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FRACTURE IN LIQUID METAL ENVIRONMENTS

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Many ductile metals fracture in a brittle manner when tested in the presence of a thin surface coating of certain liquid metals. The severity of embrittlement depends upon the metallurgical, mechanical, and physical factors and also on the chemical nature of the liquid and the solute dissolved in the liquid metals. Liquid metal embrittlement is considered a special case of brittle fracture and it is generally accepted that embrittlement is caused by the liquid metal "Adsorption Induced Reductions in the Cohesion" of atomic bonds at the crack

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tip. This report describes the phenomena of fracture in liquid metal environments and discusses the effects of variables related to the solid, the liquid, the liquid metal solutions, and to the test conditions on the severity of embrittlement. It also discusses various mechanisms of embrittlement. Also, a summary with suggestions for future work is presented.

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INTRODUCTION

One of the most interesting phenomena of degradation of the mechanical properties of metals by active chemical environments is fracture in liquid metals or liquid metal embrittlement (LME). In LME, a ductile solid metal wetted by a liquid metal when stressed, fails in a brittle manner. Both polycrystals and single crystals are embrittled (Figure 1). The stress, strain, or both at failure are significantly reduced (Figure 2). Fracture occurs by brittle intergranular or transcrystalline mode. Crack propagates very fast and rates of order 100 cm/sec have been observed. This phenomena is not caused by liquid metal corrosion or by the penetration of liquid in the grain boundaries, but fracture in liquid metal environment is considered a special case of brittle fracture (ref 1). Such a phenomena of embrittlement was reported as early as 1884. However, scientific investigations of LME were pursued in the 1930's in the USSR by Acedemitian Rebinder and his co-workers, in the United States since the 1950's, and in recent years in the United Kingdom and Japan. These investigations were reported in review papers by Rebinder et al in 1958 (ref 2), Rostoker et al in 1960 (ref 3), Westwood et al in 1967 (ref 4), Stoloff in 1968 (ref 5), Kamdar in 1973 (ref 1), Nicolas and Olds in 1979 (ref 6), Stoloff in 1979 (ref 7), and most recently by Kamdar in 1983 (ref 8) and Stoloff in 1984 (ref 9). In spite of this, LME remains an unfamiliar phenomena of brittle failure to most material scientists and engineers. This has changed significantly in the last decade by the discovery of damage to aircraft metal aluminum by liquid gallium (ref 10), cracking of

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References are listed at the end of this report.

stainless steel pipes by molten zinc (refs 11, 12) that occurred in the "Flixborough Disaster" in the United Kingdom, recent observations in the nuclear reactor industry of cracking of zircoloy nuclear fuel cladding tubes by the fission product cadmium (refs 13,14), and cracking of leaded (ref 15) and hot cracking of telluride (ref 16) free machining steels.

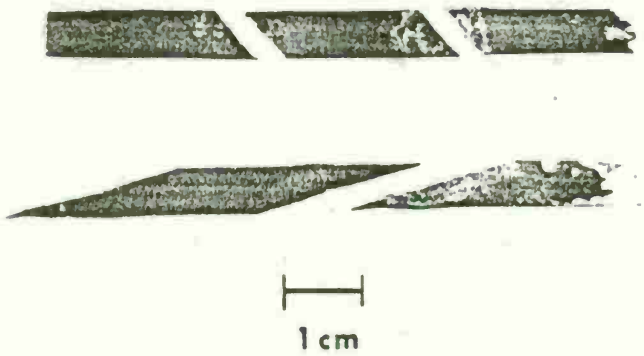

Figure 1. Demonstrating cleavage of cadmium monocrystals at 25°C after coating with mercury - 60 at.% indium solution (from Kamdar (ref 76) and Kamdar and Westwood (ref 77)).

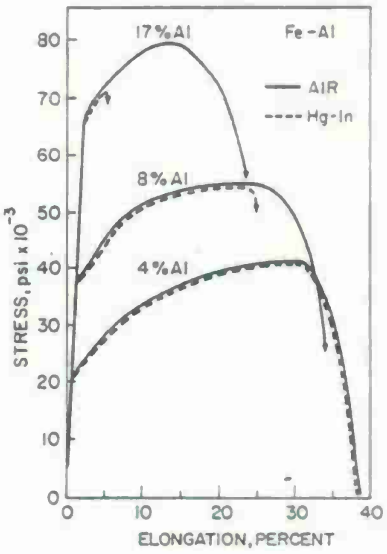

Figure 2. Absence of the effects of environment on the yield stress and strain-hardening on various iron-aluminum alloys tested in mercury-indium solution (from Stoloff et al (ref 25)).

In addition to LME, a new phenomena of solid metal induced embrittlement (SMIE) was reported where a liquid metal, at a temperature well below its melting point, embrittled the solid metal (refs 15,17-19). Examples of such embrittlement are steel by cadmium, indium, tin, zinc, lead, etc. (refs 18-21), and titanium by cadmium (refs 21,22). The occurrence of LME and SMIE induced failures in metals and alloys used in industry indicate that these

phenomena are no longer a laboratory curiosity, but are important brittle fracture processes that occur in important industries such as nuclear power generation, steel, and hence, are of interest to engineers and scientists. Therefore, there is considerable interest in these phenomena, as is evident from the first conference held in 1982 on "Liquid and Solid Metal Induced Embrittlement of Metals" (ref 23).

The purpose of this report is to review the effects of metallurgical, physical, and mechanical parameters on the embrittlement susceptibility, the role of liquid on crack propagation and embrittlement, new developments in the rather quiescent area of the mechanisms of embrittlement, and the specificity or otherwise of liquid metal embrittlement (i.e., why only certain liquid metals embrittle only certain solid metals). In addition, we will also review what is currently known about the solid metal induced embrittlement of metals (ref 87).

