *Environmental Research* 24 (1981), pp. 425–431.

Fischbein, A., J. Wallace, S. Sassa, A. Kappas, G. Butts, A. Rohl, and B. Kaul. "Lead Poisoning from Art Restoration and Pottery Work: Unusual Exposure Source and Household Risk." *Journal of Environmental Pathology, Toxicology and Oncology* 11 (1992), pp. 7–11.

Fitzhugh, E.W. "Red Lead and Minium." pp. 109–139 in *Artists' Pigments: A Handbook of their History and Characteristics. Vol. 1* (edited by R.L. Feller). Washington, DC: National Gallery of Art, 1986.

Gaver, C.C. "Tin and Tin Alloys." pp. 105–122 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 24*. New York, NY: John Wiley & Sons, 1997.

Gayle, M., and D.W. Look. "Lead." pp. 8–11 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite). Washington, DC: National Park Service, 1992.

Gettens, R.J., H. Kühn, and W.T. Chase. "Lead White." *Studies in Conservation* 12 (1967), pp. 125–139.

Gettens, R.J., and G.L. Stout. *Painting Materials: A Short Encyclopedia*. New York, NY: Dover Publications, 1966.

Glass, A. "The Albert Memorial: Saved but Not Restored." pp. 197–203 in *Monuments and the Millennium* (edited by J.-M. Teutonico and J. Fidler). London, UK: James & James Science Publishers, 2001.

Goodwin, F.E. "Lead and Lead Alloys." pp. 767–792 in *Uhlig's Corrosion Handbook, 2nd ed.* (edited by R.W. Revie). New York, NY: John Wiley & Sons, 2000.

Gottlieb, B., C. Gottlieb, A. Sjögren, and T. Jakobsen. "A New Method for Cleaning and Conservation of Lead Objects using Hydrogen and Oxygen Plasma." pp. 767–771 in *ICOM Committee for Conservation, 10th Triennial Meeting, Washington, DC* (edited by J. Bridgland). Paris, France: International Council of Museums Committee for Conservation, 1993.

Graedel, T.E. "Chemical Mechanisms for the Atmospheric Corrosion of Lead." *Journal of the Electrochemical Society* 141 (1994), pp. 922–927.

Graham, J.A.G., D.G. Maxton, and C.H.C. Twort. "Painter's Palsy: A Difficult Case of Lead Poisoning." *The Lancet* 8256 (1981), pp. 1159–1160.

Green, L. "A Re-evaluation of Lead Conservation Techniques at the British Museum." pp. 121–130 in *Conservation of Metals: Problems in the Treatment of Metal-organic and Metal-inorganic Composite Objects* (edited by M. Járó). Budapest, Hungary: Központi Muzemi Igazgatóság, 1989.

Greninger, D., V. Kollonitsch, and C.H. Kline. *Lead Chemicals*. New York, NY: International Lead Zinc Research Organization, 197-.

Grzywacz, C.M., and N.H. Tennent. "Pollution Monitoring in Storage and Display Cabinets: Carbonyl Pollutant Levels in relation to Artifact Deterioration." pp. 164–170 in *Preventive Conservation: Practice, Theory and Research* (edited by A. Roy and P. Smith). London, UK: International Institute for Conservation of Historic and Artistic Works, 1994.

Heath, D., and G. Martin. "The Corrosion of Lead and Lead/Tin Alloys occurring on Japanese Lacquer Objects." pp. 137–141 in *The Conservation of Far Eastern Arts* (edited by J.S. Mills, P. Smith, and K. Yamasaki). London, UK: International Institute for Conservation of Historic and Artistic Works, 1988.

Hofmann, W., and J. Maatsch. "Lead as a Corrosion-resistant Material." pp. 268–320 in *Lead and Lead Alloys*. Berlin, Germany: Springer-Verlag, 1970.

Keisch, B. "X-ray Diffraction and the Composition of Lead White." pp. 121–133 in *Studies in the History of Art*. Washington, DC: National Gallery of Art, 1971.

Kühn, H. "Lead–Tin Yellow." *Studies in Conservation* 13 (1968), pp. 7–33.

Lambert, J.B. "Metals." pp. 168–213 in *Traces of the Past; Unraveling the Secrets of Archaeology through Chemistry*. Reading, MA: Perseus Books, 1997.

Landau, M. "Driers and Metallic Soaps." pp. 432–445 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 8*. New York, NY: John Wiley & Sons, 1993.

Leveque, M.A. "The Problem of Formaldehyde — A Case Study." pp. 56–65 in *Preprints to the 14th Annual Meeting of the AIC*. Washington, DC: American Institute for Conservation, 1986.

MacLeod, I.D. "Identification of Corrosion Products on Non-ferrous Metal Artifacts recovered from Shipwrecks." *Studies in Conservation* 36 (1991), pp. 222–234.

MacLeod, I.D., and R. Wozniak. "Corrosion and Conservation of Lead in Sea Water." pp. 884–890 in *ICOM Committee for Conservation, 11th Triennial Meeting, Edinburgh, Scotland* (edited by J. Bridgland). London, UK: James & James Science Publishers, 1996.

Maryon, H. *Metalwork & Enamelling, 5th revised ed.* New York, NY: Dover Publications, 1971.

Naylor, J. "The Conservation and Restoration of Lead Based Statuary." *SSCR Bulletin* 1 (1983), pp. 9–11.

North, N.A. "Conservation of Metals." pp. 207–252 in *Conservation of Marine Archaeological Objects* (edited by C. Pearson). London, UK: Butterworths, 1987.

Nriagu, J.O. *Lead and Lead Poisoning in Antiquity*. New York, NY: John Wiley & Sons, 1983.

Oddy, A., and S.M. Bradley. "The Corrosion of Metal Objects in Storage and on Display." pp. 225–243 in *Current Problems in the Conservation of Metal Antiquities* (edited by S. Aoki). Tokyo, Japan: Tokyo National Research Institute of Cultural Properties, 1993.

Olby, J.K. "The Basic Lead Carbonates." *Journal of Inorganic and Nuclear Chemistry* 28 (1966), pp. 2507–2512.

Pant, B.C., J.R. Harrison, G.W. Long, and S. Gupta. "Exposure to Lead in Stained Glass Work. An Environmental Evaluation." *The Science of the Total Environment* 141 (1994), pp. 11–15.

Park, S.C., and D.C. Hicks. *Appropriate Methods for Reducing Lead-paint Hazards in Historic Housing*. Preservation Briefs, No. 37. Washington, DC: National Park Service, 1995. See also the Web site of the National Park Service (www2.cr.nps.gov/tps/briefs/brief37.htm).

Prengaman, R.D. "Lead Alloys." pp. 113–132 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 15*. New York, NY: John Wiley & Sons, 1995.

Rabinkin, A. "Solders and Brazing Filler Metals." pp. 482–497 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 22*. New York, NY: John Wiley & Sons, 1997.

Robinet, L., and M.-C. Corbeil. "The Characterization of Metal Soaps." *Studies in Conservation* 48 (2003), pp. 23–40.

Rossol, M. *The Artist's Complete Health and Safety Guide, 3rd ed.* New York, NY: Allworth Press, 2002.

Ruth, J.H. "Odor Thresholds and Irritation Levels of Several Chemical Substances: A Review." *American Industrial Hygiene Association Journal* 47 (1986), pp. A-142 – A-151.

Shoesmith, D.W., M.G. Bailey, and P. Taylor. "Anodic Oxidation of Lead in Aqueous Carbonate Solutions. II. Film Formation and Dissolution in the pH range 9 to 14." *Canadian Journal of Chemistry* 66 (1988), pp. 2941–2946.

Smith, J.F. "Lead." pp. 784–792 in *Metals Handbook, 9th ed. Vol. 13. Corrosion* (edited by J.R. Davis). Materials Park, OH: ASM International, 1987.

Street, A., and W. Alexander. *Metals in the Service of Man, 10th ed.* London, UK: Penguin Books, 1995.

Tennent, N., J. Tate, and L. Cannon. "The Corrosion of Lead Artifacts in Wooden Storage Cabinets." *SSCR Journal* 4 (1993), pp. 8–11.

Tétreault, J. *Coatings for Display and Storage in Museums*. Technical Bulletin, No. 21. Ottawa, ON: Canadian Conservation Institute, 1999.

Tétreault, J. *Airborne Pollutants in Museums, Galleries, and Archives: Risk Assessment, Control Strategies, and Preservation Management*. Ottawa, ON: Canadian Conservation Institute, 2003.

Tétreault, J., J. Sirois, and E. Stamatopoulou. "Studies of Lead Corrosion in Acetic Acid Environments." *Studies in Conservation* 43 (1998), pp. 17–32.

Thickett, D., S. Bradley, and L. Lee. "Assessment of the Risks to Metal Artifacts posed by Volatile Carbonyl Pollutants." pp. 260–264 in *Metal 98* (edited by W. Mourey and L. Robbiola). London, UK: James & James Science Publishers, 1998.

Tranter, G.C. "Patination of Lead: An Infra-red Spectroscopic Study." *British Corrosion Journal* 11 (1976), pp. 222–224.

Turgoose, S. "The Corrosion of Lead and Tin: Before and After Excavation." pp. 15–26 in *Lead and Tin: Studies in Conservation and Technology*. Occasional Papers, No. 3. London, UK: United Kingdom Institute for Conservation of Historic and Artistic Works, 1985.

Tylecote, R.F. "The Behaviour of Lead as a Corrosion Resistant Medium Undersea and in Soils." *Journal of Archaeological Science* 10 (1983), pp. 397–409.

Vogel, N.A., and R. Achilles. *The Preservation and Repair of Historic Stained and Leaded Glass*. Preservation Briefs, No. 33. Washington, DC: National Park Service, 1993. See also the Web site of the National Park Service (www2.cr.nps.gov/tps/briefs/brief33.htm).

