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Review
Liquid metal embrittlement

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Liquid metal embrittlement is the reduction in the elongation to failure that can be produced when normally ductile solid metals are stressed while in contact with a liquid metal. This review describes its principal characteristics and the several models which have been advanced in attempts to explain the occurrence and different features of the process. Comparison between theory and experiment indicates that many, but not all, of its aspects are consistent with a mechanism which operates by reducing the fracture surface energy of the solid metal. Literature reports show that liquid metal embrittlement can occur with a very wide range of material combinations, and while most of the data refer to laboratory studies, it is clear that the phenomenon is also of technological significance as a potential cause of plant damage.

1. Introduction

Liquid metal embrittlement, LME, is the reduction in elongation to failure that can occur when normally ductile metals or alloys are stressed while in contact with liquid metals. In severe cases, the ductility may be so reduced that the normal ultimate tensile strength is not achieved and thus the load needed to produce failure is decreased. Such effects are illustrated by the curves shown in Fig. 1 for aluminium stressed in contact with mercury and a number of mercury alloys [1].

LME has been studied by materials scientists for several decades, Huntington [2] describing the embrittlement of brass by mercury on the eve of the first World War. This and subsequent work has identified LME as one of the spectrum of environmental effects producing mechanical degradation that includes hydrogen embrittlement, and in some respects stress-corrosion cracking and temper embrittlement. However, despite the publication of major reviews by Eldred in 1955 [3], Rostoker, McCaughey and Markus in 1960 [4], Stoloff in 1968 [5] and Kamdar in 1973 [6], LME remains an unfamiliar failure mechanism for many materials scientists. This relative unawareness has been sharply illustrated by the recent concern and attentive discussion of damage caused by liquid gallium in an aircraft [7] and the notorious effect of molten zinc on stainless steel piping during the Flixborough disaster [8]. It is therefore appropriate that LME should be reviewed in the light of more recent work to provide a current assessment of a phenomenon which is both a subject for scientific study and a cause for concern to technologists.

This review will first describe the effects that characterize a failure process as LME and distinguish it from other environmentally induced degradation processes. We shall then discuss its occurrence, and the various rules and models that have been developed to predict its incidence and severity. In presenting experimental results we shall refer to the original papers rather than to summaries because there has been a confusing tendency to simplify the information – for example alloy data [4] has been requoted as referring to the parent metal [5, 6].

2. Characteristics

LME failure occurs by the nucleation of a crack at the wetted surface of the solid and its subsequent propagation into the bulk. The failure process does not involve bulk chemical or structural modification of the solid and hence it differs from other liquid metal degradation processes such as grain boundary penetration or high temperature corrosion. Stoloff [5] has argued that LME is unique among the liquid metal degradation processes in that it does not depend upon the liquid–solid contact time or temperature in a simple manner. Thus the time for a solid to fail in an inert atmosphere can be described frequently as a monotonic, exponential, function of the applied tensile stress, but the time for failure in a liquid metal environment can decrease abruptly when a critical, threshold, stress level is exceeded [9, 10]. This implies that the probability of LME occurring cannot be predicted from reaction rate data and that stress transients are as likely to initiate failure after short as after long exposures.

2.1. Prerequisites for LME

There are two necessary, but not sufficient, conditions that must be satisfied simultaneously for LME to occur. The first of these is an applied stress sufficient to produce plastic deformation. We know of no examples of LME failure of material stressed elastically without dislocation motion, although Parikh [11] observed failure of nickel, palladium, silver and copper alloys in lithium well below their bulk yield stresses. The threshold deformation for LME, therefore, may be very small for some systems, but is usually substantial as illustrated in Fig. 1.

While many of the data characterizing LME have been obtained from tensile tests, pure tensile stressing of the complete component is not a prerequisite for failure. Complex stress patterns can also cause LME and bend tests have been used to screen materials for their susceptibility [4] although we are unaware of any evidence of LME in compression. Similarly, it has been reported that notched tensile samples can be embrittled in conditions under which smooth samples are immune [12].

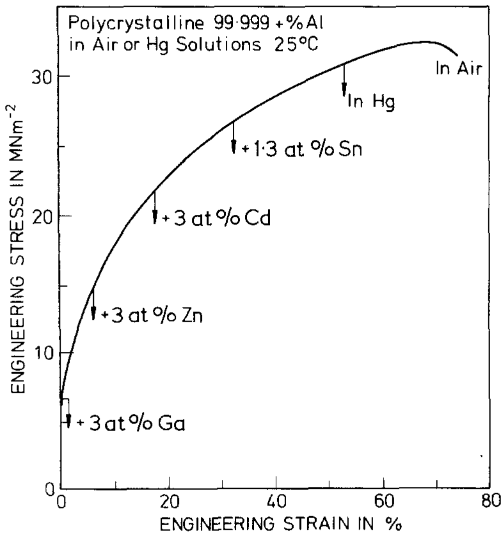

Figure 1 Embrittlement of polycrystalline pure aluminium by various mercury solutions at room temperature (after Westwood, Preece and Kamdar [1], copyright 1969 by American Society for Metals).

The second prerequisite for LME is direct contact on an atomic scale between the stressed solid and the embrittler. This implies that the liquid must flow into any crack which may form and propagate. Direct experimental observations have shown liquid metal to penetrate to the tips of growing cracks [13]. Crack growth will stop if the supply of liquid is exhausted, except in the case of notch brittle materials if the critical flaw size has been exceeded. Similarly, interruption of the supply of the embrittling liquid leads to crack arrest in all but a few circumstances which will be commented upon later (Section 2.3).

Contact between the embrittling liquid and the ductile solid can often be prevented by the presence of oxide films. Unless these are ruptured or dispersed, embrittlement may be delayed or inhibited. Thus unstressed AISI 321 stainless steel resists penetration by zinc even at 1050° C, while the stressed steel is embrittled at 780° C [14]. Similarly, Hancock and Ives [15] have shown that copper–8% aluminium alloys are embrittled by the application of mercury during but not after straining. Both of these reports are consistent with embrittlement being caused by rupture of oxide films to permit the liquid to make contact with fresh, atomically clean, solid surfaces. Thus an additional function of stressing can be to rupture surface films which inhibit direct contact.

2.2. Fracture behaviour

By definition, LME causes a loss in ductility but other mechanical characteristics are usually unaffected. Elastic moduli are believed to be always unchanged, but in severe cases the UTS and even the proof strength may be decreased, as illustrated in Fig. 1. Any reduction in the engineering UTS depends on the extent to which ductility is curtailed and on the work-hardening characteristics of the solid; a material which shows a fairly flat stress–strain curve in the plastic region will be less weakened than one which work-hardens extensively.

