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IMPURITY LIMITS FOR CAST COPPER ALLOYS

— A Literature Survey of Tin Bronzes

A. Couture

AUGUST 1976



MINERALS RESEARCH PROGRAM
PHYSICAL METALLURGY RESEARCH LABORATORIES
CANMET REPORT 76-37

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Available by mail from:

Printing and Publishing
Supply and Services Canada,
Ottawa, Canada K1A 0S9

CANMET
Energy, Mines and Resources Canada,
555 Booth St.,
Ottawa, Canada K1A 0G1

or through your bookseller.

Catalogue No. M38-13/76-37
ISBN 0-660-00987-0

Price: Canada: \$2.25
Other countries: \$2.70

Price subject to change without notice.

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En vente par la poste:

Imprimerie et Édition
Approvisionnement et Services Canada,
Ottawa, Canada K1A 0S9

CANMET
Énergie, Mines et Ressources Canada,
555, rue Booth
Ottawa, Canada K1A 0G1

ou chez votre libraire.

N° de catalogue M38-13/76-37
ISBN 0-660-00987-0

Prix: Canada: \$2.25
Autres pays: \$2.70

Prix sujet à changement sans avis préalable.

IMPURITY LIMITS FOR CAST COPPER ALLOYS -
A LITERATURE SURVEY OF TIN BRONZES

by

A. Couture*

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SUMMARY

This literature survey is part of a larger project whose (main) objective is to determine if the existing specifications regarding the maximum impurity contents allowed in cast copper alloys, are adequate or too stringent. The present survey is however limited to tin bronzes. The effects of impurity elements on the properties of these alloys are surveyed, an analysis is made of the ISO, ASTM and BS specifications and the methods used to remove (or neutralize) such impurities are summarized.

The elements covered are: aluminum, antimony, arsenic, bismuth, carbon, iron, lead, magnesium, manganese, nickel, phosphorus, silicon and sulphur. Many inconsistencies were found as to the compositional levels above which these elements become harmful, particularly when several such elements are present together. As materials recycling becomes mandatory for energy and economic reasons, the importance of specifying impurity limits which are neither too loose nor too stringent cannot be over-emphasized.

* Research Scientist, Physical Metallurgy Research Laboratories, Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources, Ottawa, Canada.

TENEUR MAXIMALE EN IMPURETES DES ALLIAGES
CUIVREUX DE FONDERIE - REVUE DE LA DOCUMENTATION
SUR LES BRONZES A L'ETAIN

par
A. Couture*

- - -

RESUME

Cette revue de la documentation fait partie d'un projet d'études entrepris en vue d'accroître, si possible, la teneur maximale en impuretés, permise par les normes, pour les alliages cuivreux de fonderie; le présent rapport ne traite toutefois que des bronzes à l'étain. L'auteur essaie de déterminer l'influence de ces éléments sur leurs propriétés, fait une analyse et une comparaison critiques des normes internationales (ISO), américaines (ASTM) et anglaises (BS), et présente un résumé des méthodes employées pour purifier le métal, le cas échéant.

Les éléments touchés par cette revue sont les suivants: l'aluminium, l'antimoine, l'arsenic, le bismuth, le carbone, le fer, le plomb, le magnésium, le manganèse, le nickel, le phosphore, le silicium et le soufre. On verra que les travaux consultés sont loins d'être toujours d'accord quant à l'influence de ces éléments. Vu que le recyclage est devenu une nécessité économique et énergétique, il est impératif de soumettre ces éléments à des normes qui sont assez restrictives, sans l'être à l'excès.

* Chercheur scientifique, Laboratoires de recherche en métallurgie physique, Centre canadien de la technologie des minéraux et de l'énergie, Ministère de l'énergie, des Mines et des Ressources, Ottawa, Canada.

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1. INTRODUCTION

Products have to conform to an ever-increasing number of standards or specifications of all kinds: strength, size, finish, conductivity, etc. In many cases such standards or levels of reliability (taken in its widest interpretation) cannot be reached and maintained if the chemical composition of the base material is not carefully controlled. Specifications for the chemical composition of metal products traditionally are of major importance, and products are accepted or rejected on this basis. Standards are revised from time to time to take advantage of new knowledge or new technology. Standards may be too loose to define the exact compositions which must be maintained to meet corresponding mechanical property requirements. Alternatively, the standards may be too rigorous for routine or light-duty applications, thus unnecessarily increasing costs. In some instances, composition limits may be set by tradition or custom as can be seen by comparing various national standards.

Certain elements, which are purposely added in one class of copper alloys, are to be avoided as impurities in another class of copper alloys (this is not confined to copper alloys). For example, lead is limited to a maximum of 0.3% in ASTM alloy #905 (1A)* whereas in alloy #937 (3A) its upper limit is 11.0%. However, the most striking example is aluminum which is very detrimental to the properties of tin bronzes and is best kept under 0.005%, whereas the aluminum content of aluminum bronzes can be as high as 11.5%. Similar comments can be made about silicon, iron, nickel, manganese, phosphorus, etc.

* The ASTM (American Society for Testing and Materials) specifications refer to those found in Part 6 of the 1975 Annual Book of ASTM Standards (unless otherwise indicated); the BS (British Standards) specifications to BS 1400:1973, and ISO (International Standards Organization) specifications to Draft International Standard ISO/DIS 1338:1976. Alloy numbers correspond to the new ASTM designations and the designation previously used is given in brackets.

Depending upon the alloy concerned, this apparent discrepancy can be explained in a number of ways. For instance, the presence of lead is highly desirable in bearing alloys because of its properties as a solid lubricant and self-alignment characteristics, but it is undesirable when tensile strength is an important factor because lead, as will be seen later, gradually weakens the structure. In the case of aluminum, the situation is different. Aluminum possesses a high affinity for oxygen and therefore readily forms alumina skins during the pouring operations and in the mould. In long-freezing range⁽¹⁾ alloys, such skins may become trapped between grains and then cause regions of discontinuities which are extremely detrimental to tensile strength, elongation, pressure-tightness, etc. However, in aluminum and manganese bronzes where the freezing range⁽¹⁾ is, relatively speaking, very short, alumina skins tend to float out into areas of the castings (like risers) where their presence is not detrimental. Therefore, aluminum can play its full role as an alloying element in the latter class of alloys, but has to be avoided in the former. Similar explanations can be applied to other elements which are beneficial in some alloys and detrimental in others.

This review deals only with cases where certain elements are considered as impurities and not as alloying elements. Copper alloys can become contaminated in a number of ways of which the following are only a few examples: the use of contaminated scrap in the charge; improper segregation of the various alloys in foundries where several alloys are cast; accidental contamination of the melt; use of contaminated stirring or skimming equipment, furnace or crucible lining, sand, etc., etc.

Another area where the amount of unwanted elements is important is that of recycling which is vital to the conservation of our resources. One of the main problems in the recycling of secondary metals is that of contamination by foreign substances or by other alloys containing elements which are undesirable when the end product is considered. The removal of such contaminants is expensive in terms of time, money and energy and is usually accomplished in one or more of the following ways:

1. prior analysis or identification and sorting by a variety of means ranging from hand picking to heavy media separation;
2. blending and/or dilution so that the impurities are below the maxima for the particular alloy;
3. chemical or possibly other treatment of the bath to remove impurities;
4. in special cases, heat treatment or alloying to render the impurity innocuous.

It follows that if a given product can tolerate a higher percentage of impurities than the current specifications permit then appreciable savings can be realized.

This research was therefore undertaken with the purpose of determining if the impurity limits now imposed by specifications to copper casting alloys are realistic or unduly strict, and, to study the possibility of neutralizing such impurities by proper additions or treatments.

Because of the large number and variety of copper casting alloys, this study has been limited, at least for the present, to tin bronzes and gunmetals.

As a first step, it was thought necessary to conduct a literature survey on the influence of impurities on the properties of these alloys to see if the present specifications are consistent with the findings of investigators who worked in these areas.

2. ALUMINUM

2.1. Influence on Properties

Aluminum is a very harmful impurity in all types of tin bronzes. It forms aluminum oxide which is insoluble in the molten alloy and exists as tough films or skins. These films impair fluidity and channel feeding in the last stages of solidification and, therefore, promote micro-porosity and reduce pressure-tightness. Furthermore, these oxide skins act as planes of weakness between the grains, resulting in a loss of mechanical properties.

Although P. J. LeThomas⁽²⁾ says that alumina films are seen at as low an aluminum content as 0.025%, aluminum is detrimental to both pressure-tightness and mechanical properties at much lower contents. LeThomas claims that sand castings are not pressure-tight as soon as aluminum exceeds 0.005%. Gardner and Saeger⁽³⁾ found that the addition of 0.005% Al to #836 (4A) gunmetal reduced the tensile strength and elongation by 2 to 12 kpsi* and 5 to 40% respectively. When 0.025% Al was present, reductions of 10 to 14 kpsi and 20 to 40% respectively, were recorded.

Winterton⁽⁴⁾ cast sticks (12 in. long x 1 in. diam) in a cast iron mould dressed with resinous aluminum paint. The addition of 0.005% Al to the following alloys: Cu-10.5% Sn, 0.75% P, #905 (1A), #836 (4A) and Cu-7% Sn, 2% Pb, 5% Zn, reduced the tensile strength and elongation by 10 to 15% and 10 to 45% respectively. Reductions of 20 and 70% respectively were observed in the only case where the aluminum content was 0.1% (Cu-10.5% Sn, 0.75% P).

In Larsson's⁽⁵⁾ experiment with DTD test bars and pressure discs cast in Cu-6% Sn, 5% Pb, 6% Zn, it is reported that the proportion of pressure-tight discs was 42% when less than 0.005% Al was present and only 4% with 0.01% Al. With 0.02% or 0.2% Al no disc was pressure-tight. Similarly, 0.01 and 0.02% Al reduced the tensile strength by 8 and 12% respectively, and

* 1 kpsi = 7/N/mm²

the elongation by 15 and 40% respectively.

Hanson and Pell-Walpole⁽⁶⁾ report that, in chilled castings, very small amounts (0.02%) of aluminum seriously reduce the strength and elongation, the effect being greatest in those bronzes which are normally very fluid (high-phosphorus or high-lead bronzes) and least in lead-free zinc bronzes. The upper limit proposed for the aluminum content is 0.005% for the phosphorus, tin and lead bronzes and 0.01% for zinc bronzes (Table 1).

Hudson and Hudson⁽⁷⁾ suggest a limit of 0.005% Al to obtain maximum quality in gunmetal castings produced under the least favourable conditions (Table 2).

2.2 Specified Limits

The ASTM specifications for ingots give a maximum aluminum content of 0.005% and this has remained the same for at least thirty years. Specifications for castings give a maximum aluminum content of 0.005% whereas thirty years ago there was no specified maximum. This is much stricter than the ISO and BS specifications which allow a maximum of 0.01% for both gunmetal ingots and castings; under rounding-off rules, this could be the equivalent of 0.014% Al. It appears that a maximum aluminum content of 0.01% is overly generous. The maximum of 0.005% allowed by the ASTM specifications seems to be reasonable, although investigators have found that even this amount can be highly detrimental.

2.3 Removal

It is fortunate that the most detrimental impurity in tin bronzes can be readily oxidized. This is most effectively carried out by the use of an oxidizing agent which converts aluminum into alumina, and, in combination with certain fluorides, a slag cover is formed which will dissolve and remove the unwanted oxide⁽⁸⁾. The following chemical compounds will provide the

necessary oxygen: manganese dioxide, potassium permanganate, sodium nitrate, sodium sulphate and calcium sulphate⁽⁹⁾.

Glassenberg, Mondolfo and Hesse⁽¹⁰⁾ found that a bronze ($3\frac{1}{2}\%$ Sn, $3\frac{1}{2}\%$ Pb, 9% Zn), which had been intentionally loaded with impurities, could be purified by bubbling air or oxygen through the bath at 1150°C , but this is a long process. Although the oxidizable impurities are removed simultaneously, they are oxidized at different rates. The following elements are listed according to their decreasing rate of elimination: aluminum, manganese, silicon, phosphorus, iron and zinc. However, nickel, lead, tin, antimony and sulphur were not affected in their experiments.