Wainwright, I.N.M., J.M. Taylor, and R.D. Harley. "Lead Antimonate Yellow." pp. 219–254 in *Artists' Pigments: A Handbook of their History and Characteristics. Vol. 1* (edited by R.L. Feller). Washington, DC: National Gallery of Art, 1986.

Waite, J.G. "Lead Preservation and Repair." pp. 101–103 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite). Washington, DC: National Park Service, 1992.

Wesson, H.C., and E. Littauer. "Lead and Lead Alloys." pp. 4:68–4:85 in *Corrosion. Vol. 1, 2nd ed.* (edited by L.L. Shreir). Boston, MA: Newnes-Butterworths, 1976.

Wicks, Z.W. "Drying Oils." pp. 519–532 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 8*. New York, NY: John Wiley & Sons, 1993.

Willies, L. "Lead: Ore Preparation and Smelting." pp. 84–130 in *The Industrial Revolution in Metals* (edited by J. Day and R.F. Tylecote). London, UK: The Institute of Metals, 1991.

Wilson, D. "Gilding Conservation in an Architectural Context." pp. 27–32 in *Gilding: Approaches to Treatment*. London, UK: James & James Science Publishers, 2001.

Zahner, L.W. "Lead and Zinc." pp. 262–284 in *Architectural Metals: A Guide to Selection, Specification, and Performance*. New York, NY: John Wiley & Sons, 1995a.

Zahner, L.W. "Metallic Coatings on Metals." pp. 299–334 in *Architectural Metals: A Guide to Selection, Specification, and Performance*. New York, NY: John Wiley & Sons, 1995b.

Zhang, X. "An Unusual Corrosion Product, Pyromorphite, from a Bronze *AN*: A Technical Note." *Studies in Conservation* 47 (2002), pp. 76–79.

CHAPTER 10. NICKEL

Agarwal, D.C. "Nickel and Nickel Alloys." pp. 831–851 in *Uhlig's Corrosion Handbook, 2nd ed.* (edited by R.W. Revie). New York, NY: John Wiley & Sons, 2000.

Antonsen, D.H. "Nickel Compounds." pp. 18–42 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 17*. New York, NY: John Wiley & Sons, 1996.

ASM International. *ASM Handbook. Vol. 3. Alloy Phase Diagrams*. Materials Park, OH: ASM International, 1992.

Bradbury, J. "Nickel 1900–1950." *Historical Metallurgy* 19 (1985), pp. 65–71.

Child, R. "The Identification of Post-Industrial Revolution Metals." pp. 7–14 in *Modern Metals in Museums* (edited by R.E. Child and J.M. Townsend). London, UK: Institute of Archaeology, 1988.

Child, R. "Modern Electroplating and Electrofinishing Techniques." pp. 291–300 in *Metal Plating and Patination* (edited by S. La Niece and P.T. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Evans, T.E. "Nickel and Nickel Alloys." pp. 4:116–4:156 in *Corrosion. Vol. 1. Metal/Environment Reactions, 3rd ed.* (edited by L.L. Shreir, R.A. Jarman, and G.T. Burstein). Oxford, UK: Butterworth-Heinemann, 1994.

Gayle, M., and D.W. Look. "Nickel and Nickel Alloys." pp. 35–41 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite). Washington, DC: National Park Service, 1992.

Graedel, T.E., and C. Leygraf. "Corrosion Mechanisms for Nickel exposed to the Atmosphere." *Journal of the Electrochemical Society* 147 (2000), pp. 1010–1014.

Krulik, G.A. "Electroless Plating." pp. 198–218 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 9.* New York, NY: John Wiley & Sons, 1994.

MacLeod, I.D. "Identification of Corrosion Products on Non-ferrous Metal Artifacts recovered from Shipwrecks." *Studies in Conservation* 36 (1991), pp. 222–234.

Persson, D., and C. Leygraf. "Analysis of Atmospheric Corrosion Products of Field Exposed Nickel." *Journal of the Electrochemical Society* 139 (1992), pp. 2243–2249.

Persson, D., and C. Leygraf. "Metal Carboxylate Formation during Indoor Atmospheric Corrosion of Cu, Zn, and Ni." *Journal of the Electrochemical Society* 142 (1995), pp. 1468–1477.

Rossol, M. *The Artist's Complete Health and Safety Guide, 3rd ed.* New York, NY: Allworth Press, 2001.

Trelstad, D.H. "Monel." pp. 52–57 in *Twentieth-century Building Materials* (edited by T.C. Jester). Toronto, ON: McGraw-Hill, 1995.

Tundermann, J.H., J.K. Tien, and T.E. Howson. "Nickel and Nickel Alloys." pp. 1–17 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 17.* New York, NY: John Wiley & Sons, 1996.

Waite, J.G. "Nickel and Nickel Alloys; Preservation and Repair." pp. 128–129 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite). Washington, DC: National Park Service, 1992.

Zahner, L.W. "Monel and Titanium." pp. 285–298 in *Architectural Metals: A Guide to Selection, Specification, and Performance*. New York, NY: John Wiley & Sons, 1995.

CHAPTER 11. SILVER

Ankersmit, H.A. (Conservation Scientist, Netherlands Institute for Cultural Heritage, Amsterdam, Netherlands). Personal communication, March 2002.

Ankersmit, H.A., G. Noble, L. Ridge, D. Stirling, N.H. Tennent, and S. Watts. "The Protection of Silver Collections from Tarnishing." pp. 7–13 in *Tradition and Innovation: Advances in Conservation* (edited by A. Roy and P. Smith). London, UK: International Institute for Conservation, 2000.

ASM International. *ASM Handbook. Vol. 3. Alloy Phase Diagrams.* Materials Park, OH: ASM International, 1992.

Bailey, R.A., and J.A. Zaccardi. "Corrosion of Copper and Other Metals by Perspiration." *Journal of Electroanalytical Chemistry* 144 (1983), pp. 443–448.

Barger, M.S., A.P. Giri, W.B. White, and T.M. Edmondson. "Cleaning Daguerreotypes." *Studies in Conservation* 31 (1986), pp. 15–28.

Barger, M.S., and W.B. White. *The Daguerreotype: Nineteenth-century Technology and Modern Science.* Washington, DC: Smithsonian Institution Press, 1991.

Birnie, L. "Special Finishes on Non-ferrous Metals at the National Maritime Museum." pp. 148–154 in *Metal Plating and Patination* (edited by S. La Niece and P.T. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Blair, C. (editor). *The History of Silver.* London, UK: Little, Brown and Company, 2000.

Bly, J. *Discovering Hallmarks on English Silver.* Buckinghamshire, UK: Shire Publications, 2000.

Brimblecombe, P., D. Shooter, and A. Kaur. "Wool and Reduced Sulphur Gases in Museum Air." *Studies in Conservation* 37 (1992), pp. 53–60.

Butts, A., and C.D. Coxe (editors). *Silver: Economics, Metallurgy, and Use*. New York, NY: Robert E. Krieger Publishing, 1975.

Canadian Conservation Institute. *Basic Care of Coins, Medals and Medallic Art*. CCI Notes, No. 9/4. Ottawa, ON: Canadian Conservation Institute, 1997.

Cappel, C.R. "Silver Compounds." pp. 179–195 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 22*. New York, NY: John Wiley & Sons, 1997.

Child, R. "Modern Electroplating and Electrofinishing Techniques." pp. 291–300 in *Metal Plating and Patination* (edited by S. La Niece and P.T. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Cope, L.H. "Surface-silvered Ancient Coins." pp. 261–278 in *Methods of Chemical and Metallurgical Investigation of Ancient Coinage* (edited by E.T. Hall and D.M. Metcalf). London, UK: Royal Numismatic Society, 1972.

Costa, V. "The Deterioration of Silver Alloys and Some Aspects of their Conservation." *Reviews in Conservation* 2 (2001), pp. 18–34.

Cronyn, J.M., and W.S. Robinson. *The Elements of Archaeological Conservation*. London, UK: Routledge, 1990.

De Witte, E. "The Protection of Silverware with Varnishes." *Bulletin de l'Institut Royal du Patrimoine Artistique* 14 (1973/74), pp. 140–151.

Drott, J. "Growth of Silver Sulphide Whiskers." *Acta Metallurgica* 8 (1960), pp. 19–22.

Eggert, G., and U. Sobottka-Braun. "Black Spots on Bronzes and Elemental Sulphur." pp. 823–827 in *ICOM Committee for Conservation, 12th Triennial Meeting, Lyon, France* (edited by J. Bridgland). London, UK: James & James Science Publishers, 1999.

Etris, S.F. "Silver and Silver Alloys." pp. 163–179 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 22*. New York, NY: John Wiley & Sons, 1997.

Evans, U.R. "Film Growth." pp. 1–12 in *An Introduction to Metallic Corrosion, 3rd ed.* London, UK: Edward Arnold Publishers, 1981.

Forbes, J.S. *Hallmark: A History of the London Assay Office*. London, UK: Unicorn Press, 1998.

Fox, R. *Presentation Pieces and Trophies from the Henry Birks Collection of Canadian Silver*. Ottawa, ON: National Gallery of Canada, 1985.

Fredrickson, N.J., and S. Gibb. *The Covenant Chain: Indian Ceremonial and Trade Silver*. Ottawa, ON: National Museums of Canada, 1980.

Glanville, P., and J.F. Goldsborough. *Women Silversmiths 1685–1845: Works from the Collection of the National Museum of Women in the Arts, Washington, DC*. Washington, DC: National Museum of Women in the Arts, 1990.

Graedel, T.E. "Corrosion Mechanisms for Silver exposed to the Atmosphere." *Journal of the Electrochemical Society* 139 (1992), pp. 1963–1970.

Hamilton, M.W. *Silver in the Fur Trade: 1680–1820* (edited by J.D. Hamilton and R.P. Lydick). Chelmsford, MA: Martha Hamilton Publishing, 1995.