Metals failing by LME usually fracture intergranularly as shown in Fig. 2, and this phenomenon has been used to reveal grain facets in structural

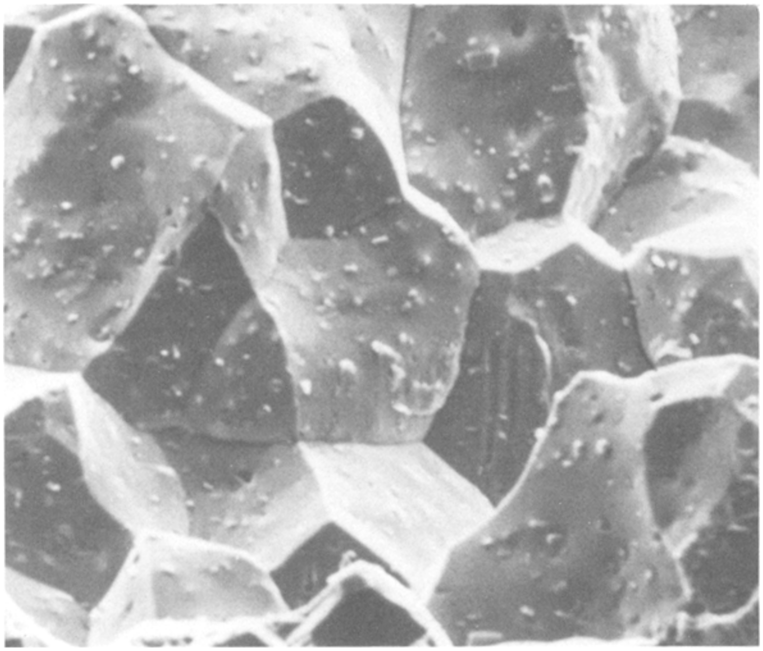

Figure 2 The intergranular fracture surface of commercially pure aluminium embrittled by gallium. The second phase particles are iron-rich intermetallics (X 320).

studies [16]. However, some cases of transgranular fracture have been observed [17–19] showing that the presence of grain boundaries is not a necessity. This conclusion has been confirmed by studies showing that stressing single crystals in contact with liquid metals can cause cleavage along low index planes [20–23].

LME-induced cracks propagate along grain boundaries or across grains at very variable speeds depending on the testing conditions. Propagation rates may reach several m sec^{-1} [24] if substantial amounts of elastic strain energy are present in the stressed solid, thus giving rise to descriptions of LME failure as "catastrophic brittle fracture". On the other hand, if little strain energy is available, the crack propagation speed will be low and depend upon the extension rate of the sample as demonstrated in Fig. 3 [25].

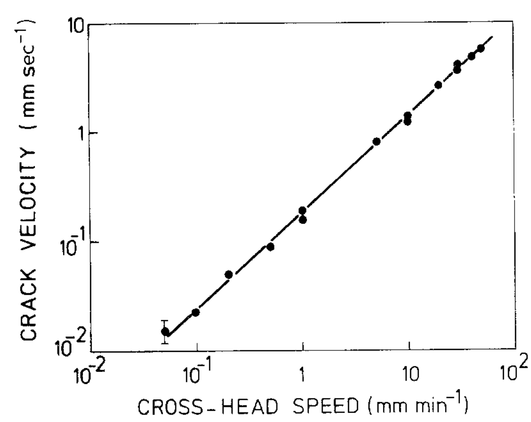

Figure 3 Crack growth rate versus extension rate for aluminium single crystals embrittled by liquid gallium (after Old [25]).

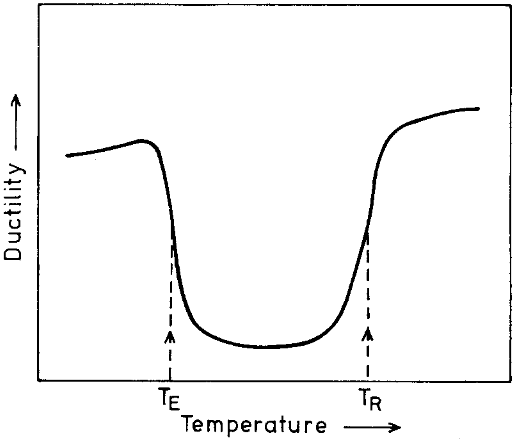

Figure 4 The effect of LME on the variation of ductility with temperature (schematic).

2.3. Dependence on temperature and strain rate

LME usually occurs just above the melting point of the embrittler and thus causes a form of ductile–brittle transition as the temperature increases. With a further rise in temperature, ductility frequently returns. In this review, the onset temperature and the ductility recovery temperature are defined as T_E and T_R respectively, as shown in Fig. 4. There is thus a "ductility trough" over a particular temperature range but the width and depth of the trough can vary considerably from system to system and also to some extent with the strain rate used during the tests on a given system. Thus studies of the brass–mercury system have revealed troughs extending over 300° C [26] while recent work at Harwell has identified troughs in the zinc–tin system extending over only a few degrees [27].

The minimum temperature for the onset of embrittlement is usually the melting point of the embrittler, presumably because its atoms are far more mobile in the liquid than the solid. However, some instances have been reported of the onset of embrittlement prior to melting. Lynn *et al.* [28] observed the embrittlement of an AISI 4140 steel to commence at 0.75 T_m for cadmium, 0.85 T_m for lead and tin and 0.9 T_m for indium and zinc, where T_m is the melting point in degrees Kelvin. In contrast, some embrittlers do not become active until temperatures much above their melting points are reached. Thus the embrittlement of austenitic stainless steel by zinc only becomes significant at about 750° C, 1.48 T_m [14], and of pure iron by indium at 310° C, 1.36 T_m [29].

Most experimenters have used low or unmeasured strain rates in tests assessing the susceptibility of material systems to LME, but there is some evidence that increased embrittlement is produced by high strain rates. Fig. 5 shows the dependence of T_R on strain rate for an aluminium alloy in mercury–3% zinc [4, 30], and titanium 55A in cadmium [31]. Similarly, the severity of embrittlement of aluminium 2024 by indium tended to be increased by faster straining, Fig. 6 [4]. There is also some evidence that failure can be produced at zero strain rates under constant load conditions by "static fatigue". This has been observed for copper–2% beryllium in mercury [32], for AISI 4140 in contact with solid indium and cadmium [33], and for AISI 4340 [34] and several titanium alloys [35, 36] in contact with solid cadmium.

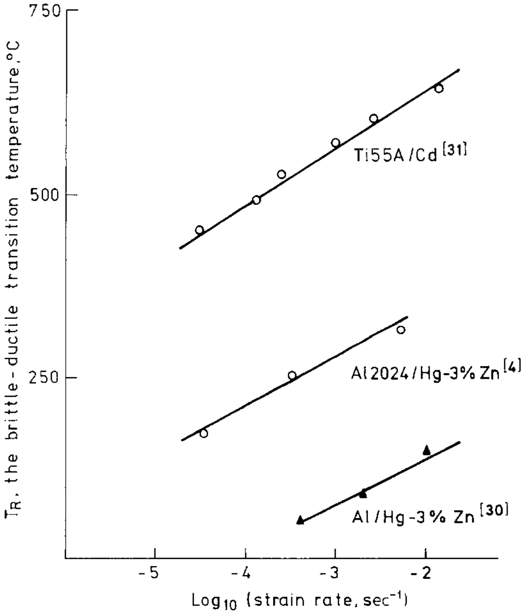

Figure 5 Observations on the effects of strain rate on the brittle–ductile transition temperature for LME.

