CANADA

EMBRITTLEMENT OF SOLID METALS IN A LIQUID METAL

by

W. A. MORGAN
PHYSICAL METALLURGY DIVISION

REPRINTED FROM METAL TREATMENT AND DROP FORGING
VOL. 26: NO. 168

DEPARTMENT OF MINES AND TECHNICAL SURVEYS, OTTAWA

MINES BRANCH
RESEARCH REPORT

R 49

PRICE 25 CENTS

SEPTEMBER 1959

Embrittlement of solid metals in a liquid metal

W. A. MORGAN

This review of the published work on the embrittlement of solid metals by lower melting-point liquid metals is published by permission of the Director, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Ontario, Canada. The author is Head, Ferrous Metals Section, Physical Metallurgy Division of the Department.

MANY SERVICE FAILURES resulting from soldering and brazing operations on stressed materials have been reported. Generally the fracture surfaces followed an intercrystalline path and were often wetted by the lower melting-point metal. This review is a summary of the published work on the embrittlement of solid metals by lower melting-point liquid metals and discusses some of the theories for this type of failure.

The intergranular failure of high melting-point metals when stressed in contact with a low melting-point molten metal or alloy has often been compared with the phenomenon of season-cracking. Possibly the similarity is borne out by the fact that Rogers[1] developed the use of mercury-salt solutions for the detection of internal stresses in brass. The simultaneous effects of internal stresses in the material and the interaction of deposited mercury with the grain boundaries of the brass causes cracking along intercrystalline paths. The method was used by Heyn[2] and later thoroughly investigated by Rawdon.[3] Huntingdon[4] reported the complete intercrystalline disintegration of a β-brass containing about 2% aluminium when treated with mercury. Desch[5] obtained individual crystals from a similar brass by immersing it in mercury, but was unable to obtain the same effect with zinc, tin or lead. Moore and Beckinsale[6] showed that brass could be made immune from mercurial penetration and season-cracking by a low-temperature anneal.

Mercury penetration

A very thorough investigation into the whole problem of season cracking was reported by Moore, Beckinsale and Mallinson[7] in 1921. The authors quoted results of mechanical tests on specimens coated with mercury which had been deposited from a mercurial salt. They found that the mercury alloys with the brass, but the action was confined to only a very thin surface layer. Fracture began at grain boundaries on the surface of the specimens and followed the crystal surfaces which became covered with mercury. The level of stress at which the intercrystalline cracks formed was shown to be dependent on the amount of free mercury and the time available for penetration. Slower rates of loading give lower values for the maximum stress and elongation. Very little deleterious effect was brought about by immersion in mercury and then testing after removal of the liquid. They concluded that little or no intergranular penetration occurred in the absence of stress. Finally the results of tests are given which show that copper was not embrittled by mercury, but that the susceptibility to failure increased with the zinc content.

Edmunds[8] confirmed this finding in the range 10—40% zinc. In his investigation he also showed that 'as-rolled' mercury-coated tensile specimens and specimens of large section possessed superior resistance to penetration than recrystallized and small-section test-pieces. He correlated the grain size of 70/30 brass with its mechanical properties in mercury, showing that the properties decreased with increase of grain size. A single crystal, however, failed in a completely ductile manner and showed no deleterious effect.

Investigations into the effect of alloying elements on the susceptibility to penetration of brass by mercury have shown that no really marked effect was produced. Lynes[9] tested annealed 70/30 brass containing 0·1 and 0·3% arsenic, and Bassett[10] investigated the effect of 0—0·2% cadmium. Wilson, Edmunds, Anderson and Peirce[11] alloyed 36 elements with cartridge brass. In all cases the authors concluded that none of the added elements accelerated failure and the beneficial effect, if any, was small.

Strachan, Jones and Harris[52] studied the effect of prior immersion in mercury at 300°C. and 500°C. on the room temperature mechanical properties of Inconel (80 Ni, 14 Cr, 6 Fe), Nimonic 75 (75 Ni, 20 Cr, 5 Fe), nickel-iron 50 Ni/50 Fe, an 18/8 stainless steel, a 3·5 Si/8 Cr valve steel, mild steel sheet, a pure iron sheet produced from powder, molybdenum and tungsten. At 300°C. no changes in the mechanical properties were observed. At 500°C., however, nickel was the only material which showed a decrease in mechanical properties. Further tests on the 20 Ni/25 Cr steel and the mild steel, after immersion in mercury at 300°C. for 2,000h. under a stress of 12,200 lb. sq. in., showed no decrease in mechanical properties. An interesting facet of this work was the effect of 30 kc./s. ultrasonic vibrations on these materials. The authors showed that they were all susceptible to cavitation-erosion in mercury at room temperature.