OCCURRENCE OF EMBRITTLEMENT

Embrittlement appears to be a specific phenomena in that only certain liquid metal embrittles certain solid metals and its alloys. For example, liquid gallium and mercury both embrittle zinc and aluminum, but not magnesium. Also, gallium is a more severe embrittler of both zinc and aluminum than mercury. This suggests that the severity of embrittlement depends upon the chemical nature of the embrittling species (ref 1). Also, all liquid metals do not embrittle all solid metals. Nevertheless, it has been suggested (refs 6,9) that LME may not be a specific phenomena as has been indicated here. In any event, some empirical deductions, certain conditions,

and prerequisites are helpful in allowing one to guess possible embrittlement couples and specifically to assure the occurrence or otherwise of embrittlement in a particular embrittlement couple of interest.

Inspection of many known embrittlement couples provides an empirical deduction that the phase diagrams of most embrittlement couples are simple binary eutectic with very limited or no solid solubility, with no intermetallic compounds, and in some instances complete immiscibility between both metals even in the liquid state. The presence of many intermetallic compounds is not necessarily a requirement, since some embrittlement couples do form intermetallic compounds. It is noted, however, that when many intermetallic compounds are formed it is less likely that constituent metals will form an embrittlement couple. Next, for the occurrence of embrittlement, a critical condition which must be fulfilled is that the liquid should wet the surface of the solid metals and must be in intimate contact with it. In order to promote wetting, a virgin metal surface free of oxide film or any other contaminent should be prepared by cleaning the surface chemically or ultrasonically, by polishing electrolytically, or by preserving in a chemical solution or an inert organic liquid which removes or prevents reformation of a surface film. The cleaned surface should be immediately contacted with liquid to promote good wetting.

Other methods which promote wetting are additions of nonembrittling impurities to the embrittling liquid, fluxing the surface and soldering the embrittling metal, and other techniques described by Rostoker et al (ref 3). However, in many instances, these methods may not provide good wetting in which case a new technique developed by Kamdar (ref 8) can be used. In this

method, the difficult to wet surface is cleaned and is then electroplated with a few micron thin plating of a metal which is readily wetted by the liquid metal. During the mechanical test, initial plastic deformation of the solid metal produces slip steps which break through the electroplated metal. The clean, freshly created surfaces of the slip steps then become coated with the liquid metal. This method has been used to promote wetting in copper plated steel specimens by mercury and liquid lead and to prevent dewetting that occurs in aluminum when tested in mercury (ref 8). A metal surface can also be cleaned by ion bombardment under ultra high vacuum and the cleaned surface can then be coated with embrittling metal by vapor deposition. Good wetting requirements indicate that embrittlement is related to the surface chemical or electronic interaction between the solid surface and the liquid metal. Whether, in fact, embrittlement will occur or not will be determined by other prerequisites which are given below.

PREREQUISITES FOR EMBRITTLEMENT

Certain prerequisites must be fulfilled before fracture can initiate in a solid in liquid metal environment. For a ductile, unprecracked metal specimen these are: (i) an applied tensile stress, (ii) some measure of plastic deformation, and (iii) the existence in the specimen of some stable obstacle to dislocation motion, capable of serving as a stress concentrator. This obstacle can be either pre-existing (e.g. a grain boundary) or created during deformation (e.g. a kink band). In addition, there should also be a sufficient supply of the active liquid metal to ensure adsorption at this obstacle, and subsequently at the propagating crack tip. A specimen which is

normally brittle when tested in tension in a liquid metal environment is found to be immune when tested in compression or pure shear, e.g. zinc in mercury. Also, fracture in an amalgamated specimen tested in a three-point bend test invariably initiates in the face under tensile stress, but not in the face which was under compressive stress. However, Stoloff (ref 9) has recently reported fracture initiation in compression in amorphous metals tested in liquid metal environments. These observations are in accord with prerequisite (i). Also, in accord with prerequisite (ii), fracture in most embrittlement couples is invariably preceded by yielding (refs 1,3,24-26). However, fracture initiated below the flow stress in coarse grain polycrystalline zinc tested in liquid mercury environment (ref 27). An examination of the apparently undamaged specimen loaded just below the fracture stress revealed the presence of microcracks only in the grains in which local yielding had occurred. Thus, in some instances, local yielding can be a sufficient prerequisite for the initiation of fracture. If the specimen contains a pre-existing crack, the prerequisites (ii) and (iii) are no longer necessary. If the solid is notch brittle, it may not be necessary for the liquid metal to keep up with the propagating crack once it is greater than critical size.

The presence of a stress concentrator in a solid, such as grain or a twin boundary, or a kink band, etc. from which the crack may initiate in a liquid metal environment, has been shown to be an important prerequisite for the initiation of brittle fracture (refs 1,8). However, transgranular fractures have been observed in LME of aluminum, zinc, and iron (ref 1). A stressed zinc single crystal coated or contacted with liquid mercury has been shown to fracture by cleavage on basal plane and aluminum in gallium on a low index

plane (refs 1,28). This clearly indicates that grain boundaries are not the prerequisite for the nucleation of a crack, but other barriers or obstacles such as a kink or a twin band can act as crack nucleating obstacles. Most all failures in LME, however, occur by intergranular fracture mode (refs 1,8), and hence grain boundary is a major crack nucleating site in solids. A possibility exists that diffusion, penetration, or even corrosion of liquid in the grain boundaries may cause embrittlement. This will be discussed later.

Besides these initial conditions, factors that induce brittle behavior in a solid, such as the presence of a stress raiser or a sharp notched or a sharp fatigue crack, increase in strain rate, grain size, microstructure, alloying, temperature of test, and type of mechanical test are all known to promote or increase the embrittlement susceptibility of the solid (refs 1,8,9). Thus, the effects of metallurgical, physical, and mechanical parameters will determine whether a brittle crack will nucleate and/or propagate in a liquid metal environment. All these factors in conjunction are responsible for the actual observance or otherwise of embrittlement in a given liquid-solid metal couple. In the following sections, we will discuss the mechanisms of embrittlement, the effects of metallurgical, physical, and mechanical parameters, and the effects of liquid and its solutions on liquid metal embrittlement.