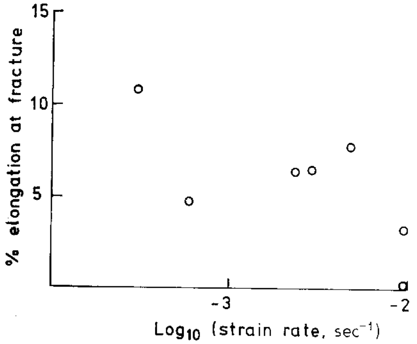

Figure 6 The effect of strain rate on the elongation to failure of aluminium alloy 2024-T4 stressed in indium at 160 to 171° C (after Rostoker, McCaughey and Markus [4]).

2.4. Effect of alloying the liquid embrittler

Alloying a liquid metal can cause it to embrittle or change the severity if it does so already, but substantial additions are often needed to produce significant effects. For example, cadmium is not embrittled by mercury at room temperature but its ductility and fracture stress decrease if the liquid is alloyed with more than 5 to 10% of indium, while the opposite effect is observed for the embrittlement of silver [10]. Thus, although embrittlement is often described as an adsorption phenomenon [6, 153], the evidence suggests that major effects will not be produced by small quantities of an active component in the p.p.m. range and in that sense the term adsorption may be misleading.

The concept that low melting metals can act as inert carriers for embrittling species may explain a number of experimental observations. Thus lack of embrittlement could be due to the T_R temperature for the particular solid metal/liquid metal combination being less than the melting point of the embrittler. However, additions of the embrittler to a lower melting carrier could result in LME. A possible example of this is provided by the observations that aluminium is not embrittled by tin–zinc solders at 250° C [37], and only slightly embrittled by mercury at room temperature, but is severely embrittled by mercury–1.3% tin and mercury–3% zinc as illustrated in Fig. 1 [1].

2.5. Effect of the metallurgical condition of the solid

Because LME failure is usually intergranular it is to be expected that variations in the grain size or structure, or the grain boundary chemistry should influence the susceptibility of stressed solids. The expectation is borne out by the available experimental evidence although the reported effects are sometimes contradictory. Thus increasing the grain size worsens the embrittlement of copper and α-brass by mercury [26, 38, 39], and of aluminium by tin–zinc alloys [40], but the reverse behaviour was observed for prestrained aluminium stressed in contact with mercury–3% zinc [30]. Similarly, while small amounts of prior deformation ($<10\%$) increased the embrittlement of an aged aluminium alloy in mercury, further deformation reduced the severity [41]. The effect of prestrain on the embrittlement of α-brass by mercury depended on its grain size [39], while Watkins *et al.* found lead embrittlement of AISI 4145 steel to be eliminated by cold work [42]. Changes in grain boundary chemistry may be responsible for the observation by Costas [43] that embrittlement of copper–nickel alloys by mercury could be suppressed by additions of phosphorus and subsequent annealing. A beneficial decrease in T_R temperatures was produced by grain boundary segregation of phosphorus, and arsenic to a lesser extent, in AISI 3340 steel, in contact with molten tin and lead, but segregation of traces of tin and particularly antimony were detrimental [44].

The hardness and deformation behaviour of the stressed solid can affect its susceptibility to LME, the harder materials normally being more severely embrittled. Preece has pointed out that although alloying can inhibit or reduce embrittlement in isolated cases, the usual effect is to make the solid harder and more readily embrittled [45]. Thus alloying copper with aluminium, germanium, gold or zinc and alloying iron with aluminium or silicon increases susceptibility to embrittlement by mercury [38]. This increase correlates with a lowering of the stacking fault energies of the alloys which in turn indicates restricted dislocation cross-slip and hence reduced plasticity. Similarly, the embrittlement of an aluminium 2024 alloy by mercury was most severe after ageing to produce a peak hardness and was reduced by overageing [46].

3. Occurrence

The examples given in the previous section demonstrate that LME does not occur every time a pure metal or alloy is stressed while in contact with a liquid metal. Nevertheless a wide range of materials have been found to be embrittled by liquid metals. Laboratory studies and plant failure analyses have shown that pure metals and industrially important alloys such as brasses and bronzes, carbon and stainless steels may be embrittled by molten metals with both low and moderate melting points including mercury, gallium, solders and even copper base alloys. Whether or not LME occurs on a particular occasion depends not only upon the composition of the solid/liquid combination but also upon the metallurgical state of the solid and the exposure conditions. It is not surprising therefore that there are conflicting reports in some cases about whether a particular combination is embrittled. Thus some workers found copper to suffer LME when stressed in contact with mercury [39], while others using fine grain material reported no effect [38]. Because a wide variety of laboratory conditions have been used in LME studies it is not possible to present a simple summary of which systems do and which do not embrittle. If there is an interest in the possibility of LME occurring with a certain combination, it is always advisable to consult the original literature to check whether the conditions employed are relevant.

The scientific literature describing studies of the susceptibility or immunity of various specific combinations to LME is extensive but scattered. To provide a guide to the location of this literature, we present in Table I what we believe to be a reasonably complete assembly of references to original work. It should be emphasized that citation in the Table does not necessarily mean that the combination suffers LME, but merely that it has been studied. Similarly, it cannot be assumed that a system will be immune to LME because no reference to it appears.

The distribution of references in the Table is notable in that less than half relate to steels despite their dominant position as materials for stressed structures. This follows from the historical development of scientific interest in the phenomenon. The earliest studies of LME were concerned

TABLE I Some references to studies of liquid metal embrittlement

Liquid metal or main alloy component	Aluminium and its alloys	Copper and its alloys	Zinc and its alloys	Other non-ferrous metals and alloys	Steels
Alkali metals	[4, 47]	[4, 11, 47]		(Ag, Ni, Pd, [11]), (Mg, [4])	[4, 166–118]
Bismuth		[4, 66–71]	(Mg, [4])	(Mg, [4]) (Mg, [4]), (Ti, [31, 35, 114]), (Zr, [18, 115])	[4, 12, 28, 117, 119] [4, 28, 35, 120, 122, 123]
Gallium	[4, 7, 16, 22, 48–58]	[23, 71]	[66, 92–96]	(Ag, [85]), (Cd, [13]), (Mg, [4])	[4, 121]
Indium	[4]	[71]			[28, (111), 124]
Lead	[4]	[4, 69, 72]	[66, 97]		[4, 28, 42, 44, 123, 125–129]
Mercury	[1, 4, 17, 30, 41, 59–62]	[4, 15, 26, 32, 39, 43, 59, 65, 73–86]	[20, 21, 95, 98, 100–113]	(Ag, [10, 85]), (Cd, [10, 23, 66]), (Mg, [4])	[4, 38, 117, 130]
Solder	[37, 40, 63–65]	[63, 69, 87–90]	[97]		[63, 131–133, 147]
Tin	[4, 37, 40]	[64, 66, 69, 88, 91]	[66, 97]		[4, 12, 28, 63, 119, 123, 125, 133–135]
Zinc	[4, 37]	[66]		(Mg, [4]), (Ni, [67]), (Ti, [4])	[4, 14, 28, 136–149]
Others	(Se*, Te*, Tl*, 4]	(Se*, Te*, Tl*, 4)		(Mg/Se*, Te*, Tl*, [4]) (Ti/Se*, Te*, Tl*, [4])	(Ag*, [105, 119]), (Al*, [108, 123, 134, [42]), (Cu*, [134, 137, 138, 142–146, 148]), (Se*, Te*, Tl*, [4])

*Asterisked elements inside brackets are liquids; the others are the stressed solids.

with the intergranular failure of internally stressed brass initiated by contact with mercury [2]. By 1920, Moore and Beckinsale [75] among others had identified many of the primary characteristics of LME from such studies. Reports of solder materials producing embrittlement of brasses and steels began to appear in the 1920s and 1930s and embrittlement of aluminium and its alloys from 1936, reflecting the growth of the aircraft industry.