Penetration of molten solders

The researches of the early workers on mercury penetration into brass and season-cracking led Dickenson[12] to report the failure of a manganese bronze by intercrystalline penetration of molten solder. He later published the first account[13] of an investigation into the embrittlement of a solid metal by a low melting-point metal. The results of his tests showed that the behaviour of different brasses varied with their microstructure. With a tin/lead solder a β-brass failed at a lower stress than an α-brass, an $\alpha + \beta$ brass occupying a midway position. For molten lead/tin/bismuth alloys containing 50% bismuth, α-brasses were much more seriously affected. Dickenson[13] offered no explanation for this. Further examples of failure as a result of such penetration followed; the embrittlement of malleable cast iron by zinc in hot-dip galvanizing was reported.[14] Duncan[15] found that molten brass penetrated nickel steel. Hall[16] reported the embrittlement of a mild steel by solder under alternating stresses at a temperature below 60°C. It is surprising that the penetration should have occurred at a temperature when the solder is solid. Probably some overheating and localized melting must have occurred at the point of penetration.

In 1927, Miller,[17], Hartley[18] and Genders[19] published three papers covering a wide range of nonferrous and ferrous metals. Miller tested specimens of 60/40 and 70/30 brasses in mercury at room temperature and in 50% lead—50% tin solder, pure tin and pure lead at temperatures of 220°C. and 350°C. He found that failure occurred by a process of intercrystalline penetration, and concluded that although a much higher stress was necessary for brass to crack in molten tin solder or lead, the process was similar to that of cracking and embrittlement by mercury. In agreement with previous workers his results showed that α-brass was more resistant than β-brass to penetration by mercury and lead-tin solder.

Hartley's work was similar to that of Miller except that he extended his range of copper/zinc alloys from pure copper to 60/40 brass. In addition, he measured the time to fracture at various stresses and compared the results obtained with values from short-time tensile tests in air at the same temperature. An analysis of his results showed that the strength of pure copper was not so drastically reduced in molten tin as were the 70/30, 64/36 and 61/39 brasses, the exception being the 80/20 brass. The stress required to fracture a test-piece was time-dependent and the stress-duration curves were of parabolic form. The author showed that the tin content of the solders used had an effect on the penetration, increasing tin content giving more rapid failure. On this finding, he based an explanation of the failure by postulating that alloying occurred at some grain boundaries which contained segregated impurities more rapidly than at others. In this way a brittle film may be formed which fractured easily under the applied stress; at this point further alloying and subsequent fracture took place.

Effect of brazing solders

Genders studied the failure of mild steel when coated with commercial brazing solder. A ½-in. rod could be fractured easily by bending it at 800°C. Molten copper also produced such an effect, but surprisingly he reported that zinc, tin and tin/lead alloy had no effect. He indicated that the experiments he had carried out showed a small amount of penetration of brazing solder at grain boundaries of armco iron in the absence of stress. In a discussion on Genders' paper, Williams[20] reported the failure of a 50/50 nickel-iron alloy in brazing solder. Anderson and Poole[21] quoted results showing that molten copper was much more severe than brazing metal on mild steel and that, although zinc had the strongest solvent action on steel, it did not give rise to embrittlement. They showed that a critical stress level had to be exceeded to produce embrittlement.

Riede[22] described cracks which developed in steel during dip-brazing and showed that normalizing could be used as a preventative. Stresses which arise during the hot-dipping process have been suggested by Albert[23] as a cause of penetration. Kreitz[24] found cracks after brazing articles which he believed to be free from internal and external stresses. Failures due to intercrystalline penetration have been reported by Ffield[25] in the welding of certain alloy steels which had been galvanized. Sparagen and Claussen[26] extended these findings to include both plain and alloy steels. Straight chromium and 18/8 stainless steels have been shown by Henry and Schroeder[27] to be susceptible to embrittlement by zinc, tin and Tobin bronze in both the molten and gaseous states. Zinc showed the most severe attack. The use of zinc coatings on nickel/chromium steels was shown to be undesirable if they were to be subsequently heated.[28] In order to determine at what temperature intergranular penetration of galvanized steel by zinc might take place, Craig[29] conducted a series of high-temperature tests on coated and uncoated steels. He found that in the temperature range from 20—800°C, low-carbon and high-carbon steels suffered no adverse effect due to zinc coatings. In stainless steel the coating had no effect up to 550°C. Above this temperature the zinc coating appeared to cause a marked decrease in ductility, but a less pronounced loss in strength.