MECHANISMS OF EMBRITTLEMENT

Many mechanisms have been proposed to explain failure in liquid metal environments. Some of these are increased pressure in the crack due to capillary effects of liquid, reduction in the surface tension or the decrease

in the surface free energy of the solid by the wetting liquid metal (refs 3, 6), stress-assisted dissolution at the crack tip (ref 29), formation of weakly bonded alloying zone (refs 30,31), or solid solution by the liquid (ref 32). Liquid metal adsorption induced reduction in cohesive forces at the crack tip causing brittle tensile failure at reduced stress (refs 1,8,9,33-35), or alternatively, adsorption induced enhanced plasticity, i.e., ingress and egress of dislocations at the crack tip causing embrittlement via ductile dimpled rupture mode (refs 36-38). Diffusion of liquid into the grain or twin boundaries is yet another possibility.

In addition to these mechanisms, recently a common cracking mechanism for environmentally induced failure in hydrogen, stress corrosion cracking, and temper, liquid and solid metal induced embrittlement in combination of several of these environments has been proposed by Telelman and Kunz (ref 39), Lynch (ref 38), Bernstein (ref 40), Spiedel (ref 41), Kamdar (ref 42), and Stoloff (ref 43). Kamdar (refs 8,42) has suggested that some commonality may exist between hydrogen temper, and liquid and solid metal embrittlement, since chemical or electronic interaction must occur between the embrittling species, whether in gaseous, liquid, or solid state, and the crack tip of the solid. The reduction in cohesion must prevail although the rate controlling processes may differ depending upon the specific environment-solid metal couple. It is sufficient to indicate that such attempts have been made for a common mechanism, but it has also become clear that this is a difficult task since the mechanism(s) in any of these environments are not yet clearly understood. We will therefore concentrate only on the mechanisms of liquid metal embrittlement. Many of the proposed mechanisms do not predict or compare well

with observed embrittlement behavior of liquid-solid metal couples. Stress-assisted dissolution models predicted that the severity of embrittlement will increased with temperature. The opposite is, however, observed in most all embrittled couples. Rostoker in 1960 (ref 3) and recently in Old and Trevena in 1979 (ref 44), and Nicolas and Old (ref 6) have suggested that embrittlement is related to the lowering of the interfacial surface tension of the solid by the liquid and have shown correlation for zinc wetted by several liquid metals. The energy at fracture is 100-1000 times greater than the surface energy. It is difficult to see how lowering the surface energy will lead to embrittlement. Interfacial surface tension will decrease with increase in temperature predicting increase in the severity of embrittlement with increase in temperature which is not in agreement with observations on LME.

The most obvious mechanism is diffusion of liquid in the grain boundary of polycrystals or sub-boundaries of single crystals either as a result of stress or as a result of increased diffusion by the presence of dissolved solute in the embrittling liquid. The embrittling atoms enter or diffuse in the grain boundary from the surface adsorbed state. When sufficient concentration of these atoms is present in the grain boundary, the cracking resistance of the boundary is lowered and embrittlement occurs. The reasons for the lower strength of grain boundary have not been given. This model is proposed by Gordon and An (ref 45) and is a variation of similar mechanisms proposed by Kristal (ref 46). The principal features of such a model is that the embrittlement is time and temperature dependent delayed failure type of phenomena. Gordon and An (ref 45) made a detailed investigation of the crack

nucleation and propagation by studying delayed failure in 4140 steel in liquid and solid indium environment as a function of stress, time, and temperature. The results provided activation energies which corresponded to that for volume diffusion. They indicated that this model also explains the known phenomenology of LME namely, presence of brittle-ductile transition, effects of strain rate, grain size, and cold work. An incubation period for crack nucleation corresponds to diffusion of liquid in the grain boundary and explains delayed failures in LME. Since crack nucleation and propagation are the same process, the same mechanism should apply to both processes. The incubation time would predict discontinuous fracture propagation and striation on the fracture surface. This is not what is usually observed, but it should be investigated. Also, stressed zinc polycrystals and single crystals fail instantaneously when contacted with liquid mercury (Figure 3), and the fracture strength of aluminum and brass is independent of the time of immersion in liquid mercury prior to testing to failure (Figure 4). These and some other results on LME are at a variance with the diffusion type delayed failure mechanism.

It is necessary to postulate a mechanism for the weakening of the grain boundary by the liquid which has diffused in the grain boundary because diffusion may not necessarily lead to weaken but even strengthen the grain boundary. Delayed failure of amorphous metals which do not have grain boundaries and which can be stressed to high levels should aid volume diffusion of liquid. This may provide better understanding of the diffusion-controlled failure in liquid metal environments. Rennovetore et al (ref 47) investigated delayed failures in aluminum and brass in liquid mercury.

Penetration of the mercury in the grain boundary was observed, but results could not be correlated with Griffith type analysis. In spite of some of these difficulties, the author believes that diffusion-controlled embrittlement is a viable process for LME.

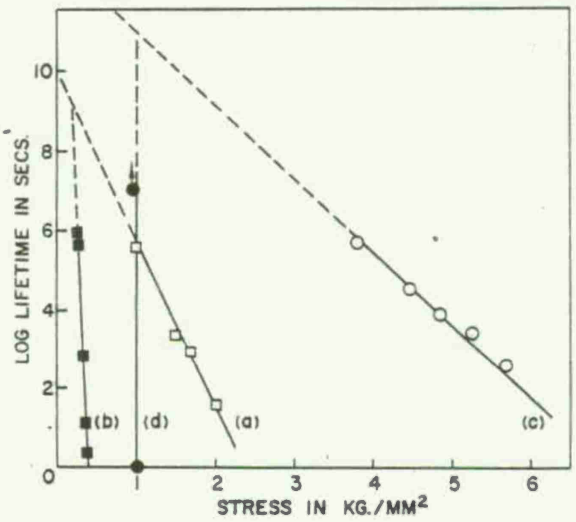

Figure 3. Variation of time to failure with applied stress for zinc at room temperature. Curves (a) and (b) for uncoated and mercury coated monocrystals (x = 50°, ~ 1 mm dia.), respectively; curves (c) and (d) for uncoated and mercury coated polycrystals, respectively (from Bryukhanova et al (ref 70)).