Blanc and LeThomas⁽¹¹⁾ were relatively successful by vigorously stirring into the bath potassium nitrate and manganese oxide singly or in combination at 1200°C .

Hanson and Pell-Walpole⁽⁶⁾ were able to reduce the aluminum content of tin bronzes from 0.10% to 0.002% by melting under a flux consisting of 33% copper oxide, 33% sand and 33% borax, the amount of flux being 4% of the charge.

Tyrie⁽¹²⁾ recommends the use of barium sulphate to remove aluminum, barium peroxide to remove aluminum and antimony, and cupric oxide to remove aluminum, antimony, arsenic and zinc.

Larsson⁽⁵⁾ tested a number of slag types of which the following mixture was the most efficient although other types were also good⁽¹³⁾: 30% sodium fluoride, 20% calcium fluoride, 20% cryolite, 20% sodium sulphate and 10% sodium carbonate. Adequate agitation of the bath was necessary and the treatment was more efficient at high temperature. In Cu-6% Sn, 5% Pb, 6% Zn gunmetal, an amount of slag equal to $1\frac{1}{2}\%$ of the charge reduced the aluminum content from 0.3% to less than 0.01% in 10 min. In modern practice, slag treatments are often combined with air blowing⁽¹⁴⁾.

Muller and Buchen⁽¹⁵⁾ found that chlorine bubbling reduces the magnesium, aluminum, manganese, zinc, iron, lead and silicon contents.

A wide variety of other refining techniques, mentioned by Versagi⁽¹⁶⁾, are shown in Table 3.

2.4 Comments

As would be expected from Ellingham's diagrams⁽¹⁷⁾ showing the change with temperature of the free energy of formation of oxides from their elements, aluminum is readily removed by oxidation techniques which, in general, require some form of fluxing action in order to collect and subsequently remove the aluminum oxide formed. It will be appreciated, however, that because of the relatively small amount of aluminum present (less than 0.005% to meet specifications) there is a partition coefficient effect, and other desirable elements such as copper, tin and zinc may also be removed, with attendant economic loss.

3. ANTIMONY

3.1 Influence on Properties

It would appear that the main influence of antimony is to increase the amount of delta in the structure⁽¹⁸⁾, thus making the alloy harder and more brittle. According to Loiseau, Lemoine and Picard⁽¹⁹⁾, 0.5% Sb is equivalent to 1% Sn as far as the delta-forming tendency is concerned.

Gardner and Saeger⁽³⁾ found that additions of 0.1, 0.15, 0.20 and 0.25% Sb to #836 (4A) bronze had little influence on the tensile strength, ductility, hardness and porosity, and caused a slight increase in electrical resistance and fluidity. They claim that it is not harmful to the pressure-tightness.

Smith and Bolton⁽²⁰⁾ claim that up to 0.4% Sb, per se, is not detrimental to the physical properties at room or elevated temperature (290°C) (557°F) of steam or valve bronze - #922 (2A).

Tests conducted by Reichelderfer, Gonser and Blalock⁽²¹⁾ on ASTM Crown Type test bars of #905 (1A), #903 (1B) and #937 (3A) bronzes showed that the addition of up to 0.5% Sb did not affect

the ultimate strength, yield strength nor elongation of any alloy. The hardness and impact strength of both #905 and #903 bronzes were not affected, but the hardness and deformation resistance of #937 bronze were increased by antimony additions. The effect of antimony on the impact strength of #937 was not determined. The addition of up to 0.5% Sb did not have any harmful effects on the casting characteristics of these bronzes and it did not increase their tendency toward gassing or segregation. Tensile tests at elevated temperatures - up to 260°C (500°F) - on these alloys were extended only to 0.3% Sb. The mechanical properties were little affected by varying antimony contents.

Eggenschwiler⁽²²⁾ added up to 0.58% Sb into #937 (3A) bronze sand castings and found that antimony decreased the Izod impact values, the decrease with increasing antimony content being greater at room temperature than at elevated temperature. Deformation under pounding decreased when the antimony content was present to the extent of 0.2 or 0.58%. The addition had no effect on the size or distribution of lead particles but produced a slight increase in the size of the delta constituent and slightly increased the hardness of the alloys.

LeThomas and Arnaud⁽²³⁾ found that up to at least 0.4% antimony had no influence on the mechanical properties of the following tin bronzes: #908, #905 (1A), #836 (4A) and a composition close to that of #932 (3B).

Rolfe⁽²⁴⁾ says that in sand-cast gunmetal, the effect of a progressive increase in antimony is a decrease in strength and ductility and the maximum permissible amount appears to be 0.75%.

Stolarczyk et al⁽²⁵⁾ estimated that the presence of 0.3-0.5% Sb in #905 (1A) could decrease the tensile strength by 1 kpsi and the elongation by 5%, while 0.5% Sb would reduce these properties by 2 kpsi, or 10% elongation in a columnar structure. The addition of 0.1% Sb in a coarse equiaxial structure and of 0.25% in a fine equiaxial structure of #836 (4A) bronze reduces

the tensile strength by 1 kpsi and the elongation by 5%; 0.4% Sb with a columnar or fine equiaxial structure or 0.25% with a coarse equiaxial structure reduces the properties by 2 kpsi or 10%, respectively. These results are for sand-cast test bars as the effect of individual impurities on the properties of plate castings was not determined. The presence of up to 0.5% Sb did not affect the pressure-tightness or hot-tearing susceptibility of these alloys.

According to Winterton⁽⁴⁾, the influence of antimony on the mechanical properties is much more pronounced than other investigators have found. This is perhaps surprising in that his tests were made on bars machined from 1-in. diameter sticks cast in cast iron moulds. However, the effect of 0.1% Sb was tested only in Cu-10.5% Sn, 0.2% P and the losses of tensile strength and elongation were 12 and 33% respectively; 0.5% Sb gave the same results. The addition of 0.2% Sb to #905 (1A) and #903 (1B) - only alloys tested - reduced the tensile strength and elongation by 20 and 60% respectively. Increasing the antimony content of #905 (1A) to 1% did not cause any further decrease. Winterton's results indicate that the alloys with the highest tin equivalent are in general the most affected by the presence of antimony, and that the influence of antimony is more marked on the elongation than on the tensile strength.

Hanson and Pell-Walpole⁽⁶⁾ found that, in chill-cast phosphorus bronze and low-tin leaded bronzes, the tensile strength is diminished very slightly by up to 1% Sb, but that, in high-tin bronzes and gunmetals, an appreciable weakening (4 to 6 kpsi) is produced by as little as 0.2% Sb, whereas higher contents have little further effect. The elongation is appreciably reduced as the antimony content increases in all types of bronzes. They add that these effects are in agreement with the observed increase in the amount of alpha-delta eutectoid produced by antimony. This increase weakens only those bronzes which already contain sufficient delta to form semi-continuous intercrystalline

films. Bronzes with only isolated areas of eutectoid are not much weakened, although their ductility is reduced. Antimony does not affect fluidity or the residual oxygen content; it only increases the amount of delta. Their suggested antimony limit for chill castings is 0.05% for high-tin bronzes and zinc bronzes and 0.5% for phosphorus bronzes and low-tin bronzes (Table 1).

Hudson and Hudson⁽⁷⁾ claim that, to obtain maximum quality under least favourable conditions, the safe antimony limits for gunmetal castings are 0.05% for #905 (1A) and 0.10% for leaded gunmetals (Table 2).

3.2 Specified Limits

The maximum antimony content allowed by the ASTM specifications for ingots has remained either unchanged over the past thirty years or has been lowered by 0.05%, with two exceptions. The limit was raised from 0.25 to 0.30% in #935 (3C) and lowered from 0.75 to 0.50% in #938 (3D). The latter is somewhat anomalous in that the maximum level for castings has been increased to 0.8%.

ASTM specifications for castings thirty years ago did not give limits for antimony for any tin bronze with the exception of the high-leaded bronzes. The maximum antimony content remained the same for #937 (3A), #932 (3B) and #935 (3C) and was raised by 0.05% to 0.8% in #938 (3D) and #943 (3E).

Where the ASTM, BS and ISO specifications can be compared (Appendix "B") the antimony limits are practically the same with the following exceptions: #935 (3C) where it is 0.30% in the ASTM and 0.5% in BS and ISO specifications, #938 (3D) castings where it is 0.8% in the ASTM and 0.5% in the ISO specifications, and #905 (1A) where the maximum is 0.20 and 0.3 in the ASTM and ISO specifications respectively.

The maximum antimony content allowed by both the ASTM and ISO standards for #836 (4A) bronze is 0.25% although its tin equivalent⁽¹⁹⁾, which is a measure of the delta-forming tendency

of the alloy, is only 7½% compared with 11% for #905 (1A) which has the same antimony limit. On this basis, the limit for #836 bronze is too strict and might safely be raised to a maximum of 0.5%.

Another complicating factor is the influence of grain size on the formation of delta. It was reported in earlier work⁽²⁶⁾ that the delta phase is more concentrated at grain boundaries in fine-grained than in coarse-grained structures of the same alloy. This is in agreement with Cibula's⁽²⁷⁾ observation that intergranular eutectoid films, which cause a drastic reduction in ductility, are most pronounced in the alloys of the finest grain size at a given tin content. He adds that such films were not observed when the tin content was 10% or less in the coarse-grained alloys and 8% or less in the fine-grained. It would therefore seem that antimony is more likely to be detrimental in alloys with a higher tin content.

3.3 Removal

It would appear that the removal of antimony below 0.35% is not practicable⁽¹⁶⁾, although Tyrie⁽¹²⁾ claims that aluminum and antimony can be removed by barium peroxide. Hanson and Pell-Walpole⁽⁶⁾ had little success (a reduction from 0.34 to 0.29%) by melting under a flux consisting of 50% cupric oxide, 25% sand and 25% borax, and Glassenberg, Mondolfo and Hesse⁽¹⁰⁾ found that air and oxygen bubbling did not reduce the antimony content of a tin bronze which contained 0.12% Sb.

3.4 Comments

There is some controversy regarding the harmful effects of antimony as an impurity, and its permissible levels in different alloys. This is probably a function of the amount and distribution of delta phase (tin content) and the lead content since there may be some partition of antimony between the two. It is likely that some of the deleterious effects noted could be negated by deliberately lowering the tin content

if the antimony content was known to be high.

The most common source of antimony is secondary lead derived from battery scrap. This source of contamination may decrease in the future with the advent of the "zero maintenance" automotive battery utilizing 'calcium lead'.

4. ARSENIC

4.1 Influence on Properties

The effect of arsenic in tin bronzes is very similar to that of antimony; it increases the amount of alpha plus delta eutectoid, thus making the alloy harder and more brittle. According to Loiseau, Lemoine and Picard⁽¹⁹⁾, its delta-forming tendency is the same as that of antimony, 0.5% As being equivalent to 1% Sn.

Two early investigators, Johnson⁽²⁸⁾ and Rolfe⁽²⁹⁾, disagree as to the effect of arsenic on the mechanical properties of #905 (1A) bronze. In an experiment of limited scope, Johnson, who tested the influence of up to 0.94% As, claims that arsenic improves the elongation. Rolfe, on the contrary, found that arsenic is detrimental. He claims that in sand-cast gunmetal the effect of a progressive increase in arsenic is a decrease in strength and ductility and that the maximum permissible amount is 0.3%⁽²⁴⁾

Winterton⁽⁴⁾ found that arsenic is detrimental to the mechanical properties of chill-cast tin bronzes but not to the same extent as antimony. However, the effect was similar in Cu-10.5% Sn, 0.75% P and #836 (4A) bronzes.

According to Stolarczyk et al⁽²⁵⁾, arsenic has a detrimental effect on both #905 (1A) and #836 (4A) sand-cast test bars. The amount of arsenic required to reduce the UTS by 1 kpsi and/or 5% elongation in #836 is at least 0.6% with both columnar and fine, equiaxial structures, whereas a similar decrease is produced

by approximately 0.2% As in a coarse, equiaxial structure. In the case of #905 the amount of arsenic for a similar reduction with a columnar structure is 0.3%.

Hanson and Pell-Walpole⁽⁶⁾ found that in chill-cast high-phosphorus bronze and Admiralty gunmetal, 0.5% As produced an appreciable decrease in strength (4 kpsi) but, in other compositions, notably in leaded bronzes, only a very slight decrease in strength occurred with up to 1% As. Elongation was appreciably reduced by arsenic in all bronzes except the high-lead compositions.