Effect of other metals

Schottky, Schichtel and Stolle[30] investigated the effect of a whole range of metals on plain carbon steels, 4% silicon steel and on 22% and 32% chromium steels. The tests were made by bending bars, in the range 1,000—1,200°C. and sprinkling metal powder on the side in tension. Tin, zinc, antimony, copper, 5% tin bronze, a 5% tin, 10% zinc brass, and white bearing metals caused marked red-shortness at all temperatures in the above range. Bismuth, cadmium, lead, silver, and nickel seemed to have little or no effect. The carbon content in the range 0·1—0·5% carbon had no effect on the resistance to penetration. No red-shortness was observed in the 32% chromium steel with any of the metals used. A short time after this investigation was published, Schuster[31] reported the penetration of brass into a steel shaft.

Van Ewijk[32] in 1935 reported that stressed nickel-chromium high-tensile steels were embrittled by molten solder, lead, tin, zinc, cadmium or Lipowitz alloy (tin 4, lead 8, bismuth 15, cadmium 3 parts; melting point 60°C.). For carbon steels no such liability was observed. In order to obtain wetting of the steels he used a zinc chloride flux; no cracking was observed on specimens in which the flux had not been used. The liability to failure in the molten metal was greatly reduced by tempering at 700°C., but normal ranges of tempering temperature produced little effect. Pattermann[33] confirmed Van Ewijk's[32] results and reported that chromium/molybdenum steel was much more resistant to embrittlement than the nickel/chromium and nickel/chromium/molybdenum steels. Rust-proof chromium steels and nickel/chromium/titanium steels only showed the effect to a very slight degree.

Variables affecting penetration

An investigation of such variables as temperature, rate of application of load, tensile properties, degree of temper-brittleness and microstructure has been made for the attack of molten white metal on steels, by Goodrich.[34] By means of a bend test he plotted load deflection curves for four different steels uncoated and coated with lead/tin solder at 250°C. and a bearing metal at 350°C. The steels used were an oil-hardened and tempered plain carbon, 1% nickel and nickel/chromium/molybdenum steel. With increase in the rate of loading for these materials there was a gradual decrease in the yield and maximum loads, the smallest decrease being shown by the plain carbon steel. An increase of temperature brought about a more rapid decrease of these properties and again the plain carbon steel seemed more resistant to penetration.

Goodrich further showed that addition of nickel up to 1·2% to carbon steels was deleterious. However, the resistance of nickel-chromium steels was either better or worse than carbon steels depending on the microstructure, a small amount of free ferrite and small sorbitic grains decreasing the liability to embrittlement. Generally, carbon steels were more uniformly resistant to penetration than alloy steels. Quenched and tempered structures gave better results than normalized or annealed structures. Addition of molybdenum to the nickel/chromium steels conferred no added resistance. In agreement with other workers, Goodrich reported that the resistance to penetration varied inversely as the grain size. Finally, temper brittleness, as determined by the Izod impact test, appeared to have no influence on the resistance to penetration.

The resistance to penetration of steels by molten white bearing-metal solder and brazing alloys was also investigated by Wang.[35] His results confirmed that alloy steels were more susceptible than plain carbon steels. Intercrystalline attack by low melting-point metals did not occur above about 400°C. The test of the load extension curves obtained, showed that penetration did not occur until the elastic limit had been exceeded, and that the degree of stress required to produce penetration was critical. The rate of application of load when increased, increased the tendency of molten brazing alloys to penetrate steels; the tendency for such penetration was diminished above 950°C.

Comparative tests in solder and oil

A very extensive range of engineering materials were tested in molten solder and oil by Austin.[36] His tests were carried out in a tensile testing machine and a complete autographic load-extension curve was plotted for each specimen. In this way it was possible to determine at what stage of the curve (elastic, general extension to maximum load, or necking) the effect, if any, occurred and whether the normal tensile flow curve was interrupted only, or modified. Generally, it was shown that the molten metal did not modify the curve, but stopped it earlier than comparative tests in oil. The presence of molten solder, therefore, did not apparently affect the general resistance of the material to deformation, but decreased the amount of deformation before fracture.

Iron, nickel and copper were slightly affected; monel metal and cupro-nickel were unaffected. The strength of silver, zinc, aluminium, aluminium/bronze, 70/30 and 60/40 brass was reduced. The plain, low-carbon steels and the lower carbon pearlitic and austenitic heat- and rust-resisting steels did not appear to be as liable to penetration as similar steels with higher carbon. Increasing hardness and secondary grain size were deleterious, but neither the temper brittle nor the burnt state appeared to increase the embrittlement. Bassett[37], in the discussion on this paper, reported the penetration of bearing metal into a steel railway wagon axle due to local overheating and alternating stress.