The rather diffuse body of data generated by the early studies were ably summarized by Eldred in 1955 [3] and updated by Rostoker *et al.* in 1960 [4], and Stoloff in 1965 [5]. Since that time, Rostoker and Stoloff, and their co-workers have continued to publish papers on a variety of aspects of LME, but most recent studies of LME have tended to be concentrated at a few laboratories concerned with restricted ranges of materials. Thus Westwood and his co-workers at RIAS, Baltimore conducted an intensive study of the mechanism of LME using model systems, particularly single and polycrystalline zinc stressed in contact with mercury and gallium and their alloys. Lacombe and his colleagues at l'Université de Paris-Sud at Orsay, have investigated the embrittlement and interdiffusion behaviour of aluminium and aluminium alloys in contact with gallium and, to a lesser extent, mercury, Similarly, while the THEMIS project commissioned work at US Universities and research institutes, the materials studied were restricted to a few low alloy steels and solder constituents.

The main results of these and other studies will be discussed later in the context of theoretical analyses of LME. It might be commented in passing however, that although these studies have improved our understanding of the mechanism of LME, most of these projects used materials combinations which were known to show LME, thus enhancing the uneven distribution of literature defining its presence. This may well have given the false impression to a casual reader that it is restricted to relatively few combinations.

Although much of the work so far has tended to be on model systems, LME is far from being merely a laboratory curiosity. For example, Rostoker *et al.* [4] were able to quote twenty published descriptions of failures caused by LME, mainly the embrittlement of steels by solder materials. Reports of industrial damage have

TABLE II Qualitative observations of Rostoker, McCaughey and Markus [4] on the embrittlement of various unspecified engineering alloys

Engineering alloy	Temperature (° C) with liquid in brackets												
	30 (Hg*)	50 (Ga)	125 (Na)	180 (In)	210 (Li)	250 (Se)	260 (Sn)	300 (Bi)	325 (Tl)	350 (Cd)	380 (Pb)	450 (Zn)	475 (Te)
Aluminium alloys	E	E	E	E	N	N	E	N	N	N	N	E	
Magnesium alloys	N	N	E	N	N	N	N	N	N	N	N	E	
Steel	N	N	N	E	E	N	N	N	N	E	N	E	E
Titanium alloys	N	N	N	N	N	N	N	N	N	E	N	N	N

*Hg – 3% Zn amalgam. E = embrittled. N = not embrittled.

continued to be published since that 1960 reveiw, the most intensive recent analysis being that of the zinc embrittlement of stainless steel found in the aftermath of the Flixborough disaster. In addition, smaller incidents also occur as illustrated by the damage to a generator shaft, a pressure vessel and a boiler by contact with molten alloys reported in the space of a few years by one insurance firm [146–148]. In practice it is probable that the incidence of LME in industrial operations is greater than that indicated by these references, since some failures will not be correctly identified and many may not be described in the open literature.

4. Empirical predictions of LME susceptibility

The detailed causes and mechanisms of LME have not yet been established but several attempts have been made to identify material parameters possessed by embrittled but not by unembrittled systems and hence to permit empirical predictions of the likelihood of LME occurring in uninvestigated systems. Many parameters have been considered and rejected. Thus, while most LME data relate to low or moderate temperatures, the liquids need not have low melting points. Similarly, both very reactive and inert liquid metals, such as lithium and indium, can embrittle. However, examination of the results summarized in Table II of qualitative tests of LME susceptibility conducted by Rostoker *et al.* [4] led these authors to agree with Pertsov and Rebinder [66] that embrittled systems usually had two common characteristics; a low mutual solid solubility and a lack of intermetallic compounds. On this basis a tentative correlation was advanced although Rostoker *et al.* [4] pointed out that it was not completely reliable. Thus steel was found to be embrittled by zinc even though the solubility of zinc in iron at 450° C is 6.5 at% and the zinc–iron system forms intermetallic compounds. On the other hand, aluminium alloys were not embrittled by cadmium at 350° C or lead at 380° C despite their low solubilities and lack of intermetallic compound formation, but were embrittled by gallium which has a solubility in aluminium of 9 at% at 50° C. In summary, Rostoker *et al.* [4] suggested that this correlation can at best be regarded only as a necessary but not as a sufficient condition.

In the past it has appeared that these correlations were in conflict with the requirement that the liquid metal should wet the stressed solid, since experimental studies and theoretical analysis associated good wetting with some degree of mutual solubility or intermetallic compound formation. This discrepancy led Stoloff [5] to regard parameters derived from wetting data as being irrelevant to the interpretation of LME phenomena. However, this view must now be revised in the light of advances made in surface study techniques. The use of UHV systems and ion bombardment cleaning now enables wetting studies to be conducted using surfaces more closely resembling fresh crack faces than those employed previously. Barlow and Planting [171], for example, showed that excellent wetting can be achieved using these techniques even with systems such as iron–sodium that have neligible solubilities and do not form intermetallic compounds. There is, therefore, no longer any necessary conflict between the correlations of LME behaviour with low mutual solubility and chemical inertness and the requirement for wetting.

More recently, Kamdar [6] has argued that data on the embrittlement of cadmium by mercury–indium alloys [23] reveals a correlation between the occurrence and severity of LME in a given system and similarity of the Pauling electronegativity of the stressed and the embrittling metals. The proposed correlation was illustrated using the data presented in Table III. The electro-

TABLE III Observations by Kamdar and Westwood [23] of the effects of mercury, gallium and some of their alloys on the strength and ductility of cadmium

Environment	Electronegativity of the solute element	Fracture stress ($MN\,m^{-2}$)	Elongation at fracture (%)
Ga	1.6	10.1	~ 0.25
Hg–3% Ga	1.6	> 49	> 45
Hg–13% In	1.6	39.3	8
Hg–40% In	1.7	14.3	~ 0.5
Hg–60% In	1.7	6.1	Very low
Ga–13% In	1.7	5.7	Very low
Hg–40% Tl	1.8	> 47	> 45
Hg–42% Sn	1.8	> 30	> 48
Hg	1.9	> 45	> 45

negativity of cadmium is 1.7, and it is notable that the most severe embrittlement cited is that by mercury alloyed with indium which has an electronegativity of 1.7 and the least is that by mercury which has an electronegativity of 1.9. Kamdar cited other examples consistent with the correlation, but also identified some exceptions. Thus aluminium is embrittled by sodium, and iron by lithium despite the differences in their Pauling electronegativities; aluminium 1.5, sodium 0.9 and iron 1.8, lithium 1.0.

The basic deduction arising from attempts such as those of Rostoker *et al.* [4] and Kamdar [6] to correlate susceptibility to LME with other parameters is that it is a specific phenomenon. That is, some couples embrittle and other do not. However, this view has been challenged recently on the grounds that available experimental data are generally inadequate for any conclusion to be drawn about immunity [97]. Thus embrittlement would not be observed in a surveying programme of the type conducted by Rostoker *et al.* [4] unless a ductility trough coincided with the particular conditions used. It can be concluded, therefore that the use of correlations to predict the susceptibility of uninvestigated systems is hazardous and will remain so until far more experimental data are available, when the need for prediction of susceptibility will, of course, be less pressing.