In an attempt to explain why arsenic is apparently more detrimental in #905 (1A) than in #836 (4A), Hudson and Hudson⁽⁷⁾ say that arsenic increases the amount of eutectoid in #905 and apparently not in #836 and that arsenic must therefore combine with the lead constituent where its presence is less innocuous. A more likely explanation would be that arsenic increases the amount of eutectoid in both alloys but, because there is little eutectoid in #836 (with 5% Sn), a small increase such as that caused by 0.5% As⁽¹⁹⁾ is less critical in #836 than in #905 (with 10% Sn).

Hudson and Hudson⁽⁷⁾, suggest that the maximum arsenic content to obtain maximum quality under least favourable conditions in gunmetal castings be 0.10% in #905 (1A), 0.20% in #836 (4A), and 0.10% in #844 (5A) (Table 2).

Hanson and Pell-Walpole⁽⁶⁾ suggest the following limits for chill castings: 0.1% As for high-phosphorus and high-tin bronzes and gunmetal, and 0.3% As for leaded bronzes (Table 1).

4.2 Specified Limits

Neither ASTM nor ISO specifications mention arsenic. The British Standards give a maximum (for iron + arsenic + antimony) of 0.20% and 0.50% for #905 and #836 respectively. It seems that arsenic is unlikely to be present alone, and iron is the most common contaminant. However, care must be exercised ,

particularly with #905 if antimony is also present, as both arsenic and antimony form delta phase.

4.3 Removal

The only reference which could be found regarding the removal of arsenic is by Tyrie⁽¹²⁾ who says that this impurity can be removed by the addition of cupric oxide.

4.4 Comments

In summary, it seems that arsenic behaves similarly to antimony in promoting delta formation and has similar effects on properties. However, it is a far less common impurity than antimony.

5. BISMUTH

5.1 Influence on Properties

Bismuth is practically insoluble in copper and occurs in the form of small globules of a light-blue colour probably consisting of almost pure bismuth⁽⁴⁾. These - like lead globules - tend to concentrate in the eutectoid and at the grain boundaries. In wrought alloys bismuth has a markedly deleterious effect, causing hot shortness.

All the chill-cast bronzes tested by Winterton⁽⁴⁾ are detrimentally affected to various degrees by the presence of bismuth. The level of bismuth varied from 0.14% in one alloy to 1.25% in another. In all cases, the influence of bismuth on the tensile strength is appreciable, causing a reduction of 5 to 12%; its effect on the elongation is much more inconsistent, going from a reduction of 60% to an improvement of 30%.

Stolarczyk et al⁽²⁵⁾ found that, in test bars under the least favourable conditions, the maximum bismuth content which caused a reduction of less than 2 kpsi in tensile strength, or 10% in elongation, or both, was less than 0.1% Bi in #905 (1A) and in #836 (4A). They also found that bismuth, in #836, was more detrimental with a columnar structure than with a

coarse- or fine-equiaxial structure.

Results obtained by Hanson and Pell-Walpole⁽⁶⁾ in chill castings indicate that, in high-tin bronze, phosphorus bronze and lead-free gunmetals, the tensile strength and elongation diminish rapidly as the bismuth content increases to 0.2%, but that higher contents have little further effect. In leaded alloys, however, the tensile strength diminishes only slightly and gradually as bismuth is increased to 0.5%, whereas the elongation does not appreciably change. It is proposed that, in lead-free alloys, bismuth acts as any other particle which would be located at the grain boundaries, whereas in leaded alloys, bismuth either dissolves in or forms a eutectic with lead which completely neutralizes its normal embrittling action. The authors recommend, for chill castings, a maximum of 0.05% Bi in all lead-free bronzes and of 0.3% in leaded bronzes (Table 1).

Hudson and Hudson⁽⁷⁾, (Table 2), suggest that the safe maximum bismuth content for gunmetal casting to obtain maximum quality under least favourable conditions, be 0.02% for #905 (1A) and 0.05 for #836 (4A) and #844 (5A).

5.2 Specified Limits

The ASTM and ISO specifications do not mention bismuth, but the British Standards give a maximum bismuth content for both ingots and castings of 0.03% for 1A and of 0.05% for 4A. This corresponds very closely to the maxima suggested by Hudson and Hudson. Such limits appear to be too strict, particularly for sand-cast leaded bronzes.

5.3 Removal

The only reference found in the literature on the elimination of bismuth from copper alloys is the work of Muller and Buchen⁽¹⁵⁾ who had limited success with chlorine bubbling.

However, from what is said in the literature^(6,30) about the neutralization of bismuth by lead through the formation of a bismuth-lead eutectic, it seems that materials which are known

to be contaminated with bismuth should be reserved for the production of high-lead alloys.

5.4 Comments

Again, bismuth seems to be a relatively uncommon impurity. Some of the observed detrimental effects may be associated with hot-tearing in the lead-free alloys.

6. CARBON

6.1 Influence on Properties

Any carbon present in molten gunmetal may react with sulphur dioxide, to form carbon monoxide and carbon dioxide, and with oxygen during pouring operations to form carbon monoxide which will cause gas holes. Therefore, Hudson and Hudson⁽⁷⁾ suggest that the safe upper limit for carbon be 0.005% in gunmetals (Table 2).

It is highly unlikely that carbon is a source of trouble in normal tin bronzes which have for years been melted in crucibles containing graphite, under charcoal covers, etc. This may not be so with alloys containing quantities of elements with high-carbon solubilities (Fe, Ni, Mn) such as cupro-nickels and high-manganese-aluminum bronze, but these are outside the scope of this report.

6.2 Specified Limits

Carbon is not covered by any of the three specifications studied, i.e., ASTM, ISO and BS.

6.3 Removal

No references were found to the removal of carbon from tin bronzes.

It would seem that nitrogen degassing should entrain any graphite (the solubility of carbon in copper and copper alloys being extremely low), carbon monoxide or carbon dioxide present in the bath.

7. IRON

7.1 Influence

The solid solubility of iron in tin bronzes is about 0.2%. In excess of this amount it may exist either as star-like crystals of an iron-rich solid solution, as in gunmetal⁽¹⁸⁾ or as hard prismatic crystals of an intermetallic compound, probably Fe_2Sn , as in phosphor bronzes⁽⁶⁾. Another author⁽⁷⁾ suggests the possibility that the iron compound may also be iron oxide.

Gardner and Saeger⁽³¹⁾ studied the effect of 0.1 to 0.6% Fe in #836 (4A) and found that the tensile strength, hardness and electrical resistivity increased slightly with iron additions. The "fluidity" of the alloy was slightly increased at high temperatures up to an iron content of 0.3%, but decreased slightly above this content.

Johnson⁽²⁸⁾ found that the presence of 0.3% Fe improved the ultimate tensile strength and elongation of Admiralty gunmetal.

According to Stolarczyk et al⁽²⁵⁾, who determined the influence of up to 0.3% Fe in both #905 (1A) and #836 (4A) gunmetals, the maximum iron content which caused, in test bars cast under the least favourable conditions, a reduction in tensile properties of less than 2 kpsi, or 10% elongation, or both, was approximately 0.2% in both alloys. The pressure-tightness and fluidity of #836 was not affected by the addition of up to 0.3% Fe, and the hot-tearing resistance of both alloys was not affected either.

In Winterton's⁽⁴⁾ experiment on a number of bronzes cast in cast iron moulds, the effect of iron on the tensile strength was inconsistent; in some cases it improved the strength but in general it caused a slight reduction. The elongation was appreciably decreased in all cases.

Hanson and Pell-Walpole's results⁽⁶⁾ with chill-cast bronzes are as follows: in phosphorus bronzes, less than 0.3% Fe markedly

improves the strength and hardness without affecting the elongation; when larger amounts are present, the brittle iron-rich compound reduces the strength and ductility with little change in hardness. In gunmetals and leaded gunmetals, increasing the iron from 0 to 2% produces a gradual and continuous increase in strength and hardness with a corresponding decrease in elongation. In high-lead bronze, small additions of iron produce a notable and objectionable increase in hardness with a corresponding decrease in strength and ductility. They thus recommend, for chill castings, an upper limit of 0.3% Fe for tin and phosphorus bronzes, of 0.5% Fe for zinc and lead-zinc bronzes and of 0.1% Fe in leaded bronzes (Table 1).

According to Hudson and Hudson⁽⁷⁾, the iron compound in gunmetals is usually precipitated in a very finely divided state. It has been suggested that the tendency of the compound to form colonies may give rise to hard spots and difficulty in machining when the iron content exceeds 0.3%. Gunmetals containing more than this amount of iron also show a tendency to rust. They suggest that gunmetal castings of high quality should not contain more than 0.15% Fe and not more than 0.1% Fe when minimum magnetic susceptibility is required (Table 2).

LeThomas⁽²⁾ says that it is wise to keep the maximum iron content of tin bronzes at 0.2 to 0.3%. LeThomas and Arnaud⁽²³⁾ found that additions of up to 0.15% Fe did not affect the ultimate strength of 4A (#836) but had a disastrous effect on a 7% Sn- 6% Pb- 4%Zn bronze which had less than 0.25% Fe. However, in both cases, their results were very widely scattered.

7.2 Specified Limits

ASTM specifications for iron have changed little over the last thirty years with some relaxation of iron limits in a few instances.

Based on the above review it would appear that the ASTM, BS and ISO specifications for iron are realistic with the ISO being, as a rule, a little less strict than the others.

7.3 Removal

Glassenberg et al⁽¹⁰⁾ blew air or oxygen through a tin bronze melt with a high iron content of 1.23%. The method is time-consuming and not too efficient. Muller and Buchen⁽¹⁵⁾ were more successful with chlorine bubbling as, after a 50-min treatment, the iron content could be reduced from 1.63% to 0.10%. Hanson and Pell-Walpole⁽⁶⁾ reduced significantly the iron content of a phosphorus bronze (10% Sn, 0.75% P) by melting under a copper oxide/sand/borax flux. Other methods are summarized by Versagi⁽¹⁶⁾ in Table 4, and he adds that air is used in all cases, both as an oxidizing agent and as the means of agitation.

7.4 Comments

In summary, iron is the most common impurity in secondary copper alloy manufacture and occasionally occurs in amounts which require bath treatment by air blowing, usually in the presence of an oxidizing flux.

Iron has beneficial effects as a grain refiner in certain alloys, particularly in aluminum bronzes, and in increasing the strength. Indeed, over the past decade a new series of wrought copper-iron alloys containing up to 2.5% Fe has been developed for applications such as water tubes. On the negative side, iron is readily oxidized, and may give rise to difficulties with the inclusion of oxides. Iron, in high-tensile brasses, in the presence of boron and silicon,^(32,33) can form massive "hard spot" inclusions which have a disastrous effect on machine tools. It may well be that, in other alloys, dispersed iron-rich precipitates induced at high-iron levels also impair machinability (i.e., tool life) compared to low-iron materials.

While iron has been readily condemned as an impurity, there is a potential for utilizing its strengthening effect which has not been fully exploited. This may be important in the future when increasing amounts of contaminated copper are generated through increased recycling.

8. LEAD

8.1 Influence on Properties

Lead is almost insoluble in the solid copper alloys and occurs in the microstructure as dark globules⁽¹⁸⁾. The importance of lead as a major alloying constituent, especially to improve pressure tightness, is outside the scope of this review which is limited to its influence at the impurity level. Thus, the only bronzes considered here will be those tin bronzes which are essentially lead-free.

Johnson⁽²⁸⁾ and Rolfe⁽²⁹⁾ claim that up to 1% Pb does not affect appreciably the quality of #905 (1A) sand castings.

Colton, Turk and LaVelle⁽³⁴⁾ found that 0.25% Pb refines appreciably the structure of Cu-11% Sn bronze but that the effect on #905 (1A) and #903 (1B) is much less pronounced. Lead improves machining but its effect on other properties was not determined.

In Winterton's tests⁽⁴⁾ on chill-cast specimens, lead caused a gradual deterioration of the properties - particularly the elongation, which, in general, is much more seriously affected than the strength.