Hatchett, D.W., and H.S. White. "Electrochemistry of Sulfur Adlayers on the Low-index Faces of Silver." *Journal of Physical Chemistry* 100 (1996), pp. 9854–9859.

Heller, D.B. "The Coating of Metal Objects at Winterthur." pp. 57–64 in *Preprints of Papers presented at the 11th Annual Meeting of the American Institute for Conservation of Historic and Artistic Works, Baltimore, Maryland, 25–29 May 1983*. Washington, DC: American Institute for Conservation, 1983.

Hendriks, K.B., B. Thurgood, J. Iraci, B. Lesser, and G. Hill. *Fundamentals of Photograph Conservation: A Study Guide*. Toronto, ON: Lugus, 1991.

Hughes, R., and M. Rowe. *The Colouring, Bronzing and Patination of Metals*. London, UK: Crafts Council, 1982.

Jacobson, L., and W.E. Leyshon. "The Daguerrian Measles Mystery." *Graphic Antiquarian* July (1972), pp. 14–15.

Johns, P. "Firestain Resistant Silver Alloys." pp. 33–67 in *The Santa Fe Symposium on Jewelry Manufacturing Technology 1997* (edited by D. Schneller). Boulder, CO: Met-Chem Research, 1997.

Kaellgren, P. "A Guide to Researching Silver Hallmarks." *Rotunda* 32 (2000), p. 46.

Krulik, G.A. "Electroless Plating." pp. 198–218 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 9*. New York, NY: John Wiley & Sons, 1994.

La Niece, S. "Niello: An Historical and Technical Survey." *The Antiquaries Journal* 63 (1983), pp. 279–297.

La Niece, S. "Silver Plating on Copper, Bronze and Brass." *The Antiquaries Journal* 70 (1990), pp. 102–114.

La Niece, S. "Silvering." pp. 201–210 in *Metal Plating and Patination* (edited by S. La Niece and P.T. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Lewis, L. "Properties and Applications of Electro-plated Coatings." pp. 39–40 in *Modern Metals in Museums* (edited by R.E. Child and J.M. Townsend). London, UK: Institute of Archaeology, 1988.

Lins, A., and S. Malenka. "The Use of Mercury Salts in Gold Electroplating." pp. 267–282 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Lins, A., and N. McMahon. "The Inhibition of Silver Tarnishing." pp. 135–162 in *Current Problems in the Conservation of Metal Antiquities* (edited by S. Aoki). Tokyo, Japan: Tokyo National Research Institute of Cultural Properties, 1993.

Long, D. "Caring for Silver and Copper Alloy Objects." *Conserve O Gram* 10/2 (1999), pp. 1–4. Available from the Web site of the National Park Service (www.cr.nps.gov/museum/publications/conserveogram/10_02.pdf).

MacLeod, I.D. "Identification of Corrosion Products on Non-ferrous Metal Artifacts recovered from Shipwrecks." *Studies in Conservation* 36 (1991), pp. 222–234.

McNeil, M.B., and B.J. Little. "The Use of Mineralogical Data in Interpretation of Long-term Microbiological Corrosion Processes: Sulfiding Reactions." *Journal of the American Institute for Conservation* 38 (1999), pp. 186–199.

Moss, A.A. "Niello." *Studies in Conservation* 1 (1953), pp. 49–62.

Newman, R., J.R. Dennis, and E. Farrell. "A Technical Note on Niello." *Journal of the American Institute for Conservation* 21 (1982), pp. 80–85.

Oddy, A., M. Bimson, and S. La Niece. "The Composition of Niello Decoration on Gold, Silver and Bronze in the Antique and Mediaeval Periods." *Studies in Conservation* 28 (1983), pp. 29–35.

Oddy, A., and S.M. Bradley. "The Corrosion of Metal Objects in Storage and on Display." pp. 225–243 in *Current Problems in the Conservation of Metal Antiquities* (edited by S. Aoki). Tokyo, Japan: Tokyo National Research Institute of Cultural Properties, 1993.

Pobboravsky, I. "Daguerreotype Preservation: The Problems of Tarnish Removal." *Technology and Conservation* 3 (1978), pp. 40–45.

Reedy, C.L., R.A. Corbett, D.L. Long, R.E. Tatnall, and B.K. Krantz. "Evaluation of Three Protective Coatings for Indoor Silver Artifacts." *AIC Objects Specialty Group Postprints* 6 (1999), pp. 41–69.

Rudoe, J. "Oxidized Silver in the 19th Century: Its Documentary Evidence." pp. 161–170 in *Metal Plating and Patination* (edited by S. La Niece and P.T. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Sease, C., L.S. Selwyn, S. Zubiate, D.F. Bowers, and D.R. Atkins. "Problems with Coated Silver: Whisker Formation and Possible Filiform Corrosion." *Studies in Conservation* 42 (1997), pp. 1–10.

Selwyn, L. "Historical Silver: Storage, Display, and Tarnish Removal." *Journal of the International Institute for Conservation - Canadian Group* 15 (1990), pp. 12–22.

Selwyn, L. *Silver — Care and Tarnish Removal.* CCI Notes, No. 9/7. Ottawa, ON: Canadian Conservation Institute, 1997.

Selwyn, L. "Corrosion Chemistry of Gilded Silver and Copper." pp. 21–47 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Selwyn, L.S., and C.G. Costain. "Evaluation of Silver-cleaning Products." *Journal of the International Institute for Conservation - Canadian Group* 16 (1991), pp. 3–16.

Shearman, W.M. *Metal Alloys and Patinas for Castings.* Ashland, OH: Kent State University Press, 1976.

Srámek, J., T.B. Jakobsen, and J.B. Pelikán. "Corrosion and Conservation of a Silver Visceral Vessel from the Beginning of the Seventeenth Century." *Studies in Conservation* 23 (1978), pp. 114–117.

Stirling, D., G. Noble, N. Tennent, and R. Kennedy. "Sulfur: From Industry to Museum." *SSCR Journal* 11 (2000), pp. 12–13.

Strahan, D.K. "Treatment of a Silver Dragon for the Removal of Silver Cyanide and Chalconatronite." *Journal of the American Institute for Conservation* 25 (1986), pp. 73–81.

Thompson, N.R. "Silver." pp. 79–128 in *The Chemistry of Copper, Silver, and Gold*. New York, NY: Pergamon Press, 1973.

Turner, E. "Silver Plating in the 18th Century." pp. 211–222 in *Metal Plating and Patination* (edited by S. La Niece and P.T. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

van Langh, R. "The Delamination of Mercury-gilded Silver." *Met Objectives* 1 (2000), pp. 6 and 9.

Wanhill, R.J.H. *Microstructurally-induced Embrittlement of Archaeological Silver*. Report NLR-TP-2001-032. Amsterdam, Netherlands: National Aerospace Laboratory, 2001.

Weisser, T.D. "Some Practical Considerations and Solutions for Preservation in the Museum Environment." pp. 81–95 in *Cultural Property and its Environment*. Tokyo, Japan: Tokyo National Research Institute of Cultural Properties, 1990.

Wharton, G. "The Cleaning and Lacquering of Museum Silver." *WAAC Newsletter* 11 (1989), pp. 4–5.

Wharton, G., S.L. Maish, and W.S. Ginell. "A Comparative Study of Silver Cleaning Abrasives." *Journal of the American Institute for Conservation* 29 (1990), pp. 13–31.

White, W.W. "Silver Coinage and the Toning Process." *The Numismatist* June (1993), pp. 792–795, 856.

Wyler, S.B. *The Book of Old Silver: English, American, Foreign*. New York, NY: Crown Publishers, 1937.

Young, R.D., and R.A. Fennell. *Methods for Modern Sculptors*. Escondido, CA: Sculpt Nouveau, 1980.

CHAPTER 12. TIN

ASM International. *ASM Handbook. Vol. 3. Alloy Phase Diagrams*. Materials Park, OH: ASM International, 1992.

Booser, E.R. "Bearing Materials." pp. 1–21 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 4*. New York, NY: John Wiley & Sons, 1992.

Child, R. "The Identification of Post-Industrial Revolution Metals." pp. 7–14 in *Modern Metals in Museums* (edited by R.E. Child and J.M. Townsend). London, UK: Institute of Archaeology, 1988.

Corbeil, M.-C. "A Note on the Use of Tin Amalgams in Marquetry." *Studies in Conservation* 43 (1998), pp. 265–269.

Corfield, M. "Tinning of Iron." pp. 40–43 in *Lead and Tin: Studies in Conservation and Technology*. Occasional Papers, No. 3. London, UK: United Kingdom Institute for Conservation of Historic and Artistic Works, 1985.

Corfield, M. "Tin and Tinplate, Technology and Conservation." pp. 33–36 in *Modern Metals in Museums* (edited by R.E. Child and J.M. Townsend). London, UK: Institute of Archaeology, 1988.

Cotterell, H.H. *Old Pewter, its Makers and Marks in England, Scotland, and Ireland*. Rutland, VT: C.E. Tuttle Co., 1963.

Earl, B. "Tin Preparation and Smelting." pp. 37–83 in *The Industrial Revolution in Metals* (edited by J. Day and R.F. Tylecote). London, UK: The Institute of Metals, 1991.

Friesel, M., and B. Karlsson. "Material Research on Lead–Tin Alloys used for Organ Pipes." *GOArt Research Reports* 1 (1999), pp. 51–67.

Gaver, C.C. "Tin and Tin Alloys." pp. 105–122 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 24*. New York, NY: John Wiley & Sons, 1997.

Gayle, M., and D.W. Look. "Tin." pp. 12–14 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite).Washington, DC: National Park Service, 1992.

Gilberg, M. "History of Tin Pest: The Museum Disease." *ICCM Bulletin* 17 (1991), pp. 3–20.

Hadsund, P. "The Tin–Mercury Mirror: Its Manufacturing Technique and Deterioration Processes." *Studies in Conservation* 38 (1993), pp. 3–16.