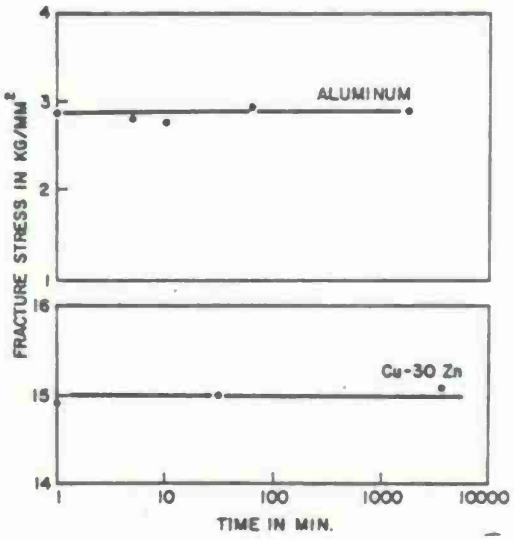

Figure 4. Fracture stress of polycrystalline aluminum or 70-30 brass as a function of time of exposure to liquid mercury prior to testing in this environment (from Ichinose (ref 86)).

Perhaps the most widely accepted mechanism of embrittlement is the "Adsorption Induced Reduction in Cohesion" proposed by Westwood and Kamdar (ref 33) and Stoloff and Johnston (ref 34). This mechanism is frequently reported as a "decohesion mechanism"*. Adsorption of liquid metal atoms decreases the density of electrons of atoms at the tip of the solid and increases that of the liquid metal atoms. The lower electron density results in reduction in cohesive forces at the tip of the crack and thereby reduces

*The author interprets this as absence of any bond strength at the crack tip due to adsorbed liquid metal in contrast to "reduction in cohesion" which means that the bond strength exists, is not absent, but is reduced. Therefore, it is appropriate to use the term "reduction in cohesion" mechanism of embrittlement.

the tensile and shear modulus at the sites of adsorption. Possibly, such electronic sharing results in a somewhat covalent bonding between liquid and solid metal. In this regard, it has been suggested that embrittlement is caused by the adsorption of liquid metal atoms or gaseous or solid metal atoms induced reduction in the tensile cohesive strength of atomic bonds at the crack tip (Figure 5) or at the sites of high stress concentrations on the surface of the solid. In the presence of tensile stress, the cracking process or crack propagation is limited by the arrival of liquid metal atoms to the propagating crack tip by diffusion of the liquid metal atoms adsorbed on the crack surface (refs 1,33). Adsorption of the liquid metal atoms can reduce the shear strength of the atomic bonds at the crack tip and this can facilitate nucleation of dislocation at the crack tip. However, adsorption effects on dislocations will be limited to several atomic spacings due to electronic screening effects, and will not be felt at larger distances in the bulk of the solid ahead or in the vicinity of the crack tip (ref 1). These effects then will be secondary in importance when compared to breaking of bonds where liquid is continuously adsorbed at the tip of a propagating crack. However, Lynch (refs 36-38) has proposed that long range effects such as extensive slip in the vicinity of cracks can occur due to reduced shear stress and can embrittle metal via ductile dimpled rupture mode. We will discuss this mechanism shortly.

Experimental evidence in support for the reduction in tensile strength of atomic bonds at the crack has been provided by Westwood and Kamdar (ref 33). The Gilman cleavage technique, which has been used to determine γ the cohesive strength of cleavage planes of ionic and metallic single crystals,

was used to determine the fracture surface energy of the basal plane in zinc single crystal in inert (e.g. liquid nitrogen) and in liquid mercury and gallium environments. The fracture energy of 90 ± 10 ergs/cm^2 is the bond energy of the basal plane in zinc (refs 1,8,33). This energy is reduced to 57 ergs/cm^2 in mercury and 42 ± 13 ergs/cm^2 in gallium (Figure 6). These reduced energies in mercury and gallium indicate reductions in the strength of the atomic bonds in the basal plane by these environments. Significantly, they indicate that embrittlement is related to the chemical nature of species adsorbed at the crack tip.

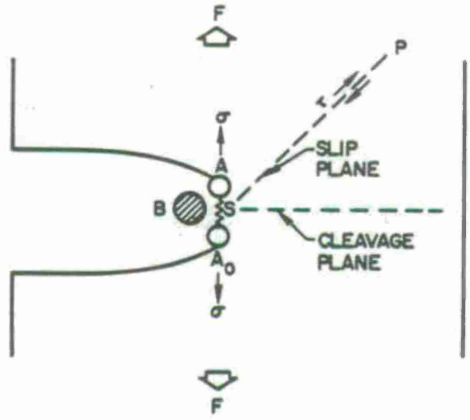

Figure 5. Equilibrium crack in a solid subjected to increasing force F. The bond A-A_0 constitutes the crack tip. B is the surface active liquid metal atom, σ is the tensile stress at the crack tip, and τ is the shear stress on a slip plane (schematic).

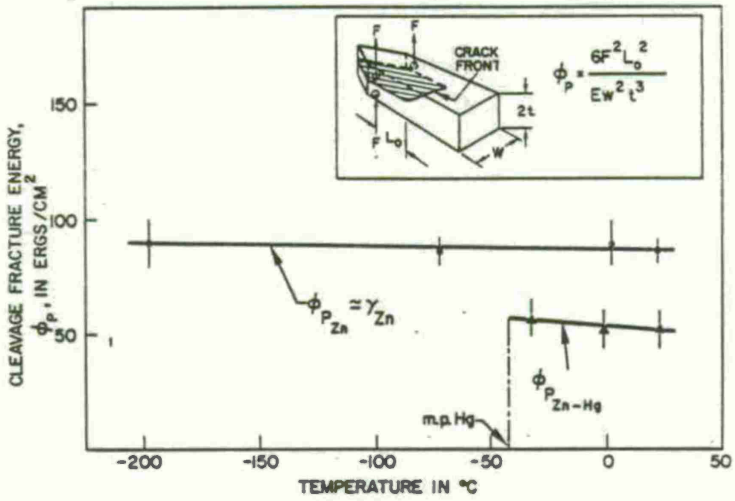

Figure 6. Effects of temperature and liquid mercury environment on the cleavage crack propagation energy, ϕ_p of the (0001) planes of zinc. The inset shows the equation and type of specimen used to determine ϕ_p (from Westwood and Kamdar (ref 33)).