Hanson and Pell-Walpole⁽⁶⁾ also found a gradual reduction of tensile strength, elongation and hardness with increasing lead content, and say that lead is objectionable in wear-resistant bushes and gears; otherwise up to 1% Pb is harmless. They recommend a maximum lead content of 0.5% in tin and phosphorus bronze chill castings (Table 1).

8.2 Specified Limits

The maximum lead content varies between 0.20% for #910 alloy (15% Sn) to 0.50% for #907 alloy (11% Sn, 0.30% P max) in the case of the copper-tin ASTM alloys Nos. 902-917, but with the exception of #915. The lead content is limited to a maximum of 0.25% in all other cases where phosphorus is present. In British

standards lead is limited to 0.50% max in PB2 and to 0.25% in PB1 and CTI alloys. Lead is also treated as an impurity in some copper-tin-nickel bronzes in both ASTM and BS specifications and in proposed ISO specifications, and may be limited to 0.1, 0.5 and 0.3% max respectively. If these materials are to be heat treated it is necessary to keep the lead to much lower levels, say 0.01%, in order to avoid quench cracking. (Similar restrictions apply to weldable alloys such as aluminum bronzes for the same reasons). It would seem that the widely used North American alloy #905 (Cu-10% Sn, 2% Zn, 0.3% max Pb) has no exact European counterpart in that their alloys permit 1.5% max Pb.

8.3 Removal

Glassenberg et al⁽¹⁰⁾ found that air or oxygen bubbling did not affect the lead content of the alloy and this was confirmed by Stolarczyk et al⁽³⁵⁾. However, the latter found the phosphate and borate slag treatments rapid and effective. Others⁽³⁶⁾ were successful with sodium fluoride and other compounds. Hanson and Pell-Walpole could reduce the lead content of a tin bronze from 0.76 to 0.31 with a mixture consisting of 50% cupric oxide, 25% borax and 25% sand⁽⁶⁾. Chlorine bubbling can also reduce the lead content of tin bronzes⁽¹⁵⁾.

8.4 Comments

In summary, lead is known to have a detrimental effect on hot shortness and for that reason must be avoided in castings which are to be stressed at temperatures in excess of the melting point of the lead phase (~ 325°C) such as in quenching or welding. Similarly, it may lead to increased deformation in bushings, etc., because of its softness.

On the positive side, lead has a marked beneficial effect on pressure tightness, is a solid lubricant, and improves machinability. The tin bronzes are notoriously difficult to cast sound, and since lead is the last constituent to freeze, it normally occupies areas which would otherwise be shrinkage cavities.

Since its strength is not less than that of a cavity, it is difficult to see how it could be detrimental in normal use, except under the circumstances noted. The above reasoning probably accounts for the European trend to avoid lead-free alloys except for phosphor bronzes and the increasing use of alloys such as BS 1400 LG4 (7% Sn, 2.5% Zn, 3% Pb) for applications for which, in North America, alloys #903 or #905 would be used. Thus, although the above two alloys form only a small fraction of the total, there would appear to be justification for increasing the permissible lead content.

9. MAGNESIUM

9.1 Influence on Properties

The solubility of magnesium in copper is 2.6% at 700°C, 1.2% at 400°C⁽³⁷⁾, and certainly much lower at room temperature and in bronzes.

Although magnesium is claimed to be detrimental to the properties of bronzes and likely to be so in tin bronzes⁽⁷⁾, there was no evidence of such an effect in grain-refined #905 (1A), #937 (3A) and #836(4A)⁽²⁶⁾ where magnesium was added to tie up sulphur in zirconium-refined alloys. The residual magnesium was as high as 0.16%. However, Cibula⁽³⁸⁾ claims that excessive magnesium additions (0.2%) made the metal stream sluggish.

Hudson and Hudson⁽⁷⁾ suggest that the safe maximum magnesium content to obtain maximum quality in tin bronzes be 0.005% (Table 2).

9.2 Specified Limits

The ASTM, ISO and BS specifications do not give limits for magnesium in tin bronzes.

9.3 Removal

Magnesium can be removed by chlorine bubbling⁽¹⁵⁾ and presumably by the same processes which are effective in removing aluminum. Magnesium also has a relatively high vapour pressure, boiling at about 1110°C. Hence, it would be expected to be removed on long standing of the melt, or by diffusion into gas bubbles during operations such as nitrogen degassing.

9.4 Comments

It may be noted that magnesium is commonly used as a deoxidizer (together with other elements) for high-nickel-copper alloys and has been suggested for materials such as aluminum bronze. Coupled with its ability to remove sulphur^(26,38), it would seem that its potential for treating copper alloys has not been fully explored.

10. MANGANESE

10.1 Influence on Properties

Appreciable amounts of manganese are soluble in copper and copper alloys, and this element is another example of elements which are intentionally added in certain copper alloys and avoided in others. Manganese tends to form manganese oxide and is thus claimed to be objectionable in tin bronzes.

References to the influence of manganese on the properties of tin bronzes are very few. LeThomas⁽²⁾, who surveyed the literature in 1955, came to the conclusion that, in tin bronzes, 0.1% Mn causes a loss of elongation of 10%, and 0.2% Mn a loss of ultimate tensile strength of 10%. From the point of view of pressure-tightness, its influence is of the same nature as that of aluminum, but to a smaller extent.

In Winterton's⁽⁴⁾ study with chilled castings, the influence of manganese was rather erratic. In leaded bronzes the effect of 0.1 to 0.2 Mn was not pronounced, in general. However,

in lead-free bronzes, the addition of manganese was, in general, very detrimental to both the tensile strength and elongation. On the other hand, it is difficult to understand why the presence of 0.01% Mn in Cu-12% Sn-0.2% P bronze would reduce the tensile strength by 11% while 0.05% Mn would restore it to its original level.

Thews⁽³⁹⁾ claims that up to 0.02% Mn in a Cu-10% Sn bronze improves the ultimate tensile strength and elongation without affecting other properties.

Hanson and Pell-Walpole⁽⁶⁾ tested chilled castings and found that up to 0.1% Mn produces an appreciable reduction of strength and elongation in phosphorus bronzes and in Admiralty gunmetal with a corresponding increase in porosity. In leaded bronzes, up to 0.2% Mn had no appreciable effect on these properties. They conclude that manganese is objectionable, if more than 0.01% is present in high-grade chill-cast phosphorus bronzes and lead-free gunmetals, while, in leaded bronzes, it is not seriously detrimental in amounts up to 0.2%.

In 1967, Hudson and Hudson⁽⁷⁾ stated: "Until the effect of manganese is more fully understood, the incidence of this element in gunmetal castings of high quality should be looked upon with suspicion, and its presence limited to 0.01% in lead-free alloys and probably 0.1% in leaded gunmetals".

10.2 Specified Limits

It is interesting to see that, in spite of the possible detrimental influence of this element, the ASTM and BS specifications do not mention manganese for gunmetals, but only for yellow brasses and some of the special alloys such as those containing silicon and nickel. The ISO specifications give a maximum of 0.2% for many of the tin bronzes.

10.3 Removal

Manganese can be removed by oxidation. Glassenberg et al⁽¹⁰⁾ were successful in removing manganese from tin bronze by air or

oxygen bubbling. They could reduce the manganese content from over 0.1% to 0.01% in 30 min with oxygen. Chlorine bubbling can also be used⁽¹⁵⁾.

10.4 Comments

The effect of manganese as an impurity seems to be poorly established and detrimental effects might be associated with possible interaction with phosphorus in phosphor bronzes and the formation of manganese oxide films or inclusions in other materials. Manganese contamination may arise from treatment by fluxes containing manganese, from the traditional manganese bronzes (high tensile brasses) and aluminum bronzes containing, say 3% Mn, and from the newer manganese-aluminum bronzes containing about 12% Mn. Assuming that these latter materials will be well segregated, and because of the relatively high oxidation potential of manganese, it is not anticipated that manganese will be a major problem to the secondary ingot maker or the foundryman.

11. NICKEL

11.1 Influence on Properties

Nickel increases the amount of eutectoid in tin bronzes⁽¹⁸⁾ and, in some cases, at higher nickel levels and particularly in the presence of lead, a nickel-rich phase was seen in such alloys⁽⁴⁰⁾.

Winterton⁽⁴⁾ found that 1% Ni in #905 (1A), #903 (1B) and in Cu-7% Sn, 5% Zn, 2% Pb alloy has no effect on the properties. This applied to up to 2.5% Ni in #836 (4A).

Hanson and Pell-Walpole⁽⁶⁾ conclude that less than 1% Ni has little effect on any property, but 1 to 2% produces a definite improvement in tensile strength, which is most marked in fluid phosphorus and leaded bronzes and rather less in #905 (1A). Their suggested upper limit for chill castings is 2%. They say that their results confirm that small amounts of nickel are beneficial in chill-cast bronzes but that its effects are not so marked as in sand-cast bronzes.

Townsend, Lloyd and Bates⁽⁴¹⁾ found that when 2% Ni is added to leaded gunmetals, the level of tin at which a brittle phase appears is reduced.

There have been many claims⁽⁷⁾ related to the deliberate addition of nickel to tin bronzes. These include increased pressure tightness, grain refinement, improved properties in heavy sections and better lead distribution. However, the arguments are not sufficiently convincing to warrant deliberate nickel additions to bronze unless this is done in association with the tin content to give increased strength and hardness because of increased eutectoid⁽¹⁸⁾ (or the nickel-rich equivalent). It may be noted that as the nickel content of the alloy increases, so does the hydrogen solubility in the liquid state.

11.2 Specified Limits

The 1975 ASTM specifications give a maximum of 1% for all tin bronzes, whereas the ISO allow as much as 2%. It seems that the limit of 1% could be raised, if not with advantage, at least without disadvantage.

11.3 Removal

Air or oxygen bubbling⁽¹⁰⁾ and chlorine bubbling⁽¹⁵⁾ did not alter the nickel content of tin bronzes. No other references were found on this subject. At the present specified levels, nickel can usually be accommodated by dilution and blending. An alternative approach at nickel levels between 1 and 2% would be to deliberately lower the tin content towards the bottom of the specification range. Nickel constitutes "cheap tin" in terms of delta formation.

12. PHOSPHORUS

12.1 Influence on Properties

Phosphorus is added to tin bronzes as a deoxidant and excess phosphorus over and above that required for deoxidation of the melt increases the degree of metal-mould reaction. This gives rise to gases which increase the amount of porosity in

the castings and thus decrease the mechanical properties, although under certain circumstances limited metal-mould reaction can improve the properties of the castings by forming distributed porosity rather than concentrated shrinkage porosity. The levels of phosphorus required to deoxidize these alloys do not give rise to a separate phase. Other work⁽¹⁸⁾ has clearly established that as little as 0.1% P in #905 (1A) bronze caused the appearance of a separate phase -- probably Cu_3P -- which at that phosphorus level is associated with the alpha + delta eutectoid. Phosphorus is also claimed to increase the amount of eutectoid⁽⁴²⁾.

Colton and Loring⁽⁴³⁾ found that phosphorus improves the properties of sand cast #903 (1B) to a maximum reached at 0.01% P for the specific gravity and Charpy impact and at 0.02% for the ultimate strength, yield strength and elongation.

Pell-Walpole⁽⁴⁴⁾ claims that phosphorus decreases the solidus temperature more than any other element added in similar amounts. He refers to high- and medium-phosphorus contents of 0.75 and 0.35%.

It is claimed⁽⁴⁵⁾ that, in the production of each casting, there is an optimum phosphorus content below which oxygen will be present in the melt and may give rise to steam unsoundness, and above which hydrogen pick-up in the mould cavity will give rise to hydrogen unsoundness. A residual phosphorus content of 0.02 to 0.03% has been considered optimum in sand-cast gunmetal test bars with the minimum of metal mould reaction. A level of 0.03 to 0.05% P is useful for the production of small gunmetal valve bodies. The optimum phosphorus content in 2- and 3-in. thick sections of #836 (4A) seems to be approximately 0.015% but in thicker castings the optimum content is probably 0.005 to 0.01%⁽⁴⁶⁾.

The influence of phosphorus on the properties of chill-cast gunmetals was also studied by Winterton⁽⁴⁾ who showed improved mechanical properties because of improved feeding properties in #836 (4A) and in Cu-7% Sn, 2% Pb, 5% Zn bronzes for

phosphorus contents of 0.1% or higher.