5. Suggested mechanisms of LME

Theories have been proposed to explain failure by LME, suggesting mechanisms as diverse as increased air-pressure in pre-existing cracks [99], stress-assisted dissolution [150], the weakening of interatomic bonds by the presence of a liquid metal at the crack tip [6, 151], the formation of a weakly bonded alloy zone ahead of the crack tip [163, 164], and enhanced plasticity at the crack tip [152]. Not all of these mechanisms, however, lead to predictions that compare well with experiment. For example, Robertson [31] points out that the stress-assisted dissolution model predicts that the severity of embrittlement will increase with the solubility of the solid in the liquid, in conflict with practical observation. Similarly, evidence of plastic deformation on LME fracture surfaces has led Lynch [152] to propose that the liquid metal facilitated dislocation nucleation and movement by reducing surface lattice distortion, but it is not easy to see how this model would account for the brittle–ductile transition. However, as with many other hypotheses, there is not yet sufficient clear evidence to confirm or disprove its validity.

The most promising models at present are those that invoke weakening of the interatomic bonds in the solid at the crack tip. Such mechanisms have been referred to as "adsorption-induced reduction in strength" by Zalkin [153] and by Kamdar as "adsorption-induced reduction in cohesion" [6]. Unfortunately, these descriptions do not permit quantitative assessment of the embrittlement nor do they provide insight into the detailed atomic mechanism. Thus Krishtal relates these models to fracture of a weakly-bonded solid solution formed in a limited volume at the crack tip [154] while Shchukin and Yushchenko [155] and Rostoker *et al.* [4] interpreted them as a lowering of the solid–liquid interfacial energy and considered the process in the context of the brittle–ductile fracture behaviour exhibited by some body centred cubic and hexagonal close packed metals. Models based on reductions in energy values make it possible to interpret many of the characteristic phenomena of LME, but this approach has been contested by Preece and Westwood [156] who considered that the brittle–ductile transition observed during the LME of some face centred cubic metals was better explained by a thermally activated desorption of the embrittler atoms from the crack tip. This interpretation is consistent with the extensive deformation that precedes LME and the higher stresses needed for fracture than yielding, but it is unlikely that the very sharp transitions observed in some systems could be explained by the desorption mechanism.

None of the mechanisms described here can account for all the varied LME phenomena, but neither can any mechanism be completely discounted. On balance, we believe that treating LME as a type of brittle fracture caused by a reduction in surface energy provides the most plausible explanation of the present, inadequate, characterization data. The theories describing brittle fracture will therefore now be summarized and their predictions compared to experimental data characterizing LME.

6. Theories of brittle fracture

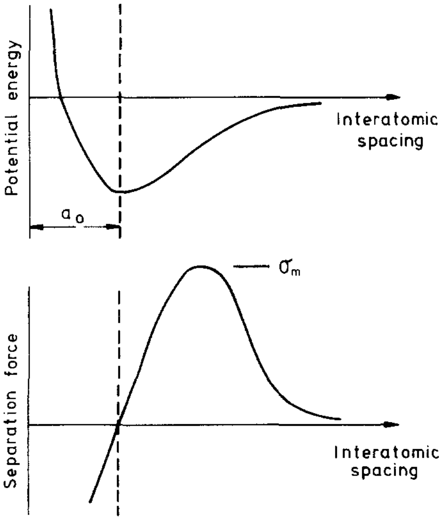

Figure 7 Schematic representation of the variation of potential energy and separation force with distance for a pair of atoms.

The simplest analysis of brittle fracture behaviour is to calculate the stress needed to fracture a perfectly elastic solid using its equilibrium interatomic separation and bonding characteristics. Fig. 7 shows schematically the relationship between the separation of a pair of atoms and their potential, and the force–displacement curve that can be derived by differentiation. By equating the elastic strain energy of the stressed solid to the work needed to create the fracture surfaces, we can derive the approximate relationship

$$\sigma_m = \left(\frac{E\gamma}{a_0}\right)^{1/2} \tag{1}$$

where σ_m is the fracture strength of the solid, γ the surface energy of the fracture faces, a_0 the equilibrium lattice spacing and E the elastic modulus, equal to the slope of the force–displacement curve at distance a_0. Substitution of reasonable values into equation 1 suggests that σ_m will be about 10% of E, but in practice this value is approached only for materials such as fine fibres or whiskers. The fracture strengths of bulk brittle materials and metals are about 1% of their elastic moduli, and this discrepancy led Griffith to postulate the presence of surface flaws at the tips of which the applied stress, σ_{app}, was concentrated [157]. Using the results of Inglis' analysis of stress distributions around elliptical cracks [158], Griffith equated the elastic energy released by the advance of an infinitely sharp crack of length c in a stressed brittle solid to the work of formation of the newly created surfaces and derived the expression

$$\sigma_{app} = \left(\frac{E\gamma}{4c}\right)^{1/2} . \tag{2}$$

In practice, cracks in brittle materials are not infinitely sharp, but the Griffith criteria for propagation can be used in a similar analysis of the behaviour of blunt cracks and leads to the expression:

$$\sigma_c = 2\sigma_{app}\left(\frac{c}{\rho}\right)^{1/2} \tag{3}$$

where σ_c is the stress at a crack tip of radius ρ. If the crack is to extend, σ_c must achieve the value σ_m given by Equation 1 and hence

$$\sigma_{app} = \left(\frac{E\gamma\rho}{4a_0c}\right)^{1/2} \tag{4}$$

which can be related to Equation 2 by the use of an effective surface energy

$$\gamma_{eff} = \frac{\gamma\rho}{a_0} \tag{5}$$

Many materials, including metals, do not normally contain the pre-existing surface cracks necessary to provide the flaws for the Griffith model of fracture behaviour. In attempting to explain how cracks could be nucleated, theoretical analyses have invoked the action of another type of flaw, i.e. dislocations. The fact that plastic deformation invariably precedes fracture is consistent with dislocation movement and the suggestion by Zener [159] that dislocations could pile up at an obstacle and coalesce to form the nucleus of a crack. The conditions needed to produce such a pile-up have been examined by many workers using the two assumptions:

(a) the array will behave elastically and hence the displacement at the head of the array (near the crack) will be related to the applied stress by the rigidity modulus, and

(b) that the resultant strain energy is transformed into the surface energy of the nucleus.