Hull, C. *Pewter*. Aylesbury, UK: Shire Publications, 1992.

Kinsela, D. "A Guide to the Conservation and Maintenance of Pipe Organs." *Heritage Bulletin* 1 (1983), pp. 1–20.

Kossolapov, A., and J. Twilley. "A Decorated Chinese Dagger: Evidence for Ancient Amalgam Tinning." *Studies in Conservation* 39 (1994), pp. 257–264.

Laughlin, L.I. *Pewter in America: Its Makers and their Marks* (3 volumes). Barre, MA: Barre Publishers, 1969–1971.

Leidheiser, H. *The Corrosion of Copper, Tin, and their Alloys*. New York, NY: John Wiley & Sons, 1971.

Lihl, F. "On the Cause of Tin Decay in the Sarcophagi of the "Kapuzinergruft"." *Studies in Conservation* 7 (1962), pp. 89–105.

Lipcsei, L., A. Murray, R. Smith, and M. Savas. "An Examination of Deterioration Products found on Tin Ingots excavated from the 14th Century B.C., Late Bronze Age Shipwreck, the *Ulu Burun*, near Kas, Turkey." pp. 451–459 in *Materials Issues in Art and Archaeology. VI* (edited by P.B. Vandiver, M. Goodway, and J.L. Mass). Materials Research Society Symposium Proceedings. Vol. 712. Warrendale, PA: Materials Research Society, 2002.

MacLeod, I.D. "Conservation, Applied Science and Why Treatments must be Monitored." *ICCM Bulletin* 10 (1984), pp. 19–41.

MacLeod, I.D. "Identification of Corrosion Products on Non-ferrous Metal Artifacts recovered from Shipwrecks." *Studies in Conservation* 36 (1991), pp. 222–234.

MacLeod, I.D., and R. Wozniak. "Corrosion and Conservation of Tin and Pewter from Sea Water." pp. 118–123 in *Metal 95* (edited by I.D. MacLeod, S.L. Pennec, and L. Robbiola). London, UK: James & James Science Publishers, 1997.

Meeks, N.D. "Tin-rich Surfaces on Bronze — Some Experimental and Archaeological Considerations." *Archaeometry* 28 (1986), pp. 133–162.

Meeks, N. "Patination Phenomena on Roman and Chinese High Tin Bronze Mirrors and Other Artefacts." pp. 63–84 in *Metal Plating and Patination* (edited by S. La Niece and P.T. Craddock). Oxford, UK: Butterworth-Heinemann, 1993a.

Meeks, N. "Surface Characterization of Tinned Bronze, High Tin Bronze, Tinned Iron and Arsenical Bronze." pp. 247–275 in *Metal Plating and Patination* (edited by S. La Niece and P.T. Craddock). Oxford, UK: Butterworth-Heinemann, 1993b.

Murphy, T.P. "Tin and Tinplate." pp. 853–862 in *Uhlig's Corrosion Handbook, 2nd ed.* (edited by R.W. Revie). Toronto, ON: John Wiley & Sons Canada, 2000.

Nadolski, D., U. Piekara, and K.-H. Barnekow. *Old Household Pewterware: Its Appearance and Function in the Course of 6 Centuries*. New York, NY: Holmes & Meier, 1987.

North, N.A. "Conservation of Metals." pp. 207–252 in *Conservation of Marine Archaeological Objects* (edited by C. Pearson). London, UK: Butterworths, 1987.

North, N.A., and I.D. MacLeod. "Corrosion of Metals." pp. 68–98 in *Conservation of Marine Archaeological Objects* (edited by C. Pearson). London, UK: Butterworths, 1987.

Oddy, A., and M. Bimson. "Tinned Bronze in Antiquity." pp. 33–39 in *Lead and Tin: Studies in Conservation and Technology*. Occasional Papers, No. 3. London, UK: United Kingdom Institute for Conservation of Historic and Artistic Works, 1985.

Organ, R.M., and J.A. Mandarino. "Romarchite and Hydroromarchite. Two New Stannous Minerals." *Canadian Mineralogist* 10 (1971), p. 916.

Payton, R. "The Conservation of Artefacts from One of the World's Oldest Shipwrecks, the *Ulu Burun*, Kas Shipwreck, Turkey." pp. 41–50 in *Recent Advances in the Conservation and Analysis of Artifacts*. London, UK: Summer Schools Press, 1987.

Penhallurick, R.D. *Tin in Antiquity*. London, UK: The Institute of Metals, 1986.

Plenderleith, H.J., and R.M. Organ. "The Decay and Conservation of Museum Objects of Tin." *Studies in Conservation* 1 (1953), pp. 63–72.

Smith, R.W. "The α (Semiconductor) ⇄ β (Metal) Transition in Tin." *Journal of the Less-Common Metals* 114 (1986), pp. 69–80.

Thornton, J. "All that Glitters is not Gold: Other Surfaces that Appear to be Gilded." pp. 307–317 in *Gilded Metals: History, Technology and Conservation* (edited by T. Drayman-Weisser). London, UK: Archetype Publications, 2000.

Tu, K.N., and K. Zeng. "Tin–Lead (SnPb) Solder Reaction in Flip Chip Technology." *Materials Science and Engineering* R34 (2001), pp. 1–58.

Turgoose, S. "The Corrosion of Lead and Tin: Before and After Excavation." pp. 15–26 in *Lead and Tin: Studies in Conservation and Technology*. Occasional Papers, No. 3. London, UK: United Kingdom Institute for Conservation of Historic and Artistic Works, 1985.

Waite, J.G. "Tin; Preservation and Repair." pp. 104–110 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite). Washington, DC: National Park Service, 1992.

Warwick, M.E. *Atmospheric Corrosion of Tin and Tin Alloys*. Greenford, UK: International Tin Research Institute, 1982.

CHAPTER 13. ZINC

Ashurst, J., and N. Ashurst. "The Repair and Maintenance of Traditional Zinc Roofing." pp. 119–125 in *Practical Building Conservation: English Heritage Technical Handbook. Vol. 4. Metals.* Aldershot, UK: Gower Technical Press, 1988a.

Ashurst, J., and N. Ashurst. "Zinc Sculpture and its Conservation." pp. 126–129 in *Practical Building Conservation: English Heritage Technical Handbook. Vol. 4. Metals.* Aldershot, UK: Gower Technical Press, 1988b.

ASM International. *ASM Handbook. Vol. 3. Alloy Phase Diagrams.* Materials Park, OH: ASM International, 1992.

Barnhurst, R.J. "Zinc and Zinc Alloys." pp. 527–542 in *ASM Handbook. Vol. 2. Properties and Selection: Nonferrous Alloys and Special-purpose Materials.* Materials Park, OH: ASM International, 1990.

Brown, H.E. *Zinc Oxide: Properties and Applications.* New York, NY: International Lead Zinc Research Organization, 1976.

Craddock, P.T. (editor). *2000 Years of Zinc and Brass.* British Museum Occasional Paper, No. 50. London, UK: British Museum Publications Ltd., 1998.

Craddock, P.T., I.C. Freestone, L.K. Gurjar, A.P. Middleton, and L. Wilkes. "Zinc in India." pp. 27–72 in *2000 Years of Zinc and Brass* (edited by P.T. Craddock). British Museum Occasional Paper, No. 50. London, UK: British Museum Publications Ltd., 1998.

Dawkins, J.M. *Zinc and Spelter.* Oxford, UK: Zinc Development Association, 1950.

Dutrizac, J.E., and J.B. O'Reilly. "The Origins of Zinc and Brass." *CIM Bulletin* 77 (1984), pp. 69–73.

Falk, T., J.-E. Svensson, and L.-G. Johansson. "The Role of Carbon Dioxide in the Atmospheric Corrosion of Zinc." *Journal of the Electrochemical Society* 145 (1998), pp. 39–43.

Gayle, M., and D.W. Look. "Zinc." pp. 15–21 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite). Washington, DC: National Park Service, 1992.

Goodway, M. "Disintegration of Zinc Die-castings." *Historical Metallurgy* 19 (1985), pp. 37–38.

Goodwin, F.E. "Zinc and Zinc Alloys." pp. 789–839 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 25.* New York, NY: John Wiley & Sons, 1998a.

Goodwin, F.E. "Zinc Compounds." pp. 840–853 in *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 25.* New York, NY: John Wiley & Sons, 1998b.

Graedel, T.E. "Corrosion Mechanisms for Zinc exposed to the Atmosphere." *Journal of the Electrochemical Society* 136 (1989), pp. 193–203.

Green, L.R., and D. Thickett. "Modern Metals in Museum Collections." pp. 261–272 in *Saving the Twentieth Century: The Conservation of Modern Materials* (edited by D.W. Grattan). Ottawa, ON: Canadian Conservation Institute, 1993.

Grissom, C.A. "The Conservation of Outdoor Zinc Sculpture." pp. 279–304 in *Ancient and Historic Metals* (edited by D.A. Scott, J. Podany, and B.B. Considine). Marina del Rey, CA: Getty Conservation Institute, 1994.

Grissom, C.A., and R.S. Harvey. "The Conservation of American War Memorials made of Zinc." *Journal of the American Institute for Conservation* 41 (2003), pp. 21–38.

Helwig, K. *Analysis of Deteriorating Metal from an Ice-skate.* CCI Analytical Report ARS 3113. Ottawa, ON: Canadian Conservation Institute, 1992.

Holm, K. "Production and Restoration of Nineteenth-century Zinc Sculpture in Denmark." pp. 239–248 in *Ancient and Historic Metals* (edited by D.A. Scott, J. Podany, and B.B. Considine). Marina del Rey, CA: Getty Conservation Institute, 1994.

Krause, C.L., and C. Mishler. *Standard Catalogue of World Coins* (edited by C.R. Bruce II). Iola, WI: Krause Publications, 1991.

La Niece, S., and G. Martin. "The Technical Examination of Bidri Ware." *Studies in Conservation* 32 (1987), pp. 97–101.