Hanson and Pell-Walpole⁽⁶⁾ found that in slowly poured chill-cast gunmetals, phosphorus in amounts of 0.05 - 0.075% produces an increase in tensile strength of from 4 to 8 kpsi and an increase in elongation which is greatest in the ductile low-tin bronzes. They conclude that "in chill-cast as distinct from sand-cast gunmetals, phosphorus is definitely beneficial, and it should be added intentionally in amounts sufficient to secure a residual phosphorus content of 0.05 to 0.075%". Phosphorus in these amounts improves the soundness of chill castings and there is no evidence that it damages the useful properties of the alloys in any way. In leaded bearing bronzes, 0.05% P increases the wear resistance and resistance to pounding while having little effect on hardness or toughness.

In phosphor bronzes, phosphorus is deliberately added to improve strength and wear resistance, with some loss of ductility at higher phosphorus levels. Because of the very high cooling rates and fine constituent size, which maintains ductility, over 1% P is commonly added to a wide range of continuously cast alloys as these are often used for bearing stock.

12.2 Specified Limits

The limits for phosphorus for the various alloys vary widely from say 0.02% max for some ingots to 1.5% max for continuous castings in the same alloy. A similar situation exists for sand casting where it is left to the discretion of the founder whether he adds phosphorus in small quantities (say 0.02%) as a deoxidizer, or at say 0.25%, where some strengthening might be anticipated. British standards permit 0.1% max P for leaded gunmetals but more stringent limits of 0.02 or 0.05% are said to be preferred for chill castings. As chill castings would have a finer structure, the reason for this additional limitation is not known.

In all cases the existing phosphorus limits are quite adequate for effective deoxidation.

12.3 Removal

Air or oxygen bubbling⁽¹⁰⁾ reduces the phosphorus content appreciably and so does the chlorine treatment⁽¹⁵⁾. Hanson and Pell-Walpole⁽⁶⁾ could reduce by 0.5% an initial phosphorus content of 0.8% with a flux consisting of 50% of copper oxide, with sand and borax.

In the author's experience, it was found that phosphorus was rapidly lost during heating or holding the metal in an induction furnace. In numerous experiments where half of the molten metal was poured and the other half was returned to the furnace for some other treatment, it was found that, to keep the residual phosphorus in the second half to the same level that it was at in the first half, approximately 3 oz of Cu-15% P master alloy had to be added to 150 lb of metal in #905 (1A), #937 (3A) and #836 (4A)⁽²⁶⁾ i.e., ~ 0.02%. In other experiments where no such addition was made, the residual phosphorus content dropped from 0.026 to 0.006%. In all these experiments, however, nitrogen was blown through the molten metal for degassing purposes and the total time elapsed between the two pours was not more than 30 min. It therefore does not seem that phosphorus removal would present any difficulty.

12.4 Comments

It seems desirable to maintain phosphorus at a relatively low level in ingot metal to reduce gas pick-up on remelting and to give the foundryman a known base point (zero) from which he can add the requisite amount of phosphorus to accomplish deoxidation or alloying. A delicate balance must be struck by the foundryman in choosing the residual phosphorus content depending on factors such as casting temperature, alloy, mould material, section thickness, gas content, and metal-mould reaction.

13. SILICON

13.1 Influence on Properties

According to Loiseau, Lemoine and Picard⁽¹⁹⁾ the delta forming tendency of 0.3% Si is similar to that of 1% Sn.

DePue and Pennington⁽⁴⁷⁾, who tested sand-cast bushings made of #903 (1B), found that the maximum pressure held by the bushing decreases with increasing silicon content to a minimum between 0.065 and 0.075% Si and thereafter increases again. For the mechanical properties determined on sand-cast test bars, the critical range occurred between 0.01 and 0.05% Si. The magnitude of reduction below specification values in the critical silicon range exceeded 25% for the tensile and yield strengths and 30% for the elongation, while the pressure-tightness was reduced by over 90%. Incidentally, the authors explain the difference in critical silicon content for pressure-tightness and mechanical properties by the difference in cooling rates between the two types of castings which, in turn, causes a different amount of eutectoid to separate out. At the critical silicon content, the microstructure contains interconnected porosity which adversely affects the properties, particularly pressure tightness.

Hudson⁽⁴⁸⁾ found that the high-lead bronzes were particularly sensitive to the presence of traces of silicon when cast into 3-in. plates, though not in DTD bars. The surface finish and porosity of the 3-in. sections were satisfactory when the analysed silicon content was 0.001% or less, but in excess of 0.002%, porosities of 8-9% were obtained. Further increase in silicon contents up to 0.03% did not cause the porosity to exceed 10%. This effect was less pronounced in #836 (4A) than in leaded bronzes containing 8-12% Sn. The severity of metal-mould reaction increased as the lead content was raised, and the 15% Pb alloy suffered pronounced metal-mould reaction when nominally free from silicon.

Bolton and Weigand⁽⁴⁹⁾ found that up to 0.07% Si in sand-cast #922 (2A) gunmetal had little effect on the tensile properties, but 0.3% caused an appreciable reduction in strength and a serious decrease in elongation, from 45 to 20%.

In a limited series of tests in which 0.01, 0.05 and 0.1% Si were added to a bronze consisting of Cu-6% Sn, 5% Pb and 6% Zn. Larsson⁽⁵⁾ found that silicon does not have the same deteriorating

influence on pressure-tightness and physical properties as aluminum. He says that it is possible that 0.05 to 0.1% Si causes a slight deterioration in elongation. Pressure-tight discs have been cast in the presence of 0.01% Si.

Winterton⁽⁴⁾ found that the influence of silicon in chill castings was erratic but, in general, it caused a decrease in mechanical properties. It seems that 0.005% Si in leaded bronzes is as detrimental to the properties as 0.01 or even 0.02 in lead-free bronzes. The deterioration of the properties is due to the formation of oxide films which interfere with proper feeding of the casting.

Hanson and Pell-Walpole⁽⁶⁾ briefly explain why silicon is more detrimental in leaded bronzes than in unleaded bronzes. Silicon tends to form oxide films in all bronzes but it is particularly harmful in leaded bronzes because it forms a flocculent silicate which seriously impairs fluidity and renders it almost impossible to obtain sound or pressure-tight castings. They found that the effects of silicon on chill-cast tin bronzes are similar to but rather less than those of aluminum. A decrease of 2 to 6 kpsi in tensile strength and from 4 to 7% elongation is produced by 0.02 - 0.05% Si whereas, further amounts have little extra effect. Silicon also increases the amount of scatter in the results of duplicate tests. They label silicon as harmful in high-tin and phosphorus bronzes, and as very harmful in leaded bronzes. Their recommended upper limit in chill castings is 0.01% Si (Table 1).

Hudson and Hudson⁽⁷⁾ suggest an upper limit of 0.005% Si for the production of high-quality castings (Table 2).

13.2 Specified Limits

The ASTM specifications allow a maximum silicon content of 0.005%, the ISO and BS standards as much as 0.01 and 0.02%, respectively, in the same tin bronzes. Such discrepancies are difficult to understand, and may in part be due to differences

in standards writing philosophy rather than technical difficulties, i.e., the values may indicate "as low as possible" in all cases.

13.3 Removal

The silicon content of tin bronzes can be reduced by chlorine⁽¹⁵⁾, or air and oxygen⁽¹⁰⁾, or by a mixture of cuprous oxide and 15% sodium chloride as recommended by Thews⁽³⁹⁾.

The slag treatment used for the removal of aluminum can also be effective as shown by Larsson⁽⁵⁾.

13.4 Comments

Like aluminum, silicon has a potential for oxide formation which is seen as dangerous, and indeed the possibility of contamination from silicon bronzes and brasses containing say 3.5% Si, is one reason why these latter alloys have never been popular.

Apart from the mention of flocculent silicates which seriously impair fluidity⁽⁶⁾, there has been no serious attempt to explain why silicon seems to be particularly deleterious in bronzes containing lead, and this factor alone may be worth further investigation if more contaminated material is to be readily used.

14. SULPHUR

14.1 Influence on Properties

Sulphur is practically insoluble in copper and copper alloys. It separates out as Cu_2S in copper-sulphur alloys and as Cu_2S plus a second sulphide phase which, in gunmetals, is probably a compound or solution of tin sulphide in cuprous sulphide containing also zinc sulphide⁽⁵⁰⁾.

There is considerable disagreement between different investigators as to the influence of sulphur on gunmetals from those who claim that sulphur is not important to those who

claim that it is undesirable even in small quantities.

Reiter⁽⁵⁰⁾ determined the influence of up to 0.3% S in #905 (1A), #836 (4A) and 90-10 phosphor bronze cast in green sand moulds. He found that sulphur up to 0.3% had no influence on porosity, tensile properties, pressure-tightness, fluidity, castability and hot-tearing resistance of all three alloys. Sulphur was present as two separate sulphide phases associated with the alpha + delta eutectoid in #905 and the 90-10 phosphor bronze and with interdendritic particles of lead in #836. Consequently, Hudson and Mantle⁽⁵¹⁾ see no reason why limits should be imposed for sulphur in gunmetals.

Bolton and Weigand⁽⁴⁹⁾, who had tested the influence of up to 0.231% S on the properties of #922 (2A), concluded that "the effects of sulphur are not marked", and a later publication by Smith and Bolton⁽²⁰⁾ claimed that up to 0.3% S has no effect on the tensile properties of sand-cast #922 bronze.

Stolarczyk et al⁽²⁵⁾ state that when 0.1 to 0.15% S is added to other impurities, the tensile strength is further decreased by 1 kpsi, a reduction which is hardly significant in view of the importance of other factors.

Gardner and Saeger⁽³¹⁾, who studied the influence of sulphur on the properties of #836 (4A) sand and chill castings, found that the effects of up to 0.1% S were slight when the pouring temperature did not exceed 1150°C, but, with a pouring temperature of 1260°C, sulphur contents of more than 0.05% caused low tensile properties and the castings contained holes due to the evolution of sulphur dioxide.

Wigy and Arnaud⁽⁵²⁾, studied the influence of sulphur on the pressure-tightness of #836 and of Cu-7% Sn, 4% Pb, 7% Zn and they found that pressure-tight specimens had a low sulphur content whereas "leakers" had a sulphur content higher than 0.1%.

Hanson and Pell-Walpole⁽⁶⁾ concluded that, in so far as the effects of sulphur on mechanical properties are concerned, the amounts of sulphur likely to be absorbed from sulphurous fuels are not seriously detrimental to slowly poured chill-cast bronzes. They suggest a maximum of 0.1% for lead-free and low-lead bronzes and of 0.5% for high-lead bronzes (Table 1).

Hudson and Hudson⁽⁷⁾ recommend a maximum sulphur content of 0.05% (Table 2).

14.2 Specified Limits

The BS standards do not mention sulphur for any copper casting alloy while the ASTM and ISO standards specify maxima of 0.05 to 0.08 and 0.1% respectively for the same alloys.

Again, as seen above, the results on this impurity are conflicting and the restrictive limits chosen appear to be more on the basis of safety than knowledge. Apart from the possible inhibiting effect on mould reaction, sulphur is not known to have any beneficial effects, although it was customary some time ago to add sulphur to high-lead bronze melts in the belief that this caused a better lead distribution. This is possible in that the sulphides have relatively low melting points and are usually associated with the lead particles in lead-containing alloys. The reduced density of the compound particle could reduce gravity segregation and there may also be surface tension effects.

14.3 Removal

Air or oxygen bubbling⁽¹⁰⁾ had no effect at all on the sulphur content, while chlorine⁽¹⁵⁾ was only moderately successful.

Thews⁽⁵³⁾ found that calcined sodium carbonate is efficient in removing sulphur when added to the green glass cover used to dissolve zinc and aluminum oxides. Calcined dolomite or calcium carbonate would probably have the same effect.

Lepp⁽⁵⁴⁾ recommends the use of barium carbonate for desulphurization, while others have used soda ash with or without

green poling⁽¹⁶⁾.