These analyses suggested that cracks could be nucleated by pile-ups of a few hundred dislocations produced by a pile-up stress, σ_{p}, such that

$$\sigma_{\mathrm{p}} = \left(\frac{AG\gamma}{(1-\nu)L}\right)^{1/2} \qquad (6)$$

where G is the shear modulus, ν is Poisson's ratio, L is the length of the dislocation array and A is an arithmetical factor, about or somewhat greater than unity, related to the geometry of the array–obstacle interaction. The pile-up stress can be related to σ_{app}, the applied stress by the equation

$$\sigma_{\mathrm{app}} = \sigma_0 + \sigma_{\mathrm{p}} \qquad (7)$$

which takes account of σ_0, the threshold or frictional stress which has to be exceeded for dislocation motion to occur. The length, L, of a dislocation array can be broadly related to the grain diameter, d, of single phase materials and the interparticle spacing of multiphase solids and hence the analysis suggests that fracture stresses are dependent upon structural features of the stressed solid in accordance with the Petch equation [160] where K is a constant

$$\sigma_{\mathrm{app}} = \sigma_0 + Kd^{-1/2} \qquad (8)$$

Given the existence of a sharp crack nucleus, the fracture behaviour will then be determined by the competing tendencies of the crack either to propagate in a brittle manner or to blunt by dislocation generation under the influence of the shear stresses at its tip [121]. Since the cleavage and plastic processes show different responses to parameters such as temperature or grain size, a sharp change in fracture behaviour may often be observed as these parameters are varied. This ductile–brittle transition phenomenon has aroused considerable theoretical interest. Stroh [161] approached the problem by considering the thermal mobility of dislocation arrays and derived a double exponential relationship for the probability, p, of the occurrence of brittle fracture rather than the relief of the stress concentration by slip rather than cleavage, of the form

$$p = \exp\left[-ft\exp-(U_\sigma/kT)\right] \qquad (9)$$

where f is a frequency factor, t the time, U_σ a stress dependent activation energy for dislocation motion, T is the temperature and k is the Boltzman constant. Equation 9 indicates that p can vary sharply with small changes in T, as would be expected of a transition effect. Further manipulation in which t was regarded as a function of the stressing and strain rates, $\dot{\sigma}$ and $\dot{\epsilon}$, and σ was related to d by Equation 8 led to the derivation of the relationship

$$\frac{1}{T_{\mathrm{R}}} = \frac{-k}{U_\sigma}\ln\dot{\epsilon} - \frac{1}{2}\frac{k}{U_\sigma}\ln d + C \qquad (10)$$

where C is a constant incorporating γ.

Petch [160] derived a relationship similar to that of Stroh [161] except that it did not define a strain rate dependence. He concluded from an analysis of stresses at a crack tip that cleavage rather than slip would occur if

$$\sigma_{\mathrm{app}} \geqslant 4G\gamma/K^*L^{1/2} \qquad (11)$$

where K^* was a constant which can be related to K by knowledge of the dependence of L on d. The thermally induced change in failure mechanisms was ascribed to the effect of temperature on γ and particularly the threshold stress component, σ_0, of σ_{app}. A simple mathematical manipulation then led to the relationship

$$\beta T_{\mathrm{R}} = \ln B - \ln\left(4qG\gamma/K^* - K^*\right) - \ln d^{-1/2} \qquad (12)$$

where β and B are material parameters, and q is a stress concentration factor.

If LME is a brittle failure process, the relationships summarized above should be generally applicable. Specific effects on fracture behaviour due to the presence of a liquid metal environment are suggested by the presence of a surface energy term, γ, in the key relationships predicting the crack initiation and propagation stresses, and brittle–ductile transition temperature, Equations 6, 4, 10 and 12. The size of the surface energy term will depend on both the material and environment. Thus for a perfectly brittle single crystal fractured in an inert atmosphere

$$\gamma = \gamma_{SV}$$

and for similar intergranular failure of a polycrystalline material

$$\gamma = 0.5\,(2\gamma_{SV} - \gamma_{GB})$$

where γ_{SV} and γ_{GB} are the surface and grain boundary energies. Since the solid surface and crack faces are covered by liquid metal during LME, the equations must be modified to

$$\gamma = \gamma_{SL}$$

and

$$\gamma = 0.5\,(2\gamma_{SL} - \gamma_{GB})$$

for trans- and intergranular failure respectively, where γ_{SL} is the specific solid–liquid interfacial energy. By definition, γ_{SL} for wetting systems is less than γ_{SV}, and hence the concept of an embrittling efficiency, η, of LME can be developed, following Kamdar [6], where

$$\eta = \frac{\gamma_{SL}}{\gamma_{SV}} \quad \text{or} \quad \frac{2\gamma_{SL} - \gamma_{GB}}{2\gamma_{SV} - \gamma_{GB}}$$

This efficiency will be as relevant to failure by blunt as well as sharp cracks if their effective surface energy, γ_{eff}, is directly proportional to γ, Equation 5. As η decreases the square roots of the stresses needed to initiate or propagate cracks decrease, and, in a more complex manner, the brittle–ductile transition temperature increases.

7. Comparison of LME phenomena with brittle fracture theory

The low ductility, cleavage-type failure and sharp brittle–ductile transition temperature characteristics of LME in some systems bear a clear resemblance to those of materials failing by brittle fracture. A firm attempt to test the resemblance can now be made by comparing the predictions about brittle fracture behaviour summarized above or implied in the equations with experimental data for LME.

The prime theoretical predictions that relate to fracture stresses are represented by Equations 4 and 6. A common factor in both equations is γ, which should be less for materials failing by LME than brittle fracture since these are wetted by the liquid metals. Such a reduction in γ_{eff} was observed by Westwood and Kamdar [103] for cleavage along (0 0 0 1) planes of zinc single crystals stressed in mercury and gallium, Fig. 8. If LME is a type of brittle fracture, these values should be a function of the thermodynamic surface and interfacial energies, γ_{SV} and γ_{SL}, of the zinc cleavage plane, and Old [25] has shown (γ_{SL}/γ_{SV}) ratios derived from wetting studies, albeit conducted in moderate vacuo, to be in reasonable agreement with the reductions in γ_{eff}, Table IV.

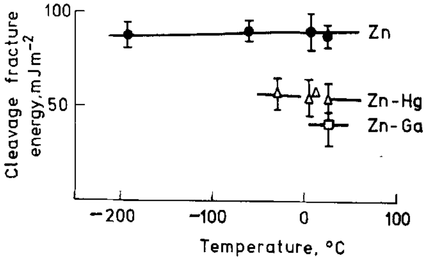

Figure 8 The cleavage fracture energies of single crystals of zinc stressed in inert and liquid metal environment observed by Kamdar and Westwood [103].

TABLE IV Coefficients of embrittlement of zinc calculated from sessile drop data [96]

Metals	Temperature (° C)	Interfacial energies (mJ m^{-2}), γ_{SL}	$\eta = \frac{\gamma_{SL}}{\gamma_{SV}}$
Embrittling			
Hg	13	340	0.41
Ga	104	228	0.27
In	250	293	0.35
Sn	256	305	0.37
Pb	370	402	0.48
Non-embrittling			
Na	232	967	1.16
Bi	295	509	0.61
Cd	362	413	0.50

γ_{SV} (zinc) was taken as 830 mJ m^{-2}.

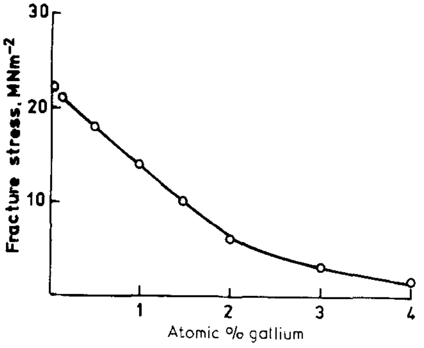

Figure 9 The influence of gallium content on the fracture stress at $-20°$ C of aluminium coated with mercury–gallium alloys (after Preece and Westwood [156]).