Lins, A. "Outdoor Bronzes: Some Basic Metallurgical Considerations." pp. 8–20 in *Sculptural Monuments in an Outdoor Environment* (edited by V.N. Naudé). Philadelphia, PA: Pennsylvania Academy of the Fine Arts, 1985.

MacLeod, I.D. "Identification of Corrosion Products on Non-ferrous Metal Artifacts recovered from Shipwrecks." *Studies in Conservation* 36 (1991), pp. 222–234.

Mottner, P., E. Assfalg, and J. Freitag. "Investigations into Intercrystalline Corrosion and Conservation of Zinc." pp. 329–340 in *Metal 98* (edited by W. Mourey and L. Robbiola). London, UK: James & James Science Publishers, 1998.

Mottner, P., H. Brückner, and J. Freitag. "Conservation of Cast Zinc Sculptures in Outdoor Exposure." pp. 251–255 in *Metal 95* (edited by I.D. MacLeod, S.L. Pennec, and L. Robbiola). London, UK: James & James Science Publishers, 1997.

Oddy, A., and S.M. Bradley. "The Corrosion of Metal Objects in Storage and on Display." pp. 225–244 in *Current Problems in the Conservation of Metal Antiquities* (edited by S. Aoki). Tokyo, Japan: Tokyo National Research Institute of Cultural Properties, 1993.

Persson, D., and C. Leygraf. "Metal Carboxylate Formation during Indoor Atmospheric Corrosion of Cu, Zn, and Ni." *Journal of the Electrochemical Society* 142 (1995), pp. 1468–1477.

Porter, F. *Zinc Handbook: Properties, Processing, and Use in Design.* New York, NY: Marcel Dekker, 1991.

Riederer, J. "Corrosion Damage to Zinc Sculptures in Germany." *European Cultural Heritage Newsletter on Research* 7 (1993), pp. 75–81.

Robinet, L., and M.-C. Corbeil. "The Characterization of Metal Soaps." *Studies in Conservation* 48 (2003), pp. 23–40.

Rossol, M. *The Artist's Complete Health and Safety Guide, 3rd ed.* New York, NY: Allworth Press, 2002.

Scott, D.A. *Copper and Bronze in Art: Corrosion, Colorants, Conservation.* Marina del Rey, CA: Getty Conservation Institute, 2002.

Sirois, J., and E. Moffatt. *Analysis of the Alloy and Patina from Two Coins and a Toy Train Fragment.* CCI Analytical Report ARS 4029. Ottawa, ON: Canadian Conservation Institute, 2001.

Street, A. "Zinc: Zinc Alloys 1900–1950." *Historical Metallurgy* 19 (1985), pp. 31–37.

Strong, S. "*Bidri* ware of India." pp. 135–147 in *Metal Plating and Patination* (edited by S. La Niece and P.T. Craddock). Oxford, UK: Butterworth-Heinemann, 1993.

Tylecote, R.F. *The Early History of Metallurgy in Europe.* London, UK: Longman, 1987.

Waite, J. "Zinc, Preservation and Repair." pp. 111–117 in *Metals in America's Historic Buildings: Uses and Preservation Treatments, 2nd ed.* (edited by M. Gayle, D.W. Look, and J.G. Waite). Washington, DC: National Park Service, 1992.

Wypyski, M.T. "Technical Examination of a 19th C. Zinc Outdoor Sculpture." In *Papers presented by Trainees at the Fifteenth Annual Art Conservation Training Programs Conference, 1989*. Cambridge, MA: Harvard University Art Museums, 1990.

Zahner, L.W. "Lead and Zinc." pp. 262–284 in *Architectural Metals: A Guide to Selection, Specification, and Performance*. New York, NY: John Wiley & Sons, 1995.

Zhang, X.G. "Zinc." pp. 887–904 in *Uhlig's Corrosion Handbook, 2nd ed.* (edited by R.W. Revie). Toronto, ON: John Wiley & Sons Canada, 2000.

GLOSSARY

Active
With an electrode potential (as in the galvanic series) lying in the negative direction.

Active corrosion
Fresh or new corrosion; often seen as spalling, cracking, or flaking.

Active metal
Metal with a high tendency to corrode (e.g. zinc, aluminum, magnesium).

Active state
Condition in which a metal reacts with its environment (i.e. freely corrodes) because it is thermodynamically unstable and the corrosion products are soluble. *Compare* "Passive state."

Age-harden
Increase the hardness of an alloy by heat treatment at moderately elevated temperature followed by rapid cooling; the hardening is caused by the precipitation of a second phase (a process that will also occur slowly at ambient temperature). *Also known as* precipitation-harden.

Alclad
Layered wrought aluminum products with an inner core of one kind of aluminum alloy (usually a high-strength material) and an outer layer of a different kind of aluminum alloy (specifically chosen to be corrosion-resistant and more anodic than the core); if the core material is exposed, it will be electrochemically protected against corrosion by the outer, more anodic aluminum alloy.

Allotrope
Any of two or more physical forms in which an element can exist (e.g. tin can exist as white tin or gray tin, and carbon can exist as graphite or diamond).

Alloy
Metallic material containing two or more elements, at least one of which is a metal (e.g. brass, bronze, pewter, steel).

Amalgam
Alloy made with mercury (e.g. gold amalgam is a mixture of gold and mercury).

Amalgam gilding
Application of a gold layer to another metal (usually a copper alloy or silver) by rubbing the surface with a gold amalgam and then heating it to drive off the mercury, leaving the gold well adhered. *Also known as* fire gilding or mercury gilding.

Amalgam silvering
Application of a silver layer to another metal by rubbing the surface with a silver amalgam and then heating it to drive off the mercury, leaving the silver well adhered. *Also known as* fire silvering or mercury silvering.

Amalgam tinning
Application of a tin layer to another metal by rubbing the surface with a tin amalgam and then heating it to drive off the mercury, leaving the tin well adhered. *Also known as* fire tinning or mercury tinning.

Amorphous
Without a crystalline structure or long-range order; amorphous materials are difficult to characterize by X-ray diffraction.

Amphoteric
Displaying both acidic and basic properties; often applied to metal oxides and hydroxides because they form cations (e.g. Al^{3+}) when they dissolve in acidic conditions and anions (e.g. AlO_2^-) when they dissolve in alkaline conditions.

Anaerobic
Without air (more specifically without oxygen).

Anion
Negatively charged ion (e.g. Cl^-, OH^-).

Anneal
Heat-treat a metal to change its physical properties (e.g. heat treatment might soften a metal by removing internal stresses caused by work-hardening).

Anode
Electrode in an electrochemical cell at which oxidation half-reactions occur and electrons flow away in the external circuit; the anode is usually where corrosion occurs and metal ions enter solution. *Compare* "Cathode."

Anodic polarization
Change in the electrode potential of a metal when it is made the anode in an electrolytic cell and current is allowed to flow.

Anodize
Produce a thick oxide layer on a metal by electrolysis (the metal is made the anode in an electrolytic cell and is forced to corrode); on aluminum, the layer of aluminum oxide that is produced is porous and can be coloured with certain dyes.

Assemble
Process (e.g. crimping, bolting, soldering, welding) used in the construction of an object to connect pre-made parts.

Austenite
Iron-rich phase (called the γFe phase) in iron–carbon alloys that have a face-centred cubic structure.

Bearing (babbitt) metal
White metal alloys (named after I. Babbitt who patented them in 1839) that contain mainly tin with some antimony and copper; used as bearing material to line steel or bronze and reduce friction.

Bell metal
Tin-rich copper alloys that generally contain 15–25 wt% tin; used for bells.

Bidri ware
Decorative metalwork that contains a zinc–copper alloy (2–10 wt% copper) patinated black and inlaid with brass, silver, or gold; it originated in India.

Blue lead
Blue pigment consisting mainly of lead sulphide (the mineral galena).

Body-centred cubic (bcc)
Crystal structure in which the unit cell has an atom at each corner of a cube and at the centre of the cube. *Compare* "Face-centred cubic (fcc)."

Bog iron ore
Iron ore deposits consisting mainly of goethite; used in early iron smelting.

Bower-Barff process
Process developed by F.S. Barff and G. Bower in the late 1870s for producing a dark black surface (consisting of mainly magnetite) on iron.

Brass
Alloy of copper with varying amounts of zinc; other metals (e.g. tin, lead) may also be present.

Braze
Join two metal surfaces together by wetting adjacent surfaces with a molten brazing (hard) solder that has a lower melting temperature than the metals to be joined; after cooling, the solidified solder holds the two metals together by adhesion. *Compare* "Soldering."

Brazing solder
Type of solder with a comparatively high melting point, typically above 450°C (e.g. copper–zinc alloys). *Also known as* hard solder. *Compare* "Soft solder."

Britannia metal
White-coloured alloy that consists mainly of tin (~90 wt%) with some antimony (~7 wt%) and copper (~3 wt%); developed around 1769.

Britannia silver
Silver–copper alloy that contains 95.8 wt% silver and 4.2 wt% copper; used in England as a standard for silver objects from 1697 until 1720.

Bronze
Alloy of copper that contains varying amounts of tin and may include other metals (e.g. zinc, lead); in modern bronze alloys, the tin may be replaced with elements such as aluminum or silicon.

Bronze disease
Corrosion reaction on copper alloys that produces powdery light green spots of copper(II) chloride hydroxides on the surface and leads to pitting of the metal; the reaction is caused by the interaction of chloride-containing species (e.g. nantokite or residual chloride-containing chemicals) with moisture, oxygen, and the copper alloy.

Burnish
Change a rough surface into a smooth and shiny one by rubbing it with a tool made from a harder material.

Cast
Pour molten metal into a mould and allow it to solidify.

Cast iron
Alloys of iron and carbon (2–4 wt% carbon) that may also contain silicon (1–3 wt% silicon) and other elements to change the properties.

Cast iron, gray
Cast iron in which the carbon content is mainly in the form of graphite; a freshly exposed surface is gray.