It seems that the most efficient and simple method is that advocated by Cirou and LeThomas⁽⁵⁵⁾ by which they could reduce the sulphur content of an 8% tin bronze from 0.24% to 0.03 in 5 min by adding 0.2% Mg. The proposed method consists of melting the charge and adding magnesium under a charcoal cover, and after skimming, reheating the charge in an oxidizing atmosphere to eliminate residual magnesium and deoxidizing with phosphorus-copper.

14.4 Comments

Sources of sulphur include high-sulphur fuels, and possibly sulphur originating in lead battery plate scrap.

15. SEVERAL IMPURITIES TOGETHER

Stolarczyk et al⁽²⁵⁾ who studied the effect of bismuth, iron, arsenic and antimony, say that when impurities are added, #905 and 836 bronze test bars show a fall in strength 10 to 30% greater than would be expected if the effect of impurities were simply additive. However, the reduction in strength and elongation of plate castings is roughly $\frac{1}{2}$ to $\frac{2}{3}$ of what it would be in test bars when several impurities are added.

Hudson⁽⁴⁵⁾ states that the effects of antimony, arsenic, bismuth, iron and sulphur appear to be simply additive.

Hudson and Hudson⁽⁷⁾ are of the opinion that if sulphur, manganese, bismuth, iron, antimony and arsenic are present together to the maximum amounts given in Table 2, they may cause a reduction in the tensile strength and elongation of sand-cast test bars of possibly 4 to 6 kpsi and 5 to 10% respectively, but they are unlikely to increase porosity - that is, when more detrimental impurities are carefully controlled.

It seems that there is insufficient evidence to draw any definite conclusions on the effects of several impurities present at the same time in tin bronzes.

16. SUMMARY AND CONCLUSIONS

The effects, specification limits and methods of removal of the impurity elements most commonly found in tin bronzes and gunmetals have been reviewed.

It is shown that, in many instances, there is conflicting evidence as to the limits above which these elements become harmful (and different limits may exist for different properties). As the impurities have no beneficial effects (with the exception of phosphorus and possibly nickel) it is believed that, in many cases, the impurity limits are based on the philosophy that "it is better to be safe than sorry".

It is noted that European specifications are generally less restrictive with regard to impurities than North American specifications. This may be due to differences in Standards writing techniques, because ASTM specifications are usually much more specific than corresponding European standards. In some instances, the low impurity levels may be specified as much to ensure that only high-grade, first-quality material be used in the make-up of the alloy, as from any conviction of the harmful effects of impurities in excess of the specified levels either singly or collectively. The less-stringent European specifications probably reflect the greater availability of high-quality material in North America, and the greater familiarity of the Europeans with processing and using a higher ratio of scrap to virgin metal. The study was undertaken in the belief that this situation will eventually arise in North America as increased recycling becomes a mandatory requirement of economic survival.

In terms of recycling, iron, aluminum and silicon stand out as being of prime importance for a variety of reasons. Although they can be readily removed by oxidation processes, this operation is wasteful of energy and materials. It is considered that there is some possibility of utilizing iron as an alloying element, as well as other elements, such as antimony and nickel, which increase the amount of delta phase in tin bronzes.

In the case of aluminum and silicon, which are restricted to 0.005% max in ASTM standards, it is noted in the literature that silicon appears less harmful than aluminum in "lead-free" bronzes and more deleterious when lead is present. These effects warrant further investigation.

Similarly, although magnesium is not a common impurity in copper alloys, it could possibly be used to remove sulphur, and it may be beneficial as a "deoxidant" with or without more traditional materials.

The literature shows that there is little factual information on the effects of impurities when present in combination.

In some specifications, groups of elements of similar chemical properties may be limited, but in many cases the limitation appears to be less logical, e.g., (Fe + As + Sb), (Sb + P + As) or (Sn + Pb + Fe + Ni + Mn), although these might be considered as groups of two different classes of impurities. This lack of knowledge of the combined effects of impurities is illustrated in specifications such as BS 1400 - SCB1, which apart from limiting aluminum to 0.01% and iron to 0.75%, simply says: Total impurities, 1.0%. The provision of such data is obviously a major task. An alternative approach might be to establish foundry tests so that material which would satisfy these "performance criteria" would be acceptable without regard to the levels of individual impurities.

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Table 1. The Relative Effects of Minor Constituents and Impurities in Various Classes of Chill-cast Bronze⁽⁶⁾.

Impurity	Bronze Type	Effect on Residual Oxygen Content	Effect on Fluidity	Effect on Constitution in Solid State	Sum Effect on Mechanical Properties	Suggested Limit(%) for Chill-castings
P	Zn bronze Zn-Pb bronze Pb bronze	None " Decrease	Improved fluidity and increased soundness	Up to 0.1% in solid solution. Excess as Cu_3P with ($\alpha\delta$)	Highly beneficial in amounts up to 0.05-0.075%. Slightly embrittling in larger quantities	0.075
Pb	P bronze Sn bronze Zn bronze	None " "	Slight increase in fluidity	Present as metallic Pb particles	Very gradual decrease in strength and ductility	0.5
Zn	P bronze Sn bronze Pb bronze	Decrease " "	No effect if excess P present. Slight decrease in fluidity in low-P bronzes	Increase in amount of ($\alpha\delta$) (1% Zn=1/2% Sn)	Slight general improvement in amounts up to 0.3-0.5%	0.3
Ni	All types	None	Slight decrease	Increased ($\alpha\delta$). Ni-Sn compounds with 2% Ni or more	Beneficial especially in amounts between 1-2%	2
Fe	Sn & P bronzes	None	Slight decrease	In solution to 0.2% Fe-Sn compound in excess of 0.2-0.3%	Beneficial to 0.3%. Severely weakening & embrittling in larger amounts	0.3
	Zn bronze Pb-Zn bronze Leaded bronze	None " "	Slight decrease	In solution to 0.2%. Excess as Fe-rich phase	Improved strength, increased hardness & decreased ductility for amounts to 2%	0.5 0.5 0.1
Al	P bronze Sn bronze Leaded bronzes Zn bronze	Decrease " " "	Severe decrease " " Slight decrease	Increased ($\alpha\delta$) (1% Al, 2% Sn) Increased ($\alpha\delta$)	Very detrimental even in amounts below 0.01% Slightly detrimental	0.005 0.01
Si	High-Sn bronze P bronze Zn bronze Leaded bronzes	Decrease " " Decrease	Harmful " " Very harmful	Increased ($\alpha\delta$) Increased ($\alpha\delta$) Increased ($\alpha\delta$)	Detrimental even in small amounts Detrimental even in small amounts	0.01 0.01 0.01
Mn	High-Sn bronze P bronze Zn bronze Leaded bronzes	Decrease " " Decrease	Harmful " " Little effect up to 0.1%. Harmful in excess	Little visible effect for amounts up to 0.5% Little visible change	Rather detrimental " " Harmless up to 0.1%. Detrimental in excess	0.01 0.01 0.05
Sb	High-Sn bronze Zn bronzes P bronzes and low-Sn(Pb) bronzes	None " None	None " None	Increased ($\alpha\delta$) Increased ($\alpha\delta$)	Detrimental due to embrittling action Relatively harmless in amounts up to 1%	0.05 0.5
As	High-P bronze High-Sn bronze Gun-metal Leaded bronzes	None " " "	None	Marked increase of ($\alpha\delta$) in embrittling form	Detrimental Hardens, otherwise harmless	0.1 0.3
Bi	All Pb-free bronzes Leaded bronzes	None "	Increased fluidity	Intercrystalline films or particles of Bi Bi forms eutectic with Pb	Very weakening and embrittling Relatively harmless	0.05 0.3
S	Pb-free & low-Pb bronzes High-leaded bronzes	None "	Decreased fluidity especially above 0.1%	Present as sulphide inclusions. Decreases segregation in leaded bronzes	Slightly detrimental Relatively harmless	0.1 0.5

Table 2 - Suggested Safe Impurity Limits (%) for Gunmetal Castings to Obtain Maximum Quality Under Least Favourable Conditions⁽⁷⁾.

	#905(1A)	#836(4A)	#844(5A)
Aluminum	0.005	0.005	0.005
Magnesium	0.005	0.005	0.005
Silicon	0.005	0.005	0.005
Carbon	0.005	0.005	0.005
Phosphorus	0.01-0.02	0.01-0.02	0.01-0.02
Sulphur	0.05	0.05	0.05
Manganese	0.01	0.05	0.05
Bismuth	0.02	0.05	0.05
Iron	0.15	0.15	0.15
Antimony	0.05	0.10	0.10
Arsenic	0.10	0.20	0.10

Table 3 - Reported Refining Procedures for Aluminum in Copper-Base Alloys(16)

Flux	% Flux in Melt	Temp, °F
40% Borax 58% Sand 2% Fluorspar	2-4	2100-2300
45% Glass 45% Salt 10% Soda ash	3-5	1900-2100
Sand Soda ash Lime	1	2000
Powdered Glass Lime	1	2100
	1	2100-2200
40% Limestone 40% Sand 20% Soda ash	1	1900
Soda ash	4 times estimated Al	1950
75% Blast furnace slag 25% Sand	5	2100
Borax*	cover	2200-2300
Salt	0.5-1	2100

* This method is slow

Table 4 - Reported Refining Procedures for Iron in Copper-Base Alloys(16)

Flux	% Flux in Melt	Temp, °F
Sand	0.5	2100
50% Sand 50% Sodium Nitrate	1	2100
25% Sodium Sulphate 25% Soda ash 50% Borax	2 times estimated Fe	2100
75% Blast furnace slag 25% Sand	5	2100
Sodium nitrate	0.5	2050-2150
57% Sand 26% Limestone 17% Soda ash*	1	1900
50% Caustic soda 50% Borax	5	2100-2250
70% Powdered glass 30% Lime	3	2100-2300
50% Glass 50% Iron oxide*	2-4	2100
40% Borax 60% Sand	2-4	2100-2300

* Listed as very effective

5. APPENDIX "A"

ASTM Specifications (1945-1975)

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A comparison of the 1945 and 1975 ASTM specifications for tin bronze ingots (Tables A-1 to A-13) shows that, with the exception of some reduction in the permissible antimony content for several alloys and a small reduction in the maximum iron content for alloy #935(3C), there has been no tightening of the ingot specifications over the last 30 years. Changes to relax the ingot specifications have been largely in the direction of higher permissible nickel content and minor adjustments in iron, zinc, phosphorus and silicon.

In the case of the ASTM specifications for tin bronze castings, the 1975 version is considerably more restrictive than the 1945. Antimony (except in the cases of alloys #937(3A), #932(3B), #935(3C), #938(3D) and #943(3E)), sulphur, aluminum and silicon are not mentioned at all in the 1945 specifications, whereas they are all subject to a maximum permissible level in the 1975 specifications. However, the later specifications may appear more restrictive than they are in practice, because, although castings should conform to the chemical requirements of Tables A-1 to A-13, a note says that chemical analysis shall regularly be made only for copper, tin, lead and nickel. Again, the major relaxation in the 1975 specifications as compared to 1945 is for nickel which is now permitted up to 1.0% for all tin bronzes. Minor relaxations exist for iron in alloys #905(1A) and #903(1B), for zinc in #937(3A) and for zinc and antimony in #938(3D) and #943(3E).

In terms of mechanical property requirements, improved properties are specified for alloys #937, 935, 938 and 943 (3A,C,D & E), and #838(4B) and #848(5B). This presumably reflects

improved foundry technology or the recognition that the properties specified in 1945 were unrealistically low. It certainly does not correspond to changes in specified composition or in permissible impurity level.

In conclusion, it is thus seen that the only major change in ASTM casting specifications over the last 30 years with regard to impurities has been the recognition that nickel is not a harmful impurity, and the larger number of elements with a specified maximum level.