The most recent report on the effect of molten solders on stressed solid metals has been published by Russian investigators.[54, 55] They studied the influence of composition and contact time of various solders on the brittle fracture of steels in tension. A beneficial effect was claimed for surface protection by nickel and copper. In the case of copper this differed from the results of Jepson and Thompson[38] discussed later in this report.

Effect of surface finish

Only a very small amount of information existed on the effect of surface finish of steel on its liability to penetration. Most of the above workers found that unless they obtained wetting of the steel by the solder with a zinc chloride, flux failure was of the normal ductile type. However, Jepson and Thompson,[38] while investigating the effect of a tensile stress on the rate of transformation of a eutectoid steel under isothermal conditions, found that specimens immersed in molten solder at temperatures between 200 and 400°C. were liable to fracture under low stresses. They, therefore, determined the time to fracture under a given load at 250°C. of specimens, each having a different surface finish. Their results showed that nickel-plating was the only effective prevention to failure, but even this failed at high stresses. An oxide skin proved the next safest and a copper-plated specimen the worst. When lead was used instead of solder no embrittlement of the steel occurred.

In the field of galvanizing particular attention has been paid to the interface reactions between molten zinc, the steel being dipped and the molten zinc bath-container materials. In 1952 Haarman[50] reported that galvanizing baths may be subject to three types of failure due to the attack of molten zinc. They were general surface attack, deep pitting and intercrystalline embrittlement. Initial results of his work showed that the higher the stress the greater was the degree of embrittlement.

Later, a more extensive investigation was reported by Radeker[51] who again showed that steel is subject to intercrystalline attack by molten zinc. Bent specimens of steel immersed in zinc baths at various temperatures between 425 and 500°C., with intermittent closing of the U-shaped strip, revealed no cracks until a notch was introduced at the bend, thus demonstrating the need for a minimum stress level. Both tensile strengths and, particularly, the reduction of area were decreased as a result of intercrystalline attack at temperatures of 425, 450, 475 and 500°C. At higher temperatures and stresses, stress-rupture tests on specimens immersed in molten zinc showed that the life was shorter than at lower stresses and temperature. The relationship between stress and time yielded a straight line on a double-log plot.

The results published by Haarman[50] and Radeker[51] differ from earlier results of Anderson and Poole who reported no intercrystalline embrittlement due to zinc. However, the former investigators agree with the work of Ffield, Henry and Schroeder, Campbell, and Craig.

Penetration of non-ferrous alloys

Service failures in four groups of non-ferrous alloys have been reported by Smith and Forsyth.[39] A high-strength brass containing aluminium having a homogeneous β-structure was easily penetrated by solder, whilst a similar brass containing manganese and possessing a duplex α-β structure was unaffected. Cracking was also observed in a completely β-brass containing lead. During annealing the lead had formed thin films around the grain boundaries and had ceased to exist as discrete globules. This type of failure has been observed to occur during the working at elevated temperatures of leaded steels.[40] Fracture of high-strength nickel-chromium steel tubes by penetration of molten solder and of austenitic steel by brazing alloy at 300°C. was also reported by Smith and Forsyth. They showed, too, that an aluminium/copper/magnesium/zinc alloy may be embrittled by Wood's metal, and that platinum alloy electrodes were susceptible to penetration by lead deposited on them during operation.

The Aluminium Development Association[41] investigated the embrittlement of aluminium and aluminium alloys in solder and brazing metal (9% tin, 10% zinc) at 250°C. Pure aluminium and aluminium/manganese alloy or annealed aluminium/magnesium/silicon alloy did not fail intergranularly. Fully heat-treated aluminium/magnesium/silicon alloy and a fully heat-treated aluminium/magnesium/zinc alloy were found to be the most susceptible.

Whitaker[42] reported the work of Voce and Bailey on the embrittlement of α-, α-β- and β-brasses up to 4% aluminium in mercury, lead, tin, and eutectic solder. With mercury, fracture occurred in all the brasses, the β-brass being most susceptible. The stress at failure increased with the aluminium content. At 200°C. each brass was embrittled by solder and again the β-brass was the most susceptible. However, in the α-β alloys preferential alloying was reported to have occurred between the α phase and the solder. Contrary to this finding, at 350°C., the alloying occurred equally with the α and β phases. Increase in the aluminium content conferred no added resistance to penetration. Lead at 350°C. did not penetrate plain 60/40, 70/30 and 53/47 brasses.