Most all fracture in liquid metal environments occurs at energies which are about two or three orders of magnitude larger than γ, the bond or the surface energy. The excess energy represents plastic work. A mechanism must explain these large reductions in plastic work energy. Westwood and Kamdar (ref 33) have shown the lowering of the elastic or surface free energy must invariably lead to proportional reductions in the plastic work energy. An equation $\sigma_p = (E\rho\gamma/4c)^{1/2}$ was derived where σ_p is the crack propagation energy, c is the crack length, γ is the surface energy, and ρ is a dimensionless ratio of (R/a_o), where R is the radius of the crack tip, and a_o is the radius of an atomically sharp crack and corresponds to the lattice spacing of

the solid. Westwood and Kamdar (ref 33) have experimentally verified this relationship by measuring the crack propagation energy on the basal plane of zinc in inert and in mercury environments. These and other results which support this mechanism and that LME is a special case of brittle fracture have been presented by the author in a planery lecture given at the Fourth International Fracture Congress and are published in the Proceedings of the Conference (ref 48).

We have discussed reductions in the tensile stress of atomic bonds at the crack tip. Alternatively, a reduction in shear stress of the atomic bonds at the tip can nucleate dislocations at the crack tip. Recently, Lynch (refs 23,38) proposed a mechanism where embrittlement occurs by the reduction in the shear strength rather than the reduction in the tensile strength of atomic bonds at the crack tip. The reduced shear strength facilitates nucleation of dislocations at low stresses. Once nucleated, the dislocations move away from the influence of the liquid metal adsorption effects and away from the crack tip, i.e., the process is dislocation nucleation limited, causing extensive slip in the vicinity of the crack tip. The localized increase in the plasticity produces a plastic zone with sufficiently large strains such that a void is nucleated ahead of the crack tip perhaps at a precipitate, inclusion in a polycrystal, or at a sub-boundary in a single crystal. The voids will grow and crack propagation will occur. Apparently, the process is repeated and the crack propagates by the growth of voids and its linkage. The fracture mode is ductile rupture with the appearance of dimples on the fracture surface. The localized plasticity at the crack tip induced void growth reduces overall strains at failure compared with that in

the absence of environment. Lower strains at failure or subcritical crack propagation by the growth and linkage of voids is then the measure of liquid metal induced embrittlement. The schematic representation of the above process is given in Figure 7.

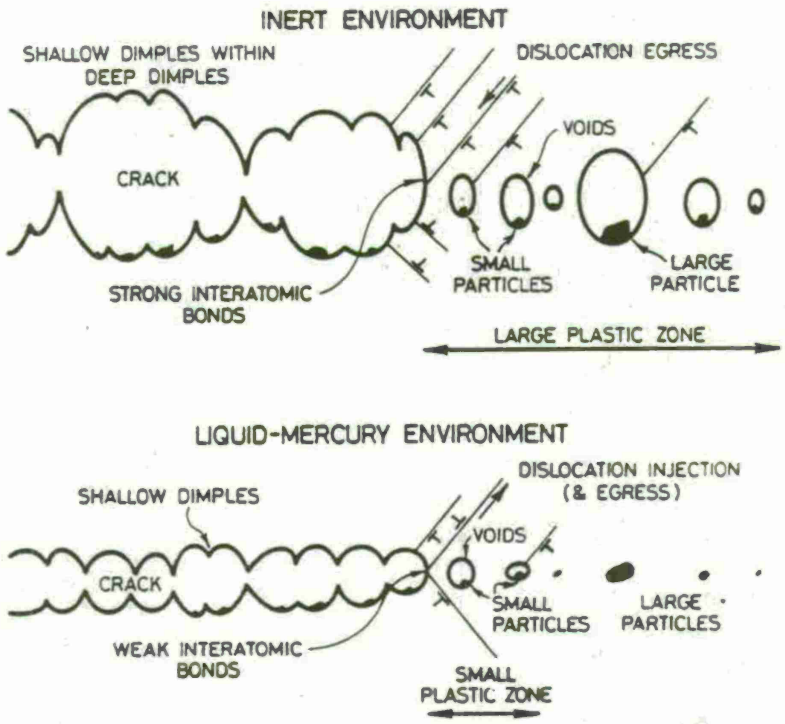

Figure 7. Schematic diagram illustrating the mechanisms of crack growth by microvoid coalescence in inert and in liquid metal environment (from Lynch (ref 37)).

In support of this model, Lynch (ref 37) has provided metallographic and fractographic evidence of slip at the crack tip and ductile dimpled rupture on the fracture surfaces of an aluminum-6% zinc-3% magnesium alloy in inert and several low melting liquid-metal embrittling environments (mercury, gallium, and bismuth-lead-zinc-tin-cadmium liquid metal solutions). The liquid metal environment caused rapid subcritical intercrystalline cracking in polycrystals

and transcrystalline cleavage fracture in single crystals. Dimpled fracture surfaces are also observed after liquid metal embrittlement for steels (ref 38) (Figure 8), α-titanium alloys and cadmium, and also steel tested in hydrogen environment.