Table A-1. Chemical requirements for #905 (1A)

Elements, %	Ingots				Castings			
	B30-45T		B30-74		B143-44T		B584-73	
	Min	Max	Min	Max	Min	Max	Min	Max
Copper	86.0	89.0	86.0	89.0	86.0	89.0	86.0	89.0
Tin	9.5	10.5	9.5	10.5	9.0	11.0	9.0	11.0
Lead	-	0.25	-	0.25	-	0.30	-	0.30
Zinc	1.5	3.0	1.5	3.0	1.0	3.0	1.0	3.0
Iron	-	0.10	-	0.15	-	0.15	-	0.20
Antimony	-	0.25	-	0.20	-	-	-	0.20
Nickel	-	0.75	-	0.8	-	1.0	-	1.0
Sulphur	-	0.05	-	0.05	-	-	-	0.05
Phosphorus	-	0.03	-	0.03	-	0.05	-	0.05
Aluminum	-	0.005	-	0.005	-	-	-	0.005
Manganese	-	-	-	-	-	-	-	-
Silicon	-	0.005	-	0.005	-	-	-	0.005

Tensile Strength, N/mm^2

275

275

Yield Strength, 0.5% N/mm^2

125

125

Elongation, % in 2 in.

20

20

Table A-2. Chemical requirements for #903 (1B)

Elements, %	Ingots				Castings			
	B30 - 45 T		B30-74		B143-44T		B584-73	
	Min	Max	Min	Max	Min	Max	Min	Max
Copper	86.0	89.0	86.0	89.0	86.0	89.0	86.0	89.0
Tin	7.75	9.0	7.8	9.0	7.5	9.0	7.5	9.0
Lead	-	0.25	-	0.25	-	0.30	-	0.30
Zinc	3.5	5.0	3.5	5.0	3.0	5.0	3.0	5.0
Iron	-	0.10	-	0.15	-	0.15	-	0.20
Antimony	-	0.25	-	0.20	-	-	-	0.20
Nickel	-	0.75	-	0.8	-	1.0	-	1.0
Sulphur	-	0.05	-	0.05	-	-	-	0.05
Phosphorus	-	0.03	-	0.03	-	0.05	-	0.05
Aluminum	-	0.005	-	0.005	-	-	-	0.005
Manganese	-	-	-	-	-	-	-	-
Silicon	-	0.005	-	0.005	-	-	-	0.005

Tensile Strength, N/mm^2

275

275

Yield Strength, 0.5% N/mm^2

125

125

Elongation, % in 2 in.

20

20

Table A-3. Chemical requirements for #922 (2A)

Elements, %	Ingots				Castings			
	B30-45T		B30-74		B143-44T		B584-73	
	Min	Max	Min	Max	Min	Max	Min	Max
Copper	86.0	89.0	86.0	89.0	86.0	90.0	86.0	89.0
Tin	5.75	6.5	5.8	6.5	5.5	6.5	5.5	6.5
Lead	1.0	1.75	1.0	1.8	1.0	2.0	1.0	2.0
Zinc	3.5	5.0	3.5	5.0	3.0	5.0	3.0	5.0
Iron	-	0.20	-	0.20	-	0.25	-	0.25
Antimony	-	0.25	-	0.20	-	-	-	0.20
Nickel	-	0.75	-	0.8	-	1.0	-	1.0
Sulphur	-	0.05	-	0.05	-	-	-	0.05
Phosphorus	-	0.03	-	0.03	-	0.05	-	0.05
Aluminum	-	0.005	-	0.005	-	-	-	0.005
Manganese	-	-	-	-	-	-	-	-
Silicon	-	0.005	-	0.005	-	-	-	0.005

Tensile Strength, N/mm^2

235

235

Yield Strength, 0.5% N/mm^2

110

110

Elongation, % in 2 in.

22

24

Table A-4. Chemical requirements for #923 (2B)

	Ingots				Castings			
	B30-45T		B30-74		B143-44T		B584-73	
Elements, %	Min	Max	Min	Max	Min	Max	Min	Max
Copper	85.0	89.0	85.0	89.0	85.0	89.0	85.0	89.0
Tin	7.75	9.0	7.8	9.0	7.5	9.0	7.5	9.0
Lead	-	0.90	0.30	0.9	-	1.0	0.30	1.0
Zinc	3.5	5.0	3.0	5.0	3.0	5.0	2.5	5.0
Iron	-	0.20	-	0.20	-	0.25	-	0.25
Antimony	-	0.25	-	0.20	-	-	-	0.20
Nickel	-	0.75	-	0.8	-	1.0	-	1.0
Sulphur	-	0.05	-	0.05	-	-	-	0.05
Phosphorus	-	0.03	-	0.03	-	0.05	-	0.05
Aluminum	-	0.005	-	0.005	-	-	-	0.005
Manganese	-	-	-	-	-	-	-	-
Silicon	-	0.005	-	0.005	-	-	-	0.005

Tensile Strength, N/mm²

250

250

Yield Strength, 0.5% N/mm²

110

110

Elongation, % in 2 in.

18

18

Table A-5. Chemical requirements for #937 (3A)

	Ingots				Castings			
	B30-45T		B30-74		B144-45T		B584-73	
Elements, %	Min	Max	Min	Max	Min	Max	Min	Max
Copper	78.0	81.0	78.0	81.0	78.0	82.0	78.0	82.0
Tin	9.25	10.75	9.3	10.7	9.0	11.0	9.0	11.0
Lead	8.25	10.75	8.3	10.7	8.0	11.0	8.0	11.0
Zinc	-	0.75	-	0.8	-	0.75	-	0.8
Iron	-	0.10	-	0.10	-	0.15	-	0.15
Antimony	-	0.50	-	0.50	-	0.55	-	0.55
Nickel	-	0.50	-	0.8	-	0.50	-	1.0
Sulphur	-	0.08	-	0.08	-	-	-	0.08
Phosphorus	-	0.03	-	0.05	-	0.05	-	0.15
Aluminum	-	0.005	-	0.005	-	-	-	0.005
Manganese	-	-	-	-	-	-	-	-
Silicon	-	0.003	-	0.005	-	-	-	0.005

Tensile Strength, N/mm^2

170

205

Yield Strength, 0.5% N/mm^2

85

85

Elongation, % in 2 in.

8

15

Table A-6. Chemical requirements for #932 (3B)

	Ingots				Castings			
	B30-45T		B30-74		B144-45T		B584-73	
Elements, %	Min	Max	Min	Max	Min	Max	Min	Max
Copper	82.0	84.0	82.0	84.0	81.0	85.0	81.0	85.0
Tin	6.5	7.5	6.5	7.5	6.25	7.5	6.3	7.5
Lead	6.5	7.75	6.5	7.7	6.0	8.0	6.0	8.0
Zinc	2.5	4.0	2.5	4.0	2.0	4.0	2.0	4.0
Iron	-	0.15	-	0.20	-	0.20	-	0.20
Antimony	-	0.30	-	0.30	-	0.35	-	0.35
Nickel	-	0.50	-	0.8	-	0.50	-	1.0
Sulphur	-	0.08	-	0.08	-	-	-	0.08
Phosphorus	-	0.03	-	0.03	-	0.15	-	0.15
Aluminum	-	0.005	-	0.005	-	-	-	0.005
Manganese	-	-	-	-	-	-	-	-
Silicon	-	0.003	-	0.005	-	-	-	0.005

Tensile Strength, N/mm^2

205

205

Yield Strength, 0.5% N/mm^2

95

95

Elongation, % in 2 in.

12

15

Table A-7. Chemical requirements for #935 (3C)

	Ingots				Castings			
	B30-45T		B30-74		B144-45T		B584-73	
Elements, %	Min	Max	Min	Max	Min	Max	Min	Max
Copper	83.0	85.0	83.0	85.0	83.0	86.0	83.0	86.0
Tin	4.5	5.5	4.5	5.5	4.5	6.0	4.3	6.0
Lead	8.5	9.75	8.5	9.7	8.0	10.0	8.0	10.0
Zinc	0.5	1.5	0.50	1.5	-	2.0	-	2.0
Iron	-	0.15	-	0.10	-	0.20	-	0.20
Antimony	-	0.25	-	0.30	-	0.30	-	0.30
Nickel	-	0.50	-	0.8	-	0.50	-	1.0
Sulphur	-	0.08	-	0.08	-	-	-	0.08
Phosphorus	-	0.02	-	0.04	-	-	-	0.05
Aluminum	-	0.005	-	0.005	-	-	-	0.005
Manganese	-	-	-	-	-	-	-	-
Silicon	-	0.003	-	0.005	-	-	-	0.005

Tensile Strength, N/mm²

170

195

Yield Strength, 0.5% N/mm²

85

85

Elongation, % in 2 in.

8

15

Table A-8. Chemical requirements for #938 (3D)

Elements, %	Ingots				Castings			
	B30-45T		B30-74		B144-45T		B584-73	
	Min	Max	Min	Max	Min	Max	Min	Max
Copper	76.0	79.0	76.0	79.0	75.0	79.0	75.0	79.0
Tin	6.5	7.5	6.5	7.5	6.25	7.5	6.3	7.5
Lead	14.0	16.0	14.0	16.0	13.0	16.0	13.0	16.0
Zinc	-	0.75	-	0.8	-	0.75	-	0.8
Iron	-	0.10	-	0.10	-	0.15	-	0.15
Antimony	-	0.75	-	0.50	-	0.75	-	0.8
Nickel	-	0.50	-	0.8	-	0.75	-	1.0
Sulphur	-	0.08	-	0.08	-	-	-	0.08
Phosphorus	-	0.03	-	0.05	-	0.05	-	0.05
Aluminum	-	0.005	-	0.005	-	-	-	0.005
Manganese	-	-	-	-	-	-	-	-
Silicon	-	0.003	-	0.005	-	-	-	0.005

Tensile Strength, N/mm²

170

180

Yield Strength, 0.5% N/mm²

95

95

Elongation, % in 2 in.

10

12

Table A-9. Chemical requirements for #943 (3E)

	Ingots				Castings			
	B30-45T		B30-74		B144-45T		B584-73	
Elements, %	Min	Max	Min	Max	Min	Max	Min	Max
Copper	69.0	73.0	69.0	73.0	68.5	73.5	68.5	73.5
Tin	4.5	5.75	4.7	5.8	4.5	6.0	4.5	6.0
Lead	22.0	24.5	22.0	24.5	22.0	25.0	22.0	25.0
Zinc	-	0.50	-	0.8	-	0.50	-	0.8
Iron	-	0.10	-	0.10	-	0.15	-	0.15
Antimony	-	0.75	-	0.7	-	0.75	-	0.8
Nickel	-	0.50	-	0.8	-	0.50	-	1.0
Sulphur	-	0.08	-	0.08	-	-	-	0.08
Phosphorus	-	0.03	-	0.05	-	0.05	-	0.05
Aluminum	-	0.005	-	0.005	-	-	-	0.005
Manganese	-	-	-	-	-	-	-	-
Silicon	-	0.003	-	0.005	-	-	-	0.005

Tensile Strength, N/mm²

145

165

Yield Strength, 0.5% N/mm²

-

-

Elongation, % in 2 in.

7

10

Table A-10. Chemical requirements for #836 (4A)

	Ingots				Castings			
	B30-45T		B30-74		B145-45T		B584-73	
Elements, %	Min	Max	Min	Max	Min	Max	Min	Max
Copper	84.0	86.0	84.0	86.0	84.0	86.0	84.0	86.0
Tin	4.25	6.0	4.3	6.0	4.0	6.0	4.0	6.0
Lead	4.0	5.75	4.0	5.7	4.0	6.0	4.0	6.0
Zinc	4.5	6.0	4.3	6.0	4.0	6.0	4.0	6.0
Iron	-	0.25	-	0.25	-	0.30	-	0.30
Antimony	-	0.25	-	0.25	-	-	-	0.25
Nickel	-	0.75	-	0.8	-	1.0	-	1.0
Sulphur	-	0.08	-	0.08	-	-	-	0.08
Phosphorus	-	0.03	-	0.03	-	0.05	-	0.05
Aluminum	-	0.005	-	0.005	-	-	-	0.005
Manganese	-	-	-	-	-	-	-	-
Silicon	-	0.003	-	0.005	-	-	-	0.005

Tensile Strength, N/mm^2

205

205

Yield Strength, 0.5% N/mm^2

95

95

Elongation, % in 2 in.