Stainless steels

Although many investigations sponsored by the U.S. Atomic Energy Commission on the solution of solid metals in molten metals have been published recently, only a comparatively small number have dealt with stressed metals. Grassi, Bainbridge and Elliot[45] investigated the stress-rupture properties of five low-alloy and stainless steels in liquid lead-bismuth alloy at 750°C. When the metals were not pre-coated before immersion in the molten metal no significant attack was noted. However, coating before testing resulted in a small decrease of the properties of the steels. The greatest decrease in strength was shown by a chromium/molybdenum/vanadium steel.

In a later publication the same authors[46] tested niobium and molybdenum in lead and bismuth. They reported that an anomalous increase in strength was noted for molybdenum in the stress-rupture tests at 850 and 750°C. in the molten metals. No significant surface attack by the liquid metals was noted. Niobium on the other hand showed a decreased strength and ductility, bismuth having the greater effect and producing fissures in the surface of the metal. The welding of niobium to molybdenum resulted in a zone between the two metals, which showed the development of large grains and broad grain boundaries containing some unknown precipitate. These boundaries were particularly susceptible to embrittlement by molten bismuth.

Pray, Peoples and Boyd[47] reported that stainless steels are relatively unattacked by pure bismuth. Stellite and some of the Haste-alloys are embrittled. Their results indicated that the presence of gases in solutions in the bismuth did not affect the attack on the steels, 'as-received' bismuth being as reactive as degassed metal. Fatigue and stress-rupture tests on stainless steels in molten sodium at 500°C. have been shown by Koenig and Vandenberg[48] to give results comparable with those obtained in helium and argon.

Penetration by sodium, gallium, potassium and lithium

Sodium, gallium, potassium and lithium have received particular study because of their potentiality as coolants in nuclear reaction. Wilkinson and Yaggee[44] showed that even in unstressed tests Monel, Inconel, mild steel (SAE·1020), Armco iron, nickel types 302, 347 and 440 stainless steels were subject to intergranular attack by lithium at 600°C. No intergranular attack was noted at 300°C. Bokros[56] showed that sodium had no effect on the hot-tensile properties of zirconium. Martin and Smith[57] have also shown that sodium did not affect the fatigue life of 18/8 stainless steels when tested at 300°C. in push-pull tension. On the other hand, these same authors reported that the fatigue limit and the life of mild steel, at stresses above the fatigue limit, was reduced, when tested in molten tin at 300°C.

Herold *et al.*[53] conducted a systematic investigation of the penetration of lithium into pure iron and mild steels (0·1%C.) at temperatures up to 1,100°C. They found that pure iron was resistant to penetration but that steels were embrittled. It was theorized that the reaction between impurities and carbon in steel produced fissures which aided penetration. Heating the steel in hydrogen for 100 h. at 900°C. rendered it impermeable.

The main work on the problem of intercrystalline failure has not been directed to an evaluation of its cause, but rather to seek systems which did not exhibit it. It was not until 1948, when C. S. Smith[49] published an account of the effect of interfacial energies on the equilibrium form of a microstructure, that any further work was carried out.

Effect of interfacial energies

Smith suggested that the interfacial energies between crystals could be considered as tensions acting along the boundaries. When several crystals meet, then their boundaries make definite angles with one another at their point of intersection so that the interfacial tensions formed a balanced system. The angle between two interphase boundaries when a crystal of one phase meets two crystals of another phase was called the dihedral angle. The dihedral angle would vary with the values of the interfacial tensions. The concept could be applied to the interface between a solid surface, solid grain boundary and a molten phase. Smith postulated that if the interphase energy was less than half that of the crystal-boundary energy in one phase, the dihedral angle would be zero and the second phase would tend to spread indefinitely along the crystal boundary.

Furthermore, he concluded that if the dihedral angle was less than 60° a liquid second phase would be expected to penetrate along grain edges (a grain edge being defined as the line forming the junction between three adjacent crystals). He tried to explain the embrittlement of copper-bismuth alloys by this concept, that since the dihedral angle of bismuth on copper was equal to zero, then molten bismuth would penetrate between the crystals completely wetting the grain faces and disintegrating the solid. Lead would not have the same deleterious effect, since the dihedral angle on copper was much greater than zero. Smith believed that no stress was necessary for such an action to occur. No indication was given of the rate at which liquid bismuth might be expected to penetrate along the grains of a piece of solid copper with which it was in contact.