Another test of the predicted relevance of $(\gamma_{SL}/\gamma_{SV})$ ratios to LME behaviour is provided by comparison with qualitative observations. Table IV suggests that ratios of less than ~ 0.5 are associated with LME of zinc, in accordance with Hondros' [162] observation that brittle fracture of grain boundaries is produced by segregation reducing the relevant energy ratio to less than 0.5.

If the stress for LME is controlled by γ_{SL}, alloying additions to the liquid that change γ_{SL} should also change the LME behaviour. Thus it is noteworthy that fracture strengths can be reduced by alloying the embrittling liquid although it must be emphasized that there is no direct evidence that these additions also reduce γ_{SL}. Examples of fracture strength reductions produced by liquid alloying are provided by the cadmium/mercury–indium system [23] referrred to previously and the aluminium/mercury–gallium system illustrated in Fig. 9, but it should also be noted that alloying mercury with indium caused the stress for LME of silver to increase [156].

Equation 6 predicts that the stress to nucleate a crack will be proportional to the inverse root of the length of the dislocation pile-up, which can be related to the grain size. Many workers have noted that coarser grained materials are more subject to LME and several have observed a variation of the fracture stress with the inverse root of the grain size, as illustrated in Fig. 10. However, experiments with prestrained brass stressed in mercury [39] and with prestrained aluminium stressed in mercury–3% zinc[30] revealed that coarser grained material is less subject to LME, possibly due to a more complex relationship of dislocation pile-up length and grain size.

Another factor which LME data show to influence the failure stress is the solid alloy

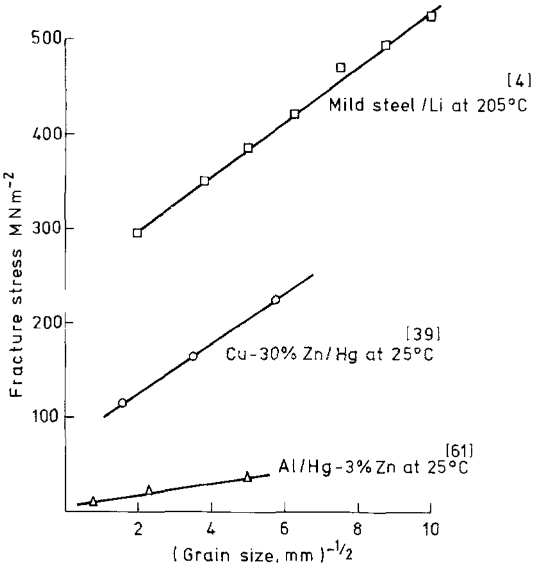

Figure 10 Observations of the influence of grain size on the fracture stress for LME of several material combinations.

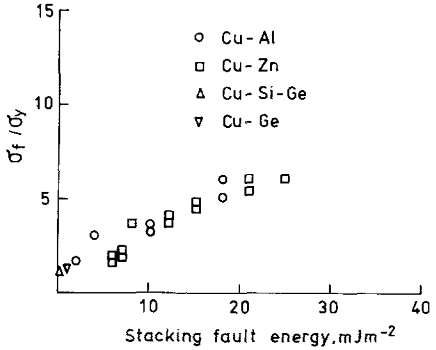

Figure 11 The effect of stacking fault energy on the ratio of the fracture stress to the yield stress for various copper alloys tested in contact with mercury at room temperature (after Johnston, Davies and Stoloff [82]).

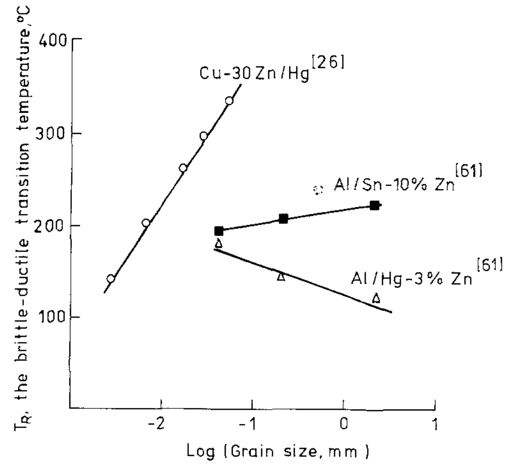

Figure 12 Observations of influence of grain size on the brittle–ductile transition temperature for LME.

composition. In some cases the changes can be related to variation in the stacking fault energy, low values of which imply restricted dislocation cross-slip and hence a greater propensity for LME. Thus Fig. 11 presents data reported by Johnston *et al.* [82] that demonstrate a clear influence of stacking fault energy on the stresses at which contact with mercury produces LME of a number of copper alloys.

Equations 10 and 12 predict that reductions in γ_{SL} values not only reduce the stresses for LME but increase the brittle–ductile transition temperatures, T_R. It is notable therefore that additions of gallium to mercury that decrease the stress for LME of a aluminium, and additions of tin and antimony to lead that decrease the stress for LME of AISI 4145 also increase their transition temperatures [156, 125].

Analyses suggest that these temperatures are also a function of the logarithm of the grain size. Data defining the effect of grain sizes on T_R temperatures are sparse and contradictory, as illustrated by Fig. 12. The Stroh [161], but not the Petch [160], analysis also suggests that the transition temperature should increase with the logarithm of the strain rate, in accord with the few relevant LME data known to us, Fig. 5.

This comparison of predictions based on analyses of brittle fracture behaviour and experimental observations of LME phenomena reveals a fair but not complete agreement. Discrepancies such as that illustrated by the grain size data plotted in Fig. 12 could be due perhaps in part to incomplete experimental characterization or to inadequacies in the present state of theoretical development.

Theoretical analyses of brittle fracture cannot yet be related to several important features of LME. For example, while the occurrence of plastic deformation prior to crack nucleation is the basis of brittle fracture analyses, no clear conclusions can be drawn about the very variable amounts of deformation associated with LME failure. Thus LME might reduce the macroscopic deformation before failure from say 40% to 0.1% in one case and only to 20% in another. While the first example could be of considerable engineering importance the second might be of academic interest only.

A further, more basic, inadequacy of existing brittle fracture theory is that it cannot analyse the factors controlling the onset of embrittlement which it is more plausible to associate with a change in the availability of the foreign atoms that alter γ values and hence fracture characteristics. The normal minimum T_E temperature is the melting point of the embrittling metal which can be associated with the onset of easy macroscopic flow, by capillary action, and enhanced atomic mobility of the embrittler as indicated by an increase of several orders of magnitude in the diffusion coefficient. T_E temperatures below the melting point may involve a mechanism such as vapour phase transport or surface diffusion and in this respect it is noteworthy that cadmium and lead, which have high volatilities, are particularly effective embrittlers in the solid state. On the other hand, Shunk [29] has shown that the T_E of iron and a series of steels embrittled by indium is very sensitive to their metallurgical structure, so an explanation based only on the mobility of the embrittler is inadequate.

8. Theoretical prediction of LME susceptibility

Even though understanding of the mechanisms controlling LME is incomplete, attempts have been made to predict the likelihood of its occurrence by assuming that this is related to the interatomic bonding characteristics that play a central role in mechanisms involving a cleavage process [6, 121, 151, 153]. General support support for this approach is provided by the empirical correlations mentioned in Section 4 since each of the factors associated with embrittlement is an indication of weak liquid–solid interaction.