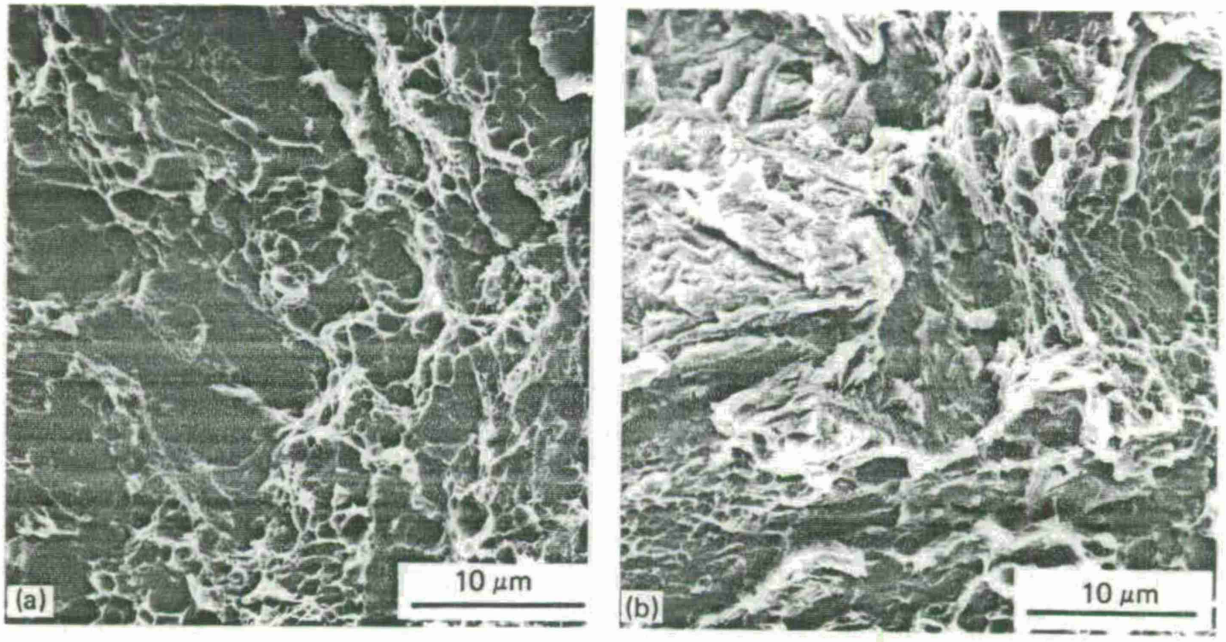

Figure 8. Scanning electron micrographs showing dimpled, transcrystalline fracture surfaces produced by cracking D6ac steel (290°C temper) in (a) air and (b) liquid mercury environments (from Lynch (refs 37,49)).

The later results suggest that LME and hydrogen embrittlement occur by a similar mechanism. On the other hand, in the most recent work Lynch (ref 49) reported that basal cleavage surfaces of zinc crystals tested in mercury were featureless, brittle, and did not have dimples (Figure 9). This suggests reduction in tensile cohesion of the atomic bonds as the embrittling mechanism. Lynch (ref 49) therefore suggests that both reduction in tensile or shear cohesion are possible mechanisms. The specific mechanisms will be determined by the ductility of the solid and the severity of the embrittling liquid, i.e., the chemical nature related interactions of the liquid at the crack tip.

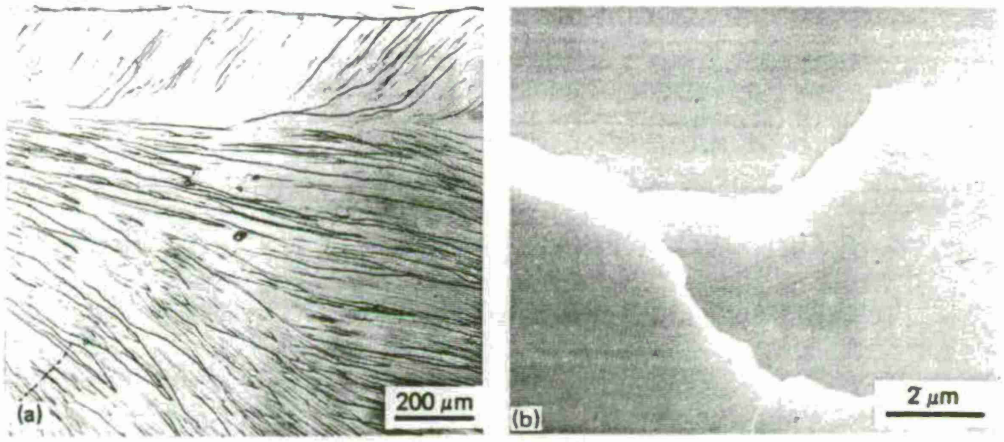

Figure 9. (a) Optical micrograph, and (b) Scanning electron micrograph showing featureless brittle surface produced by cracking zinc single crystal in liquid mercury (from Lynch (ref 49)).

The Lynch model should explain the severity of embrittlement and brittle-ductile transition. The increased reductions in the shear strength would predict faster crack growth, increase in degradation of mechanical property, and increase in the size of dimples - or pure shear failure, on the fracture surface. These can be verified experimentally by examining the fracture surfaces of embrittlement couples which are known to be most severely embrittled.

It is recognized that the localized reductions in the shear strength at a crack tip are almost impossible to measure or even estimate. However, it may be possible that nucleation and subsequent large scale motion of dislocations central to this model may be demonstrated by studying the motion of an individual dislocation in different liquid metals and in inert environments in metal single crystals using the method of Gilman and Johnston (ref 50) and Westwood (ref 51). Sensitivity of the motion of dislocation to specific liquid metal environment will provide support for the specificity of LME. Additionally, such an investigation will provide direct support for environmental induced increased plasticity since most of the studies on LME have shown that liquid metal has no effect on the yield stress or the stress-strain behavior of either the single crystal or the polycrystals, (refs 1,8,9) (Figure 2). It is necessary to separate the inherent plasticity of metal from that due to adsorbed liquid metal environment so that a more direct support can be provided for this model.

The dimpled fracture surfaces associated with embrittlement may result from high ductility and low embrittlement susceptibility of a solid in a particular liquid metal environment. Environmentally induced brittle cracks

propagate a small distance, say ~ 10 to 100°A, and subsequently are blunted by the high ductility of the solid metal by the emission of dislocations from the propagating crack tip and a void is nucleated. The reinitiation of brittle cracks from the void and subsequent void formation and linkage would repropagate the crack. Fracture surfaces could then have predominantly dimpled rupture appearance, perhaps with striation markings.