Cast iron, white
Cast iron in which the carbon content is mainly in the form of cementite; a freshly exposed surface is white.

Cathode
Electrode in an electrochemical cell at which reduction half-reactions occur; electrons flow toward the cathode in the external circuit. *Compare* "Anode."

Cathodic corrosion
Corrosion of a metal (e.g. aluminum) when it is made the cathode in an electrolytic cell; the corrosion is caused by a local increase in pH from the reduction of water at the cathode.

Cathodic polarization
Change in the electrode potential of a metal when it is made the cathode in an electrolytic cell and current is allowed to flow.

Cation
Positively charged ion (e.g. H^+, Fe^{2+}).

Cementite (iron carbide)
Hard, brittle intermetallic compound of iron and carbon; it is a constituent of certain cast irons and steels and serves to strengthen them (i.e. makes them harder).

Charcoal
Amorphous form of relatively pure carbon made by heating wood in the absence of air to drive off water and other volatiles; formerly used as fuel in ironmaking.

Chemical conversion coating
Non-metallic coating formed on a metal (e.g. aluminum) by its reaction with chemicals; often used as a preparation layer prior to painting.

Chrome
Synonym for the element chromium.

Chrome-plated nickel silver (CPNS)
Copper alloy known as nickel silver electroplated with a layer of chrome.

Close plating
Method for attaching silver foil to a metal object (e.g. iron, copper alloys) using an intermediate tin layer and soldering; this procedure was patented in England in 1779.

Coal
Naturally occurring carbon-rich mineral used as a fuel; often contaminated with sulphur and phosphorus.

Coke
Dense carbon-rich fuel made by heating coal (above 1000°C) in the absence of air to drive off volatiles, particularly sulphur; used in iron smelting.

Cold-work (work-harden)
Work, shape, or hammer a metal while it is cold; most metals become harder when cold-worked due to deformation of the crystal structure.

Corrosion
Electrochemical reaction between a metal and its environment that causes the metal to deteriorate; the electrochemical process involves the transfer of electrons from the metal to another species during simultaneous oxidation and reduction reactions.

Corrosion potential (E_c)
Electrode potential of a corroding metal surface immersed in an electrolyte measured relative to a reference electrode.

Creep
Relatively slow flow of certain metals under continuous stress (e.g. lead or zinc in large sculptures gradually flows toward the ground because of gravity).

Crevice corrosion
Localized corrosion that occurs under gasketting, deposits, and joins due to low levels of oxygen that result from the restricted access to the interior of a crevice (e.g. stacked metal sheets left outdoors often develop staining due to crevice corrosion).

Crystalline
Structure characterized by regular atomic arrangement and long-range order.

Cyanotype
Early type of photograph (developed 1842) based on paper made light-sensitive with a mixture of iron(III) salts, including potassium ferricyanide; the blue image in the developed photograph is Prussian blue, a complex iron salt.

Daguerreotype
Early type of photograph (1839 to mid-1860s) with a silver-plated copper base covered with light-sensitive silver halides; the final image (developed with mercury vapour) is captured by silver amalgam particles.

Damascene
Ornament steel by etching or inlaying, usually with gold or silver.

Damascus steel
Steel with a fine surface pattern resembling waves; the pattern is created by contrasting areas of silvery cementite and darker pearlite and can be enhanced by etching. *Also known as* watered steel.

Dealloying
Preferential corrosion of one metal constituent from an alloy, leaving the other constituents (usually the more noble ones) behind. *See* "Dezincification."

Deliquescence
Formation of a solution on the surface of an object when a solid compound absorbs water from the surrounding air and dissolves.

Dendrite
Branched, tree-like pattern of crystals formed during the solidification of metal.

Depletion gilding
Production of a gold surface on a gold alloy (e.g. copper–gold alloys) by chemically removing the alloying elements from the surface.

Depletion silvering
Production of a silver surface on a silver alloy (e.g. copper–silver alloys) by chemically removing the alloying elements from the surface.

Dezincification
Selective corrosion of zinc from a copper–zinc alloy (typically with >15 wt% zinc) leaving behind a porous copper-rich surface; the colour changes from the usual yellow of brass to the pink of copper.

Diffusion gilding
Application of a gold layer to another metal by burnishing gold leaf directly onto the metal and then heating it to allow the gold and underlying metal to diffuse into one another, forming a strong bond.

Ductile
Capable of sustaining large deformations without fracturing; ductile metals can be drawn into wires.

Efflorescence
A powdery deposit formed by a crystalline hydrated solid losing its water of crystallization or by salts coming from inside an object and accumulating on its surface (such salts are often carried to the surface in solution and remain as a powder after the water has evaporated).

Electrochemical cell
Combination of two electrodes (an anode and a cathode) in electrical contact and immersed in an electrolyte; the anode and cathode may be different metals or dissimilar areas on the same metal surface.

Electrochemical series
List of elements arranged according to their standard equilibrium potentials for reactions involving ions in solution under standard conditions and at equilibrium (no current flowing).

Electrode
Material with a high electrical conductivity (e.g. metals) in contact with an electrolyte.

Electrode potential
Potential of an electrode immersed in an electrolyte measured relative to a reference electrode.

Electroform (electrotype)
Produce or reproduce (an object) by electroplating a mould with a deposit of metal (an electrotype is a metal plate used in printing made by electroplating a mould of the page to be printed).

Electroless plating
Deposition of a layer of metal onto a solid surface using chemicals (a chemical reduction process) rather than an electric current.

Electrolysis
Production of a chemical change by passing a current through an electrochemical cell (e.g. electrolysis of water results in the formation of hydrogen gas at the cathode and oxygen gas at the anode).

Electrolyte
Ionic conductor containing positive and negative ions that migrate in an electric field (e.g. an aqueous solution containing dissolved salts).

Electrolytic cell
Electrochemical cell that consumes electrical energy from an external source.

Electromotive force
Difference in electrode potential between two electrodes immersed in the same electrolyte.

Electroplate
Deposit a layer of metal onto a conducting surface by making it the cathode in an electrolytic cell.

Electroplated Britannia metal (EPBM)
Tin alloy known as Britannia metal electroplated with a layer of silver.

Electroplated copper (EP copper)
Copper electroplated with a layer of silver.

Electroplated lead (EP lead)
Lead electroplated with a layer of silver.

Electroplated nickel silver (EPNS)
Copper alloy known as nickel silver electroplated with a layer of silver.

Electropolish
Produce a high polish on a metal surface by making it the anode in an electrochemical cell (high points corrode preferentially, leaving a smoother finish).

Electrum
Gold–silver alloys used in ancient times; they have a pale green or silvery white colour.

Equilibrium potential (E_h)
Potential at equilibrium (no current flowing) of the half-reaction of an electrode immersed under non-standard conditions; can be calculated using the standard equilibrium potential and the Nernst equation.

Eutectic
Having the lowest freezing point of all possible mixtures of the components in an alloy.

Exfoliation
Corrosion in which the corrosion products form along planes parallel to the metal surface, causing the metal to delaminate; wrought aluminum alloys that contain copper are particularly susceptible to this type of corrosion. *Also known as* layer or lamellar corrosion.

Face-centred cubic (fcc)
Crystal structure in which the unit cell has an atom at each corner and each face centre of a cube. *Compare* "Body-centred cubic (bcc)."

Ferric
Iron ions in the +3 oxidation state (e.g. Fe^{3+}).

Ferrite
Iron-rich phase (called the αFe phase) in iron–carbon alloys that have a body-centred cubic structure (*compare* "Austenite") or magnetic iron oxides with the general formula MFe_2O_4 (where M is usually a metal).

Ferrous
General term for metals in which iron is the main constituent or specific term for iron ions in the +2 oxidation state (e.g. Fe^{2+}).

Filiform corrosion
Hair-like or filamentary corrosion underneath an organic coating on metals such as aluminum or iron. *Also known as* underfilm corrosion.

Fineness
Fraction of gold in a gold-containing alloy expressed in parts per thousand by weight; pure gold has a fineness of 1000 and 18 kt gold has a fineness of 750.

Finish
Process (e.g. engraving, plating, painting) used during the final steps of constructing an object to provide decoration or further protection.

Fire gilding
See "Amalgam gilding."

Fire silvering
See "Amalgam silvering."

Fire tinning
See "Amalgam tinning."

Firestain
Dark copper oxide stains that form on sterling silver and other silver–copper alloys during the annealing process.

Flatware
Utensils (e.g. knives, forks, spoons, serving pieces) used for eating or serving; silver-coloured metal ones can be made from sterling silver, silver plate, or stainless steel.

Flux
Material (e.g. borax, zinc chloride) that keeps metal surfaces free of oxides during soldering and brazing or material (e.g. limestone) that combines with impurities and makes slag flow easily during ironmaking.

Foil gilding
Ancient form of application of a gold layer by mechanically attaching (e.g. by crimping or riveting) gold foil to a surface.

Foil silvering
Ancient form of application of a silver layer by mechanically attaching silver foil to a surface.

Fool's gold
Various yellow minerals (e.g. pyrite and chalcopyrite) that can be mistaken for gold.

Form
Process (e.g. casting, forging, rolling) used in the construction of an object to give ingots of metal their initial shape.

French plating
Method (based on burnishing) for attaching thin silver sheets to copper alloys; it was used in France in the early 1700s.

Fused plate
See "Sheffield plate."

Galvanic cell
Electrochemical cell (e.g. a battery) that is a source of electrical energy.

Galvanic corrosion
Accelerated corrosion of a metal in electrical contact with a more noble metal (or a non-metallic conductor) in an electrolyte.

Galvanic series
List of metals, alloys, and conducting materials arranged according to their electrode potentials in a specific wet environment (e.g. seawater); the series is ordered from metals with the most positive electrode potentials (e.g. noble metals such as platinum) to metals with the most negative ones (e.g. active metals such as zinc and aluminum).