Data bearing directly on mechanical aspects of interatomic bonding characteristics are not readily available, but several workers have made predictions on the basis of other parameters thought to be related to bonding. Thus Chaevskii [163] and Chaevskii and Popovich [164] related interatomic bonding to the heat of mixing of the liquid and solid and predicted embrittlement susceptibility on the basis of their crack tip alloying model. However, Zalkin [153] has criticised the use of this parameter because some systems forming eutectics, indicative of weak bonding, have large negative heats of mixing. Another approach by Toropovskaya [165] related the heat of fusion H_F to the interatomic bonding and hence to brittle/ductile fracture characteristics suggesting that

$$\frac{H_F \text{ liquid–solid solution}}{H_F \text{ solid}} = \frac{\sigma_{\text{app liquid environment}}}{\sigma_{\text{app inert eironment}}}$$

TABLE V Correlation of the ratio of the heats of fusion, K_H, with degree of embrittlement, K_σ, for pure copper [165]

Test temperature (° C)	Liquid metal	K_H	K_σ
400	Bismuth	0.16	0.42
	Lead	0.85	0.54
	Cadmium	0.68	0.63
	Tin	0.74	0.73
	Gallium	1.03	1.00
500	Bismuth	0.16	0.27
	Zinc	0.98	1.2
	Tellurium	1.3	1.0
600	Bismuth	0.16	0.28
	Antimony	0.54	0.40
	Zinc	0.98	0.80
	Aluminium	1.02	1.00

Data were cited for copper, Table V, showing impressive agreement between K_H, the ratio of the thermodynamic quantities and K_σ, the ratio of the rupture strengths. Similarly, Tetelman and Kunz [166] attempted to relate embrittlement susceptibility to the heat of solution of liquid–solid systems, but their model led only to semi-quantitative descriptions. Kelley and Stoloff [151] compared LME data with electron bond energy values, but the method could not account for the behaviour of all the systems considered.

Clearly there are difficulties in identifying the mechanism whereby the presence of foreign atoms at a surface or crack tip reduces interatomic bonding, and in accounting for the influence of metallurgical and testing variables on LME susceptibility. However, the concept that the presence of foreign atoms at a surface or crack tip can reduce interatomic bonding is attractive particularly because it is amenable to quantitative evaluation.

9. LME as an environmental failure process

The primary scientific interest in LME at present is due to its resemblence to other members of the family of processes in which the fracture behaviour of a solid is modified by its environment. Thus interpretation of LME phenomena may contribute to or gain from improved understanding of a range of fracture processes.

This viewpoint is exemplified by the proposals of Lynn *et al.* [28] of the existence of a family of environmentally induced embrittlement processes (EIE) of which metal induced embrittlement (MIE) was one class which could be subdivided into liquid metal induced embrittlement (LMIE) and solid metal induced embrittlement (SMIE). Similarly, the experiments of Cottrell and Swan [141] demonstrating the embrittlement of stainless steel by zinc vapour imply yet another subdivision, metal vapour induced embrittlement (MVIE). Despite its profusion of initials, this nomenclature helps to emphasize that the embrittlement is due to the presence of a foreign atom regardless of whether it is in a solid, liquid or vapour.

Viewed in this way, the similarities between (liquid) metal embrittlement and some other environmentally induced embrittlement processes are noteworthy. Edwards *et al.* [167], for example, have observed a 50% reduction in ductility in an En30A (4% Ni 1% Cr) steel when tested at room temperature in a low pressure atmosphere of hydrogen. Another example, from the non-metallic field, is provided by the embrittlement of polycrystalline silver chloride by aqueous solutions of various salts [168]. It is also relevant to consider whether there is any significance in the resemblance of environmentally induced embrittlement processes to temper embrittlement in steels. There is strong evidence that this is associated with the segregation of impurity elements to grain boundaries which may be regarded as producing an internal environment. Just as LME has been associated with surface energy changes, some authors have linked temper embrittlement to grain boundary energy changes. Tetelman and Kunz [166] have produced a unifying theory of temper, hydrogen and liquid metal embrittlement on this basis, although this is perhaps a little ambitious in view of alternative suggestions that hydrogen embrittlement itself may have more than one mechanism [169]. Equally interesting parallels can be drawn from studies of crack-growth rates in several different materials systems. Under some conditions, LME can display a delayed failure behaviour not unlike the static fatigue observed in glass, while in other circumstances, strong similarities with stress-corrosion cracking can be noted.

10. The technological significance of LME

Regardless of the detailed interpretation of the processes involved in LME, its technological significance relates principally to the damage it can cause by directly initiating equipment failure or more frequently, by aggravating the effects of accident conditions, such as seizure of moving parts or fires. Recent published failure analyses and newspaper reports indicate that equipment affected can range from simple but vital components like engine shafts [146] to aircraft [7] and major chemical plants [8, 140]. The presence of zinc on the fracture surface of ruptured stainless steel pipework following a refinery accident in the US and the Flixborough disaster has been interpreted as evidence of damage by LME. In both cases the suggested mechanism was the dripping of molten zinc from galvanized structures on to pipes which were stressed and at about 800° C due to a fire. The cost of damage that can be directly attributed to LME is difficult to estimate but may be substantial and therefore techniques for monitoring its onset before failure occurs and remedial action are of importance.

The early, sub-critical, stages of equipment damage produced by corrosion or fatigue sometimes can be followed by a periodic inspection programme. However, the development of a monitoring procedure for LME is complicated because the probability of crack nucleation is not related to the time for which the stressed component is exposed to the liquid, or in some cases even solid, embrittler but once a crack has been formed it can grow very rapidly. Thus a new piece of equipment is as much at risk as an ageing one and there is no tolerable level of LME induced cracking. It is very desirable, therefore, that procedures should be developed to remedy the effects of inadvertent contact with the liquid metals or at least to define the extent of damage so that replacement and recommissioning can be undertaken. The possibilities of using high temperature heat treatments to evaporate or disperse the embrittling metals have been investigated, but only partial success has been achieved. In the case of aircraft damage procedures have been investigated for the removal of mercury [170] from aluminium alloys. In most cases, however, there is no prudent course to adopt if LME has occurred but to replace completely not only components that have been damaged but also those that were or may have been in contact with the liquid metal.

11. Concluding remarks

This brief review has cited many references describing the conditions under which a wide range of metals and alloys have been observed to suffer LME. Indeed the range is so wide that it is no longer reasonable to argue that LME is a specific phenomenon and hence to assume that some material combinations are totally immune. In general, therefore, the task of the experimentalist is to define whether a combination suffers from LME in the conditions of particular interest.

Recent events have made it amply clear that the information can be not only of scientific interest but also of considerable value to technologists concerned with plant damage and safety. However, since it is virtually impossible to investigate every possible condition that a component may encounter during its operational lifetime or during the course of an accident, it is important to be able to predict the probability of LME occurring.

Several theories have been advanced and models described that attempt to account for the main characteristics of LME, but none is completely satisfactory. The major task confronting scientists interested in LME, therefore, is the acquisition and interpretation of quantitative data for well characterized material combinations. In particular, attention should be paid to metallurgical as well as chemical characteristics.

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