An investigation of the embrittlement of single-edge notched 4340 steel specimens tested in cyclic fatigue in liquid lead at various temperatures provide some support for the above suggestions (refs 42,52). At the melting point of lead, 675°F, steel is severely embrittled when tested in cyclic fatigue and the fracture mode is brittle intergranular. At 1200°F, fracture mode is ductile but embrittlement is observed as a reduction in the number of cycles to failure to half of those at failure observed in an inert argon environment. A detailed study of fracture surfaces of specimens tested at various temperatures is being conducted. A specific mechanism is not proposed at this time. It appears that the effect of temperature or temperature-induced bulk ductility of the solid metal and relative embrittlement susceptibility of liquid metal environment are synergistic effects, one counteracting the other. The observed fracture mode may result from the relative magnitudes of such effects rather than liquid metal induced "localized plasticity."

ROLE OF LIQUID IN CRACK PROPAGATION

In the previous models of embrittlement, it was implied that once a crack is nucleated, subsequent crack propagation occurs either mechanically and in the absence of the liquid at the crack tip or by the continuous presence of liquid metal atoms at the propagating crack tip via diffusion of liquid over adsorbed liquid metal substrate, i.e., diffusion of liquid over liquid or by surface diffusion (refs 1,33). Kamdar (refs 8,52) has suggested that the study of crack propagation in LME using fracture mechanics methods similar to that used in stress corrosion cracking (SCC) of metals could provide better understanding of the mechanism and role of liquid in LME. Recently Kamdar (ref 8) and Kapp (ref 53) studied the variation in the crack growth rate with stress intensity at the tip at various temperatures in brass and aluminum alloys in liquid mercury environments (Figure 10). The activation energy for the aluminum-mercury system suggested an aluminum-mercury adsorption reaction rate controlled process (Figure 11). However, the activation energy derived from the data for the brass mercury system (Figure 12) indicated that diffusion of liquid over liquid or surface diffusion is the rate controlling process, Figure 13. Gordon (ref 45) evaluated the role of embrittling liquid or metal vapor phase. His analysis and the activation energy derived from experimental data indicates that the bulk liquid flow is the transport mechanism and that the liquid metal which wet the base metal can penetrate to the tips of sharp cracks due to surface tension forces. For a few high-vapor pressure embrittlers such as cadmium, zinc, and possibly mercury, vapor transport could play a role in crack propagation.

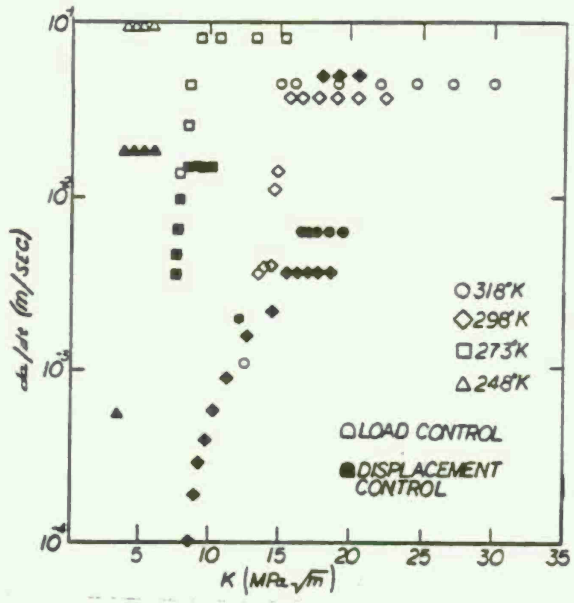

Figure 10. Crack growth rate versus stress intensity factor K tested in static fatigue for aluminum 6061-T651 in mercury at various temperatures, the circle at 318°K, diamonds at 298°K, squares at 273°K, and triangles at 248°K. The unfilled point indicates load control and filled points indicate displacement control (from Kapp (refs 53,74)).

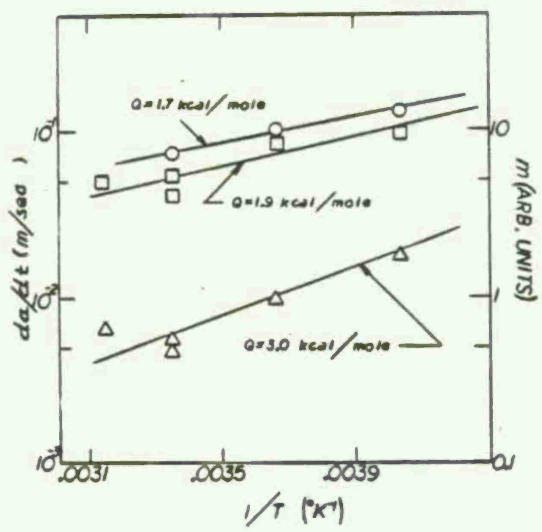

Figure 11. Steady state crack velocities in static fatigue crack growth rate as a function of temperature. The circles are the slopes m, the squares and triangles are load and displacement-controlled crack velocities (from Kapp (refs 53,74)).

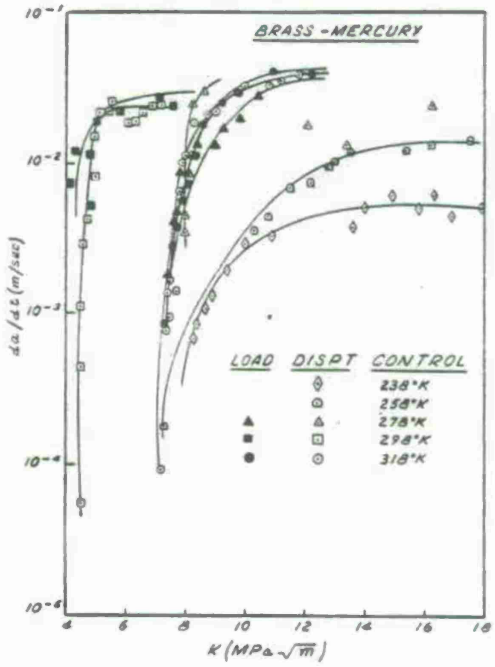

Figure 12. Crack growth under load and displacement control as a function of K in brass in liquid mercury at various temperatures (from Kamdar (ref 8)).