Galvanize
Cover (iron, steel, etc.) with a protective zinc coating by dipping into molten zinc or by electroplating.

Galvanized steel
Zinc-coated steel; if any steel is exposed, it is electrochemically protected against corrosion by the outer, more anodic zinc layer.

Gangue
Impurity minerals in metal ores, typically aluminum oxide and silicon dioxide.

Gilding
Thin layer of gold on the surface of another material.

Gold filled
Modern jewelry term for metal (usually a copper–zinc alloy) with a surface layer of gold alloy (which is usually applied mechanically) that makes up at least 1/20th of the total weight. *Compare* "Rolled gold."

Grain
Individual crystal in a polycrystalline metal; each grain contains atoms ordered in a regular geometric pattern.

Grain boundary
Junction between adjacent grains in a polycrystalline metal.

Graphite
Allotrope of carbon that is soft and has a dark gray colour; it is a good conductor of heat and electricity.

Graphitic corrosion
Deterioration of gray cast iron due to selective corrosion of iron, leaving soft graphite. *Also known as* graphitization.

Graphitization
See "Graphitic corrosion." (Note: In metallurgy the term "graphitization" means the formation of graphite by the decomposition of iron carbide; therefore the term is no longer recommended as a synonym for graphitic corrosion.)

Green gold
Modern jewelry term for gold–silver alloys with a pale green colour.

Green rust
Bluish-green iron compounds that contain both Fe^{2+} and Fe^{3+}, have a layered structure, and incorporate other anions such as carbonate, chloride, and sulphate ions.

Gunmetal
Copper alloys that contain zinc, tin, and small amounts of other elements or copper alloys that are used to make guns and have various combinations of copper, tin, zinc, and lead.

Half-reaction
One of the component reactions of a net chemical reaction. (For example, the net chemical reaction in an electrochemical process can be divided into an oxidation half-reaction and a reduction half-reaction to account for the net transfer of electrons; electrons are generated in the oxidation half-reactions (e.g. $2Fe \rightarrow 2Fe^{2+} + 4e^-$) and electrons are consumed in the reduction half-reactions (e.g. $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$).)

Hard solder
See "Brazing solder."

Heat-treatable
Capable of being hardened by heat treatment (e.g. certain aluminum alloys can be hardened by heat treatment).

Hollowware
Tableware designed to function as containers, serving dishes, and decorative pieces (e.g. bowls, vases, candlesticks, pitchers, teapots, trays, pots, jugs, kettles); silver-coloured metal ones can be made from sterling silver, silver plate, or stainless steel.

Horn silver
Silver chloride.

Hot-dip
Apply a layer of metal to an object by immersing it in molten metal.

Hydrolysis
Reaction between a compound or ion and water (e.g. $Fe^{2+} + H_2O \rightarrow Fe(OH)^+ + H^+$).

Immune state
Condition in which a metal does not react with its environment because it is thermodynamically stable.

Intergranular corrosion
Preferential corrosion at grain boundaries in a metal alloy that can lead to disintegration of the alloy as the grains fall out (e.g. aluminum alloyed with copper is sensitive to intergranular corrosion if intermetallic $CuAl_2$ particles precipitate at grain boundaries).

Intermetallic compound
Phase of an alloy that consists of two or more metals (or a metal and a non-metal) with an ordered, crystalline structure and usually a definite composition (e.g. AuCu, Fe_3C, $CuAl_2$, $FeSn_2$).

Iron earth pigments
Naturally occurring iron oxides and hydroxide oxides that are used as yellow, orange, and red pigments; yellow earth pigments (e.g. yellow ochre, raw sienna) usually contain goethite, and red earth pigments (e.g. red ochre, burnt sienna) usually contain hematite.

Karat (kt)
Fraction of gold in a gold-containing alloy expressed in parts per 24 by weight; 24 kt gold is pure gold and 18 kt gold is 18/24 parts gold (i.e. 75 wt% gold).

Lamellar corrosion
See "Exfoliation."

Layer corrosion
See "Exfoliation."

Lead burning
Localized melting of lead in a flame to form a continuous join between two pieces.

Leaf gilding
Application of a gold layer by applying thin sheets (leaves) of gold (< 1 μm thick) to a prepared surface (e.g. wood, metal, gesso).

Leaf silvering
Application of a silver layer by applying thin sheets (leaves) of silver to a prepared surface (e.g. wood, metal, gesso).

Litharge
Can refer specifically to red lead monoxide (α-PbO) or collectively to lead monoxides that can exist in two polymorphs (α-PbO and β-PbO).

Malleable
Capable of being worked, rolled, hammered, or shaped under pressure without breaking.

Martensite
Supersaturated solid solution of carbon in iron that forms in iron–carbon alloys cooled rapidly (quenched); it is hard and brittle, and has a needle-like appearance when viewed under a microscope. *Compare* "Pearlite."

Mercury gilding
See "Amalgam gilding."

Mercury silvering
See "Amalgam silvering."

Mercury tinning
See "Amalgam tinning."

Metal soap
Waxy compound formed by the reaction between metal ions and organic fatty acids present in vegetable fats, oils, and waxes; cadmium, copper, lead, and zinc can form metal soaps.

Meteoritic iron
Iron–nickel alloys (5–60 wt% nickel) originating from space.

Microbiological corrosion
Corrosion of metals caused by microorganisms.

Mill scale
Oxide layer formed on iron alloys during heat treatment or fabrication while hot.

Monel
Nickel–copper alloys with ~66 wt% nickel.

Mosaic gold
Gold-coloured pigment that consists of tin(IV) sulphide.

Native metal
Metal found naturally in the elemental form (e.g. gold, silver, and copper).

Nernst equation
An equation (found in many chemistry textbooks) to calculate the effect of non-standard temperatures, pressures, or ion concentrations on electrode potential.

Nickel silver
Copper-rich alloys that contain nickel and zinc (but no silver), have a silver-white colour, and can be highly polished; an early trade name was German silver.

Niello
Lustrous black or blue-black material used as an inlay material to fill engraved designs on silver; it generally consists of one or more metal sulphides (e.g. silver sulphide, lead sulphide, copper sulphide).

Noble
With an electrode potential (as in the galvanic series) lying in the positive direction.

Noble metal
Metal with a low tendency to corrode (e.g. gold, platinum).

Non-heat-treatable
Incapable of being hardened by heat treatment (e.g. certain aluminum alloys cannot be hardened by heat treatment).

Normal hydrogen electrode (NHE)
See "Standard hydrogen electrode (SHE)."

Oil gilding
Application of a gold layer to a surface by applying gold leaf using a water-insoluble adhesive such as an oil-based varnish. *Compare* "Water gilding."

Ore
Naturally occurring mineral from which metals can be extracted.

Ormolu
Mercury-gilded or gold-coloured copper alloys (e.g. certain brasses).

Oxidation
Chemical reaction in which the constituents lose electrons; if a metal or metal ion is oxidized, the oxidation state is increased. *Compare* "Reduction."

Oxidized silver
Silver intentionally coloured with chemicals to produce dark grays or blue-blacks.

Parcel-gilt
Partial covering of a metal (often silver) surface with gold, usually by amalgam gilding.

Passive state
Condition in which a thermodynamically unstable metal has a low corrosion rate because the metal surface has reacted with the environment to form a protective film of corrosion products. *Compare* "Active state."

Patina
Corrosion products on the surface of a metal; patina may occur naturally as a result of long-term exposure to weather, pollution, etc., or may be artificially induced through the application of various chemicals.

Pearlite
Alternating layers of iron and iron carbide that form in iron–carbon alloys cooled slowly; they have an iridescent appearance (similar to a pearl) under low magnification. *Compare* "Martensite."

Pewter
Alloy of tin (typically 80–90 wt% tin) with lead (ancient pewter) or antimony (modern pewter).

pH
Measure of the acidity or alkalinity of a solution (by definition, pH is the negative logarithm of the hydrogen ion concentration); acids have $pH < 7$, neutral solutions have $pH = 7$, and alkaline solutions have $pH > 7$.

Pitting corrosion
Localized corrosion that causes cavities or pits on the metal surface; most commonly initiated by chloride ions.

Platinotype
Early type of photograph (patented 1873) based on paper made light-sensitive with a mixture of iron(III) oxalate and a platinum salt; the black image in the developed photograph is metallic platinum.

Polymorphs
Compounds that have the same chemical formula but different crystal structures.

Potential
See "Electrode potential."

Potential-pH diagrams
See "Pourbaix diagrams."

Pourbaix diagrams
Theoretical diagrams of electrode potential plotted against pH calculated using thermodynamic information; they can be used to predict the conditions in which a metal will actively corrode, be immune to corrosion, or possibly become passivated. *Also known as* stability diagrams or potential-pH diagrams.

Precious metals
Eight scarce and costly metals, i.e. gold, silver, and the six members of the platinum group (platinum, palladium, rhodium, iridium, ruthenium, and osmium).

Precipitation-harden
See "Age-harden."

Pseudogilding
Surface layer of gold-coloured pyrite or chalcopyrite that has the appearance of gilding; often formed during burial under anaerobic conditions where sulphate-reducing bacteria thrive and produce hydrogen sulphide.

Quench
Cool rapidly, usually by plunging into a cold liquid.

Red gold
Modern jewelry term for gold–copper alloys with a reddish colour.

Red lead
Bright orange-red pigment that consists mainly of lead oxide (the mineral minium).

Reduced sulphur
Sulphur in a reduced oxidation state (e.g. hydrogen sulphide, carbonyl sulphide, and elemental sulphur).

Reduction
Chemical reaction in which the constituents gain electrons; if a metal ion is reduced, the oxidation state is reduced. *Compare* "Oxidation."

Reference electrode
Electrode with a stable and reproducible potential.

Rolled gold
Modern jewelry term for metal (usually a copper–zinc alloy) with a surface layer of gold alloy (which is usually applied mechanically) that makes up less than 1/20th of the total weight. *Compare* "Gold filled."