Robertson[43] has endeavoured to explain the intercrystalline penetration of mercury into brass by applying Smith's ideas. He pointed out that pure copper appeared to be immune from penetration at 170°C. (the temperature above which intermetallic compounds were not stable) since the measured grain boundary groove angle (about 120°) was high. Tests on specimens which were kept under a constant stress while immersed in mercury under the same conditions indicated that the dihedral angle was not appreciably affected by the presence of a stress. An unstressed brass containing 69% copper suffered deep penetration after immersion in mercury for 18 h. at 350°C.; this temperature was chosen since it was above that at which intermetallic compounds were formed. It was suggested that the attainment of the equilibrium dihedral angle at room temperature was prevented by the formation of an intermetallic compound, but that this compound may be broken down under stress.

Discussion

In the foregoing survey details have been given of materials which are susceptible to embrittlement when immersed or coated with a liquid metal. It will also aid in an appreciation of this problem if a brief account is given of the general factors which can effect embrittlement as follows: (1) The surface condition of the solid metal; (2) the grain size of the solid metal; (3) the level of stress; (4) the strain rate; (5) the composition of the molten metal; (6) the effect of temperature.

(1) *Surface condition* One of the prime requisites for embrittlement noted in all publications was that the liquid metal should wet the solid metal surface. Thus oxide films which are not soluble in the liquid metal and which will not be reduced by the liquid metal are protective. At very high deformations, however, the oxide skin may crack, thus presenting fresh unoxidized surfaces to the molten metal. Plating can be protective if the plated metal is not attacked by the molten metal. If it is attacked, then failure is enhanced by the plating, *e.g.* Jepson and Thompson's work. Any method of surface preparation which presents a clean, solid metal surface to the liquid metal can initiate failure in a suitable system.

(2) *Grain size* A large grain size is deleterious. Goodrich showed that the resistance to penetration at 250 and 350°C. varied inversely as the grain size. This effect was very pronounced at 250°C. but not so noticeable at 350°C. Van Ewijk, in a discussion on Goodrich's paper, reported also that embrittlement was increased with a coarsening of the grain size. The confirmation of this effect was provided by Genders, who showed that the degree to which a metal had been cold-worked and the shape of the grain boundaries influenced intercrystalline embrittlement by a liquid metal. The second factor was particularly important at lower temperatures. Desch supported the view that grain shape was more important than grain size. He suggested that intercrystalline embrittlement will not be found in cast metals where there are interlocked and irregular boundaries. This statement, however, seems surprising in the light of Dickenson's results which showed that an as-cast structure of intermingled α and β crystals in a manganese bronze specimen suffered intergranular failure in molten solder. It seems quite conclusive that a large grain-size is deleterious and this may be explained by the fact that crack propagation is easier if the direction of the boundary does not change within short distances.

(3) *Stress level* Many investigations have reported that the time to fracture of a solid metal in a molten metal environment is decreased with increasing stress more so than if the metal was tested in air. Hartley showed that a hyperbolic relationship existed between the stress and time to rupture. Several of the published papers have also indicated that the rate of embrittlement is slow below a critical stress. It appears that this critical stress level may correspond with the yield strength of the solid metal. It is, of course, difficult to determine accurately because local yielding will undoubtedly occur in most metals near their conventional yield or proof stress.

(4) *Strain rate* Goodrich has reported that the yield and maximum loads withstood by different steels in the presence of molten white metal decreased with slower rates of loading at constant temperature. The greatest effect, however, was obtained on the extent of deformation before fracture, which was greatly reduced at lower strain rates. Hartley, too, was able to show that the apparent strength of a solid metal tested in a liquid metal was very much higher in a rapid tensile test than in a slow test extending over about 10 h.

(5) *Composition of the molten metal* Earlier in this discussion it has been pointed out that one of the major factors initiating embrittlement was that the liquid metal should wet the solid metal surface. Lead, for example, does not wet 60/40 and 70/30 brass but solder does. Thus Whitaker showed that these brasses were embrittled by solder at 200°C.

but that lead at 350°C. had no effect. In this instance the tin in the solder promoted wetting of the surface. The wettability of a molten metal is related to the interfacial tension at the liquid/solid interface. If tin wets the surface of solid brass then the lead should readily wet the tinned surface, since tin and lead are mutually soluble.

Other investigators have confirmed this effect on steels where lead produced no intergranular failure at 250°C. but solder did.

(6) *The effect of temperature* Dickenson showed that the maximum strength and deflection of a solid metal tested in bending when coated with a molten metal was decreased by an increase in temperature. The resistance to penetration of steels has been shown to be less at 350°C. than at 250°C. At the higher temperature failure was almost instantaneous, whilst at 250°C., for the same stress the time to fracture was prolonged. Van Ewijk, however, working on the penetration of molten solders into stressed nickel/chromium steels, found that the temperature of the molten metal did not affect the degree of embrittlement. His work was carried out on internally stressed components, so the higher temperatures may have relieved the stress.