20

20

Table A-11. Chemical requirements for #838 (4B)

Elements, %	Ingots				Castings			
	B30-45T		B30-74		B145-45T		B584-73	
	Min	Max	Min	Max	Min	Max	Min	Max
Copper	82.0	83.5	82.0	83.5	82.0	83.75	82.0	83.8
Tin	3.5	4.25	3.5	4.2	3.25	4.25	3.3	4.2
Lead	5.25	6.75	5.8	6.8	5.0	7.0	5.0	7.0
Zinc	5.5	8.0	5.5	8.0	5.0	8.0	5.0	8.0
Iron	-	0.25	-	0.25	-	0.30	-	0.30
Antimony	-	0.25	-	0.25	-	-	-	0.25
Nickel	-	0.75	-	0.8	-	1.0	-	1.0
Sulphur	-	0.08	-	0.08	-	-	-	0.08
Phosphorus	-	0.01	-	0.02	-	0.03	-	0.03
Aluminum	-	0.005	-	0.005	-	-	-	0.005
Manganese	-	-	-	-	-	-	-	-
Silicon	-	0.003	-	0.005	-	-	-	0.005

Tensile Strength, N/mm^2

200

205

Yield Strength, 0.5% N/mm^2

85

90

Elongation, % in 2 in.

15

20

Table A-12. Chemical requirements for #844 (5A)

Elements, %	Ingots				Castings			
	B30-45T		B30-74		B145-45T		B584-73	
	Min	Max	Min	Max	Min	Max	Min	Max
Copper	78.0	82.0	79.0	82.0	78.0	82.0	78.0	82.0
Tin	2.5	3.5	2.5	3.5	2.25	3.5	2.3	3.5
Lead	6.25	7.75	6.3	7.7	6.0	8.0	6.0	8.0
Zinc	7.5	10.0	7.0	10.0	7.0	10.0	7.0	10.0
Iron	-	0.35	-	0.35	-	0.40	-	0.40
Antimony	-	0.20	-	0.25	-	-	-	0.25
Nickel	-	0.75	-	0.8	-	1.0	-	1.0
Sulphur	-	0.08	-	0.08	-	-	-	0.08
Phosphorus	-	0.01	-	0.02	-	0.02	-	0.02
Aluminum	-	0.005	-	0.005	-	-	-	0.005
Manganese	-	-	-	-	-	-	-	-
Silicon	-	0.003	-	0.005	-	-	-	0.005

Tensile Strength, N/mm^2

200

200

Yield Strength, $0.5\% N/mm^2$

90

90

Elongation, % in 2 in.

18

18

Table A-13. Chemical requirements for #848 (5B)

Elements, %	Ingots				Castings			
	B30-45T		B30-74		B145-45T		B584-73	
	Min	Max	Min	Max	Min	Max	Min	Max
Copper	75.0	76.75	75.0	76.7	75.0	76.75	75.0	77.0
Tin	2.75	3.25	2.3	3.0	2.5	3.5	2.0	3.0
Lead	5.5	6.5	5.5	6.7	5.25	6.75	5.5	7.0
Zinc	14.0	17.0	13.0	16.0	13.0	17.0	13.0	17.0
Iron	-	0.35	-	0.35	-	0.40	-	0.40
Antimony	-	0.20	-	0.25	-	-	-	0.25
Nickel	-	0.50	-	0.8	-	1.0	-	1.0
Sulphur	-	0.07	-	0.08	-	-	-	0.08
Phosphorus	-	0.01	-	0.02	-	0.02	-	0.02
Aluminum	-	0.005	-	0.005	-	-	-	0.005
Manganese	-	-	-	-	-	-	-	-
Silicon	-	0.005	-	0.005	-	-	-	0.005

Tensile Strength, N/mm^2	170	195
Yield Strength, 0.5% N/mm^2	85	85
Elongation, % in 2 in.	15	16

6. APPENDIX "B"

Comparison Between Most Recent
ASTM, BS and ISO
Specifications

- - -

The only alloys where the three specifications can be compared are #905(1A), #937(3A), #935(3C) and #836(4A) while the ASTM and ISO specifications only are comparable for alloys #932(3B) and #938(3D) (Tables B-1 to B-6).

As a rule, the BS and ISO specifications for chemical composition are almost equivalent and they are considerably more lenient than their ASTM counterpart. This is particularly true for nickel, aluminum and silicon, and for lead in #905 (1A) and zinc in #937(3A) and #938(3D). There is one exception however; the ISO specification is the only one to impose a maximum manganese content (0.2%) and that is in alloys #905(1A), #937(3A), #935(3C) and #938(3D).

- - -

Table B-1. Chemical requirements for #905(1A)

Elements, %	Ingots			Castings		
	ASTM B30-74	BS-1400 1973	ISO/DIS 1338 1976	ASTM B584-73	BS-1400 1973	ISO/DIS 1338 1976
Copper	86.0-89.0	REM	86.0-88.5	86.0-89.0	REM	86.0-89.0
Tin	9.5-10.5	9.7-10.5	9.2-11.0	9.0-11.0	9.5-10.5	9.0-11.0
Lead	0.25	1.5	1.3	0.30	1.5	1.5
Zinc	1.5-3.0	1.75-2.75	1.0-3.0	1.0-3.0	1.75-2.75	1.0-3.0
Iron	0.15	0.15	0.20	0.20	0.15	0.25
Antimony	0.20	-	0.3	0.20	-	0.3
Nickel	0.8	1.0	2.0	1.0	1.0	2.0
Sulphur	0.05	-	0.10	0.05	-	0.10
Phosphorus	0.03	0.02	0.03	0.05	-	0.05
Aluminum	0.005	0.01	0.01	0.005	0.01	0.01
Manganese	-	-	0.2	-	-	0.2
Silicon	0.005	0.02	0.01	0.005	0.02	0.01

Tensile Strength, N/mm ²	275	270	240
0.2% Yield Strength, N/mm ²	125(0.5%)	130	120
Elongation, % in 5.65/S	20(% in 2 in.)	13	12

Table B-2. Chemical requirements for #937(3A)

Elements, %	Ingots			Castings		
	ASTM B30-74	BS-1400 1973	ISO/DIS 1338 1976	ASTM B584-73	BS-1400 1973	ISO/DIS 1338 1976
Copper	78.0-81.0	REM	78.0-81.0	78.0-82.0	REM	78.0-82.0
Tin	9.3-10.7	9.2-11.0	9.2-11.0	9.0-11.0	9.0-11.0	9.0-11.0
Lead	8.3-10.7	9.0-11.0	8.5-10.5	8.0-11.0	8.5-11.0	8.0-11.0
Zinc	0.8	1.0	2.0	0.8	1.0	2.0
Iron	0.10	0.15	0.15	0.15	0.15	0.25
Antimony	0.50	0.5	0.5	0.55	0.5	0.5
Nickel	0.8	2.0	2.0	1.0	2.0	2.0
Sulphur	0.08	-	0.10	0.08	-	0.10
Phosphorus	0.05	0.10	0.05	0.15	0.10	0.05
Aluminum	0.005	0.01	0.01	0.005	0.01	0.01
Manganese	-	-	0.2	-	-	0.2
Silicon	0.005	0.02	0.01	0.005	0.02	0.01

Tensile Strength, N/mm^2	205	190	180
0.2% Yield Strength, N/mm^2	85(0.5%)	80	80
Elongation, % in 5.65/S	15(% in 2 in.)	5	7

Table B-3. Chemical requirements for #932(3B)

Elements, %	Ingots			Castings		
	ASTM B30-74	BS-1400 1973	ISO/DIS 1338 1976	ASTM B584-73	BS-1400 1973	ISO/DIS 1338 1976
Copper	82.0-84.0		82.0-84.0	81.0-85.0		81.0-85.0
Tin	6.5- 7.5		6.2- 8.0	6.3- 7.5		6.0- 8.0
Lead	6.5- 7.7		5.0- 7.5	6.0- 8.0		5.0- 8.0
Zinc	2.5- 4.0		2.3- 5.0	2.0- 4.0		2.0- 5.0
Iron	0.20		0.20	0.20		0.20
Antimony	0.30		0.30	0.35		0.35
Nickel	0.8		0.8	1.0		1.0
Sulphur	0.08		0.10	0.08		0.10
Phosphorus	0.03		0.03	0.15		0.10
Aluminum	0.005		0.01	0.005		0.01
Manganese	-		-	-		-
Silicon	0.005		0.01	0.005		0.01

Tensile Strength, N/mm ²	205	210
0.2% Yield Strength, N/mm ²	95(0.5%)	100
Elongation, % in 5.65/S	15(% in 2 in.)	12

Table B-4. Chemical requirements for #935(3C)

Elements, %	Ingots			Castings		
	ASTM B30-74	BS-1400 1973	ISO/DIS 1338 1976	ASTM B584-73	BS-1400 1973	ISO/DIS 1338 1976
Copper	83.0-85.0	REM	80.0-87.0	83.0-86.0	REM	80.0-87.0
Tin	4.5- 5.5	4.2- 6.0	4.2- 6.0	4.3- 6.0	4.0- 6.0	4.0- 6.0
Lead	8.5- 9.7	8.0-10.0	8.5-10.0	8.0-10.0	8.0-10.0	8.0-10.0
Zinc	0.50-1.5	2.0	2.0	2.0	2.0	2.0
Iron	0.10	-	0.15	0.20	-	0.25
Antimony	0.30	0.5	0.5	0.30	0.5	0.5
Nickel	0.8	2.0	2.0	1.0	2.0	2.0
Sulphur	0.08	-	0.10	0.08	-	0.10
Phosphorus	0.04	0.10	0.05	0.05	0.10	0.10
Aluminum	0.005	-	0.01	0.005	-	0.01
Manganese	-	-	0.2	-	-	0.2
Silicon	0.005	0.02	0.01	0.005	0.02	0.01

Tensile Strength, N/mm ²	195	160	160
0.2% Yield Strength, N/mm ²	85(0.5%)	60	60
Elongation, % in 5.65√s	15(% in 2 in.)	7	7

Table B-5. Chemical requirements for #938(3D)

Elements, %	Ingots			Castings		
	ASTM B30-74	BS-1400 1973	ISO/DIS 1338 1976	ASTM B584-73	BS-1400 1973	ISO/DIS 1338 1976
Copper	76.0-79.0		75.0-78.5	75.0-79.0		75.0-79.0
Tin	6.5- 7.5		7.2- 9.0	6.3- 7.5		7.0- 9.0
Lead	14.0-16.0		13.5-16.5	13.0-16.0		13.0-17.0
Zinc	0.8		2.0	0.8		2.0
Iron	0.10		0.15	0.15		0.25
Antimony	0.50		0.5	0.8		0.5
Nickel	0.8		2.0	1.0		2.0
Sulphur	0.08		0.10	0.08		0.10
Phosphorus	0.05		0.05	0.05		0.10
Aluminum	0.005		0.01	0.005		0.01
Manganese	-		0.2	-		0.2
Silicon	0.005		0.01	0.005		0.01

Tensile Strength, N/mm^2	180	170
Yield Strength (0.2%), N/mm^2	95(0.5%)	80
Elongation, % in 5.65/s	12 (% in 2 in.)	5

Table B-6. Chemical requirements for #836(4A)

Elements, %	Ingots			Castings		
	ASTM B30-74	BS-1400 1973	ISO/DIS 1338 1976	ASTM B584-73	BS-1400 1973	ISO/DIS 1338 1976
Copper	84.0-86.0	REM	83.5-85.5	84.0-86.0	REM	84.0-86.0
Tin	4.3- 6.0	4.0-6.0	4.2- 6.0	4.0- 6.0	4.0-6.0	4.0- 6.0
Lead	4.0- 5.7	4.0-6.0	4.0- 5.7	4.0- 6.0	4.0-6.0	4.0- 6.0
Zinc	4.3- 6.0	4.5-6.0	4.5- 6.0	4.0- 6.0	4.0-6.0	4.0- 6.0
Iron	0.25	-	0.25	0.30	-	0.30
Antimony	0.25	-	0.25	0.25	-	0.25
Nickel	0.8	2.0	2.0	1.0	2.0	2.0
Sulphur	0.08	-	0.10	0.08	-	0.10
Phosphorus	0.03	0.02	0.03	0.05	-	0.05
Aluminum	0.005	0.01	0.01	0.005	0.01	0.01
Manganese	-	-	-	-	-	-
Silicon	0.005	0.02	0.01	0.005	0.02	0.01

Tensile Strength, N/mm ²	205	200	200
0.2% Yield Strength, N/mm ²	95(0.5%)	100	90
Elongation, % in 5.65/S	20(% in 2 in.)	13	13

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