Rust
Reddish-brown corrosion products (mainly iron hydroxide oxides) on ferrous metals.

Sand casting
Casting technique in which molten metal is poured into a sand mould (formed by pressing a model into the sand).

Shakudo
Copper–gold alloys (4–5 wt% gold) that can be patinated a dark purple-black colour (often used in Japan).

Shape
Process (e.g. cutting, drilling, turning) used in the construction of an object to establish its final dimensions.

Sheffield plate
Form of plating in which a thin sterling silver slab is well bonded to the surface of a copper slab by heating and the resulting sandwich structure is then thinned by rolling and worked like sterling silver; this method was popular in Sheffield, England (heyday 1790–1830) for making silver-plated copper objects. *Also known as* fused plate.

Sheradizing
Industrial process to put an even coating of zinc on small iron or steel parts (e.g. springs, washers, nuts, bolts) by tumbling them with zinc dust and sand in a heated drum.

Shibuichi
Copper–silver alloys (10–50 wt% silver) that can be patinated various shades of gray (often used in Japan).

Siderite
Iron carbonate or iron meteorites.

Silver-gilt
Silver covered with a thin layer of gold (usually applied by amalgam gilding).

Silver plate
Metal plated with a thin layer of silver.

Slag
Glass-like compounds of comparatively low melting point that form during the extraction of metals when the impurities in the ore react with a flux.

Slush casting
Casting technique in which molten metal is poured into a mould, sloshed around, and the excess poured out so that a thin coating is left inside the mould.

Smelt
Extract a metal from its ore by heating; often a metal oxide is heated in the presence of excess carbon until the metal separates, usually by melting.

Soft solder
Type of solder with a comparatively low melting point, typically below 450°C (e.g. lead–tin alloys). *Compare* "Brazing solder."

Solder
Join two metal surfaces together by wetting adjacent surfaces with a molten soft solder that has a lower melting temperature than the metals to be joined; after cooling, the solidified solder holds the two metals together by adhesion. *Compare* "Brazing."

Solid solution
Crystalline phase in which two metals are soluble in one another and their atoms are randomly distributed over one type of crystalline lattice (i.e. are single phase).

Solid solution harden
Increase the hardness of a metal by adding another metal to form a solid solution (i.e. a single phase).

Speculum metal
Tin-rich copper alloys with a silvery-white colour that takes a high polish.

Stability diagrams
See "Pourbaix diagrams."

Standard equilibrium potential (E_h^0)
Potential at equilibrium (no current flowing) of the half-reaction of an electrode immersed under standard conditions.

Standard hydrogen electrode (SHE)
Reference electrode based on hydrogen which, by definition, has an electrode potential of zero. *Also known as* normal hydrogen electrode (NHE).

Steel
Alloy of iron with small amounts of carbon (typically less than 2 wt% carbon) and, often, other metals.

Steel, alloy
Iron–carbon alloys with small amounts of additional elements (e.g. chromium, manganese, vanadium).

Steel, carbon
Iron–carbon alloys with no or few additional elements.

Steel, stainless
Corrosion-resistant iron–carbon alloys with at least 10.5 wt% chromium as well as other metals, often nickel and molybdenum.

Steel, tool
Iron–carbon alloys that contain carbide-forming elements (e.g. tungsten, molybdenum) and have been hardened by heat treatment to produce uniformly distributed wear-resistant carbides (e.g. tungsten carbide, molybdenum carbide); used to make tools for cutting or forming.

Steel, weathering
Low-carbon steel alloyed with small amounts of other elements (e.g. copper, phosphorus, manganese); in outdoor conditions with good drainage and alternating periods of wet and dry, it develops an adherent dark brown patina that increases its resistance to corrosion.

Sterling silver
Silver–copper alloy with 92.5 wt% silver and 7.5 wt% copper.

Stress corrosion cracking
Corrosion process in which cracks form in certain alloys when they are under stress while exposed to certain corrosive environments (e.g. copper–zinc alloys can develop cracks if they contain internal stresses from forming and are exposed to ammonia).

Surface enrichment
The surface augmentation of the more noble constituent of a metal alloy through a process of dealloying.

Tarnish
Discoloration of a metal surface by a thin film of corrosion products.

Temper
Degree of hardness and strength of a metal; achieved by either heat treatment (e.g. by reheating a quenched alloy) or mechanical working (e.g. cold-rolling), or both.

Terne
Lead–tin alloy with more than 5 wt% tin that has a dull gray colour.

Terneplate
Iron coated with terne, a lead–tin alloy.

Tin cry
Sound produced when pure tin is bent.

Tin pest
Deterioration of elemental tin when it is cooled below 13°C and the phase changes (from white tin to gray tin), causing the metal to expand and crack; it is rarely identified on objects because the phase transition is inhibited by low levels of impurities.

Tin sweat
Silver-coloured layer of tin-rich material (resembling deliberate tinning) formed on the surface of cast copper–tin alloys.

Tintype
Early type of photograph (patented 1856) made from a thin sheet of iron (not tin) coated with lacquer and then covered with a light-sensitive silver salt to capture the image.

Toning
Coin collectors' term for silver coins covered with rainbow colours created by a thin layer of silver sulphide tarnish; toning is often considered to be valuable.

Trade silver
Silver trinkets and ornaments that Europeans in North America traded with Aboriginal people for goods and services during the 18th and early 19th centuries.

Tumbaga
Gold–copper alloys (10–90 wt% copper) associated with gold objects from early South American cultures.

Type metal
Alloys (e.g. lead–tin alloys) with low melting temperatures that are used to cast letters for printing.

Underfilm corrosion
See "Filiform corrosion."

Underside corrosion
Corrosion on the underside of certain metals (e.g. lead, zinc) used outdoors (e.g. roofs, sheets) where inadequate ventilation allows water to condense.

Unified Numbering System (UNS)
North American system for designating commercial metals and alloys in regular production and use; it is managed jointly by the American Society for Testing and Materials (ASTM) and the Society of Automotive Engineers (SAE).

Uniform corrosion
General even thinning of metal as it reacts with its environment (e.g. weathering steels such as Cor-Ten develop an even red-brown layer as a result of uniform corrosion).

Verdigris
Copper acetates of varying chemical composition that range in colour from green to blue or undesirable and disfiguring green corrosion products on copper alloys.

Vermeil
Sterling silver plated with a thin layer of gold.

Volatile
Easily converted into a vapour.

Water gilding
Application of a gold layer to a surface by applying gold leaf using a water-soluble adhesive such as rabbit-skin glue. *Compare* "Oil gilding."

Watered steel
See "Damascus steel."

Weld
Join two metal surfaces together by heating until they melt and flow together.

White bronze
Zinc; the term "white bronze" was used to market the metal as a low-cost alternative to bronze.

White gold
Gold–silver alloys with a pale green or silvery white colour (ancient) or modern jewelry term for gold alloys with a white colour that are used as a substitute for platinum.

White lead
White pigment consisting mainly of lead carbonate hydroxide (the mineral hydrocerussite).

White metal
General term for white-coloured alloys with relatively low melting points (e.g. pewter, zinc) or specific term for white-coloured tin–antimony alloys (e.g. bearing alloys, Britannia metal).

White rust
White staining on stacked zinc sheets after exposure to moisture; it consists of various white zinc corrosion products (zinc oxide, zinc hydroxide, zinc carbonate hydroxide).

Work-harden (cold-work)
Increase the hardness of a metal (i.e. build up internal stresses) by a mechanical process such as hammering, drawing, or other means of shaping.

Wrought
Work solid metal by hammering, rolling, extrusion, forging, or drawing; the metal is often heated before working.

Wrought iron
Form of fairly pure iron (generally less than 0.1 wt% carbon) that is mechanically shaped by heating and hammering, and contains characteristic threads of slag (traditional) or low-carbon steel that contains no slag (modern).

Yellow gold
Modern jewelry term for gold alloyed with copper and silver; it has a yellow colour.

Yellow lead
Yellow pigment that consists mainly of lead oxide (the mineral massicot).

Zinc-rich paint
Paint with a high fraction of zinc dust particles (>90 wt% zinc); when applied to a rust-free iron or steel surface, the metal is electrochemically protected against corrosion by the outer, more anodic zinc layer.

Reference material: ASM International (1987); ASTM (2001a); Beale et al. (1988).

INDEX

PHYSICAL PROPERTIES OF NINE COMMON METALS

Principal oxidation number(s)	Atomic weight (g mol^{-1})	Density at 20°C (g cm^{-3})	Melting point (°C)	Boiling point (°C)	Linear expansivity (°C^{-1})	UNS range for alloys
Al^{3+} (aluminic)	26.98	2.70	660	2519	23.1 x 10^{-6}	A00001– A99999
Cu^{1+} (cuprous) Cu^{2+} (cupric)	63.55	8.96	1085	2562	16.5 x 10^{-6}	C00001– C99999
Au^{1+} (aurous) Au^{3+} (auric)	196.97	19.3	1064	2856	14.2 x 10^{-6}	P00001– P00999
Fe^{2+} (ferrous) Fe^{3+} (ferric)	55.85	7.87	1538	2861	11.8 x 10^{-6}	many, e.g. series F, G, J, S, T
Pb^{2+} (plumbous) Pb^{4+} (plumbic)	207.19	11.35	327	1749	28.9 x 10^{-6}	L50001– L59999
Ni^{2+} (nickelous)	58.69	8.90	1455	2913	13.4 x 10^{-6}	N00001– N99999
Ag^{1+} (argentous)	107.87	10.5	962	2162	18.9 x 10^{-6}	P07001– P07999
Sn^{2+}(stannous) Sn^{4+}(stannic)	118.69	7.31	232	2602	22.0 x 10^{-6}	L13001– L13999
Zn^{2+}(zincic)	65.39	7.13	420	907	30.2 x 10^{-6}	Z00001– Z9999

ISBN 0-662-37984-5

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