One of the more interesting effects of temperature, revealed by Goodrich and Genders, was that the effect of grain size, in lowering the properties of the solid metal in a liquid metal, was greater at low temperatures than at high temperatures. The inference that can be drawn from this behaviour is that the applied stress can decrease the activation energy for grain boundary diffusion and that embrittlement is due to rapid grain boundary diffusion under the influence of stress.

A satisfactory hypothesis for this type of embrittlement has not yet been developed. Some authors believe failure is due to discontinuous cracking and attack along the grain boundaries. However, this idea does not explain all facets of the problem.

References

(1) F. Rogers (unpublished Report, 1906), see *J. Inst. Metals*, 1921, **25**, 38; 1919, **22**, 114; 1920, **23**, 244.
(2) E. Heyn, 'Internal strains in cold-wrought metals and some troubles caused thereby,' *Ibid.*, 1914, **12**, 3.
(3) H. S. Rawdon, 'The use of mercury solutions for predicting season cracking in brass,' *Proc. Amer. Soc. Testing Materials*, 1918, **18**, 2, 189.
(4) A. K. Huntingdon, *J. Inst. Metals*, 1914, **12**, 3.
(5) C. H. Desch, 'The solidification of metals from the liquid state,' *Ibid.*, 1919, **22**, 247.
(6) H. Moore and S. Beckinsale, 'The removal of internal stress in 70/30 brass by low temperature annealing,' *Ibid.*, 1920, **23**, 225.
(7) H. Moore, S. Beckinsale, and C. E. Mallinson, 'The season cracking of brass and other copper alloys,' *Ibid.*, 1921, **25**, 35-126.
(8) G. Edmunds, 'Season cracking of brass,' Symposium on stress corrosion cracking of metals, *A.S.T.M.* and *A.I.M.E.*, 1944 and 69.
(9) W. Lynes, *A.S.T.M.*, 1941, **41**, 859-885.
(10) W. H. Bassett, *Ibid.*, 1918, **18**, 2, 153-162.
(11) T. C. Wilson, G. Edmunds, E. A. Anderson, and W. M. Peirce, Symposium on stress corrosion cracking of metals, *A.S.T.M.* and *A.I.M.E.*, **1944**, 173.
(12) J. H. S. Dickenson, *J. Inst. Metals*, 1919, **22**, 274.
(13) J. H. S. Dickenson, 'Note on a failure of manganese bronze,' *Ibid.*, 1920, **24**, 315-322.
(14) U.S. Bureau of Standards Technical Paper, No. 245, 1923.
(15) H. M. Duncan, 'The action of molten brass on nickel steel,' *Metal Ind.*, 1924, 24.
(16) H. C. Hall, *J. Inst. Metals*, 1920, **24**, 326.
(17) H. J. Miller, 'The penetration of brass by tin and solder,' *Ibid.*, 1927, **37**, 183.
(18) H. J. Hartley, 'The attack of molten metals on certain non-ferrous metals and alloys,' *Ibid.*, pp. 193.
(19) R. Genders, 'The penetration of mild steel by brazing solder and other metals,' *Ibid.*, pp. 215.
(20) S. V. Williams, *Ibid.*, pp. 226.
(21) Anderson and Poole, *Ibid.*, pp. 237.
(22) W. Riede, 'The occurrence of cracks in the brazing of steel,' *Stahl u. Eisen*, 1929, **49**.
(23) W. Albert, 'Occurrence of cracking in hard soldering of steel,' *Ibid.*, 1930, **50**.
(24) K. Kreitz, 'About brazing properties,' *Ibid.*, 1931, **51**.
(25) P. Ffield, 'Alloys in shipbuilding,' *Trans. Soc. Naval Arch. Mar. Eng.*, 1937, **45**, 174-200 (M.A. **5**, 739).
(26) Sparagen and Claussen, 'Welding copper steels,' Supplement to the Journal of the American Welding Society, Sept., 1939.
(27) O. H. Henry and R. W. Schroeder, 'A study of the embrittling effect of zinc on stainless steel,' *Welding J.*, 1942, **21**, suppl. 287-290.
(28) H. A. Campbell, 'Stainless steels, hot and otherwise,' *Iron Age*, 1943, **151**, 56-58.
(29) J. H. Craig, 'Elevated temperature tests on galvanized steels,' Symposium on stress corrosion cracking, *A.S.T.M.* and *A.I.M.E.*, 1944.
(30) H. Schottky, K. Schichtel, and R. Stolle, *Arch. Eisenhuttenwesen*, 1931, 4, 541-547; *Iron Steel Ind.*, 1931, **4**, 322 and 332.
(31) L. W. Schuster, 'Mechanical breakdown of prime movers,' *Inst. of Mech. Eng.*, 1933, **124**, 337-435.
(32) L. J. G. van Ewijk, 'The penetration of steels by soft solder and other molten metals,' *J. Inst. Metals*, 1935, **56**, 241-248.
(33) O. Pattermann, *Ibid.*, p. 254.
(34) W. E. Goodrich, 'The penetration of molten white metals into stressed steels,' *J. Iron St. Inst.*, 1935, **132**, 43-64.
(35) M. S. Wang, 'The intercrystalline penetration of molten alloys into steel,' Thesis, Leeds University, June, 1943.
(36) G. W. Austin, 'The effect of molten-solder on some stressed materials,' *J. Inst. Metals*, 1936, **58**, 173-185.
(37) H. N. Bassett, *ibid.*, p. 189.
(38) M. D. Jepson and F. C. Thompson, *Ibid.*, 1951, **43**, 82.
(39) W. R. Smith and P. E. J. Forsyth, 'Grain boundary penetrations by liquid metals':
(i) 'Some service failures,' *Metallurgia*, 1946, **34**, 186-188.
(ii) 'Attack of platinum-alloy spark-plug electrodes by molten lead,' *Ibid.*, pp. 245-246.
(40) Private communication from E. C. Lloyd, G.K.B., and N. Cardiff.
(41) A.D.A. communication, 'Soldering of aluminium,' *Metallurgia*, 1950, **42**, 131.
(42) M. E. Whitaker, 'Intercrystalline failure of brasses and aluminium brasses in air, ammonia, certain aqueous solutions and molten metals,' *Ibid.*, 1948, **39**, 21-29.
(43) W. D. Robertson, *Trans. Amer. Inst. Min. Met. Eng.*, 1951, **191**, 1190-1191.
(44) W. D. Wilkinson and F. L. Yaggee, 'Attack on metals by lithium,' A. N. L. Report 4990, Oct., 1950.
(45) R. C. Grassi, D. W. Bainbridge, and R. O. Elliot, 'Metallurgical investigations concerned with the behaviour of materials in an environment of liquid lead/bismuth alloy,' *Univ. of Calif. Inst. Eng. Res. N.P.*, 1881, Sept., 1950, A.E.C.U.
(46) R. C. Grassi, D. W. Bainbridge, and R. O. Elliot, *Ibid.*, A.E.C.U. 2201, July, 1952.
(47) H. A. Pray, R. S. Peoples, and W. K. Boyd, 'Corrosion by molten bismuth,' Battelle Memorial Inst. B.M.I. 773, Oct., 1952.
(48) R. F. Koenig and S. R. Vandenberg, 'Sodium, a non-corrosive coolant,' Knolls Atomic Power Laboratory A.E.C.U., 1945.
(49) C. S. Smith, 'Grains phases and interfaces; an interpretation of microstructure,' *Trans. Amer. Inst. Min. Met. Eng.*, 1948, **175**, 15-51.
(50) R. Haarman, 'Observations on the attack of molten zinc on iron,' Second international conference on hot dip galvanizing, Düsseldorf, 1952, 123-143.
(51) W. Radeker, 'Stress-cracking in steel caused by molten zinc,' *Stahl. u. Eisen.*, 1953, **73**, 10, 654-658.
(52) J. F. Strachan, D. J. Jones, and N. L. Harris, 'The effect of mercury on the corrosion and mechanical properties of various materials,' Part 2, A.E.R.E. Report No. X/R, 1229, 1954.
(53) A. Herold, P. Mullerand, and P. Albrecht, 'On the permeability of steel to lithium,' *Compt. Rend.*, 1952, **235**, (13), 658-659.
(54) S. T. Kishkin, V. V. Nikolenko, and S. I. Ratner, 'Strength of metals in contact with fused solders,' *Zhurnal Tekhnicheskoi Fiziki*, Aug., 1954, **24**, (8), 1455-1466.
(55) I. M. Potak and I. M. Shcheglakov, 'Influence of molten metallic coatings on the mechanical properties of steels and alloys,' *Ibid.*, May, 1955, **25**, (5), 892-907.
(56) J. C. Bokros, 'Effect of sodium on the mechanical properties of zirconium,' U.S. Atomic Energy Commission NAA-SR-1867, June 15, 1957.
(57) J. W. Martin and G. C. Smith, 'A preliminary study of the fatigue of metals in liquid metal environments,' *Metallurgia*, Nov., 1956, **54**, (325), 227-232.