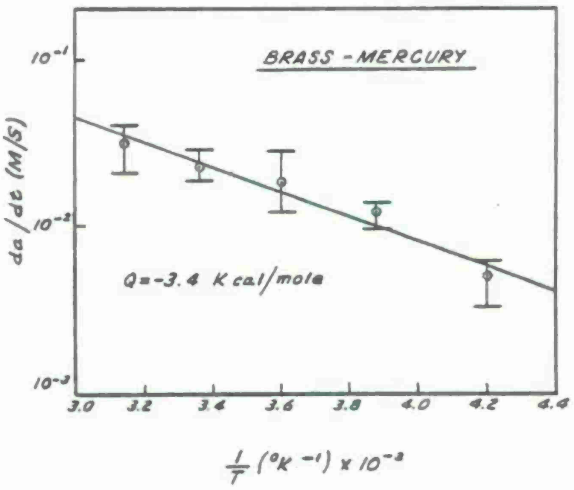

Figure 13. Crack growth in brass-mercury versus temperature activation energy, Q = -3.4 Kcal/mole (from Kamdar (ref 8)).

EFFECTS OF METALLURGICAL, MECHANICAL, AND PHYSICAL FACTORS

Kamdar and Westwood (ref 55) and Kamdar (refs 1,8,48) have used liquid metal environments and have shown that the prerequisites for liquid metal adsorption-induced brittle fracture are the same as that for brittle fracture in inert environments and that these environments can be used instead of low temperatures and inert environments to test the validity of several fracture criteria. The embrittlement of zinc and dilute zinc alloy monocrystals, bicrystals, and polycrystals tested in liquid mercury and in inert liquid nitrogen have provided support for a brittle fracture criteria for the blocked dislocation model of crack nucleation (refs 55-58).

From these investigations, it was concluded that adsorption-induced liquid metal embrittlement can be regarded as a special case of brittle fracture. Therefore, it is apparent that those factors (e.g. grain size, strain rate, temperature, alloying additions, etc.) which tend to induce brittle behavior in a metal in an inert environment also increase the susceptibility of a solid to liquid metal embrittlement. The effects of these factors on variations in susceptibility to liquid metal embrittlement can be better appreciated by considering ideal experimental conditions, where most all of the energy due to stress concentrations at the sites of crack nucleation or at the tip of a crack is used in the nucleation and propagation of a sharp crack to fracture and little energy is used in relaxation by plastic deformation processes. Under this condition, one may assume that maximum embrittlement has occurred. The severity of embrittlement may not increase further in a pure solid-pure liquid metal couple except by selecting a new chemical species, that is a new liquid metal environment thereby altering

the magnitude of reduction in the cohesive strength of atomic bonds at the crack tip. Thus, a decrease in the magnitude of the critical resolved shear stress or the yield stress, σ_y, may cause stress relaxation and hence a decrease in the susceptibility to embrittlement (i.e., it may increase the stress or strain at fracture or change the fracture characteristics from being nucleation to propagation-controlled). If the decrease is high enough, a brittle to ductile transition may occur in the solid with the result that inhibition of embrittlement will occur. Alternatively, an increase in σ_y may cause an increase in the relative susceptibility to embrittlement. σ_y is known to vary with grain size, temperature, strain rate, and other factors such as Taylor orientation factor m, the number of available slip systems to satisfy von Mises criterion for ductility in polycrystals, etc. A quantitative relationship between σ_y and grain size relating to the ductile-brittle transitions in a solid can be described by the well-known Cottrell-Petch equation $\sigma_y K_y d^{1/2} > \beta\mu\gamma$.* Thus, the variation of σ_y and hence that in the susceptibility to embrittlement of a pure solid can be related to all these factors. In addition to these factors, the magnitude of σ_y can be significantly affected by solute additions to solid via solute locking of dislocation sources, solid solution hardening, order-disorder reactions, and the presence and dispersion of second phases. The magnitude of the cohesive strength of bonds at the tip, however, may also be affected when large additions of solute are made. In any event, the effects of some of these factors are simultaneous and interrelated. In this section, wherever

*Here K_y is the slope of the linear plot of σ_y against grain size, β is a factor expressing state of stress, μ is the shear modulus, and γ is the effective fracture-surface energy.

possible, we will use the above considerations while discussing the effects of these various metallurgical and physical factors on the susceptibility of a solid to liquid metal embrittlement.

Effects of Grain Size

The grain size dependence of fracture stress have been investigated for zinc-mercury (ref 59) (Figure 14), cadmium-gallium (ref 34), brass (ref 60), copper-alloys (ref 61) in mercury, and mild steel in lithium (ref 3). In these and other instances reported elsewhere (refs 1,5,6,8,9), the fracture stress varies linearly with the reciprocal of the square root of the grain size and thus follows the well-known Cottrell-Petch relationship for grain size dependence of the fracture stress. In zinc-mercury fracture is nucleation-controlled in region I and propagation-controlled in region II (Figure 14). In cadmium-gallium (ref 34) and many other couples, fracture is propagation-controlled. The stress-strain behavior of polycrystals as well as single crystals is identical in both the liquid metal and the inert environments. Specifically, the yield stress is not affected by testing in liquid metal environments (refs 1,7-9) (Figure 3). Plastic flow, yielding, or slip in few grains is a prerequisite for embrittlement as discussed earlier, and thus fracture can occur both above and below the macroscopic yield or flow stress of the solid, usually with a decrease in the fracture stress, strain, or both. Fracture path is usually intergranular, but transcrystalline cleavage type failure, or mix mode of failure, has been observed in hexagonal closed-packed (HCP) metals and some body-centered cubic (BCC) metals. In face-centered cubic (FCC) metals such as copper and nickel, grain size dependence could not be observed in inert environments because the metals fail

by ductile shear mode at low temperatures. It is worthy to note that in LME grain size dependence of fracture stress has been observed (ref 13). These results indicate that brittle fracture in LME is the same as that in inert environments and probably occurs by the reduction in cohesion mechanism rather than by a diffusion or dissolution-controlled process.

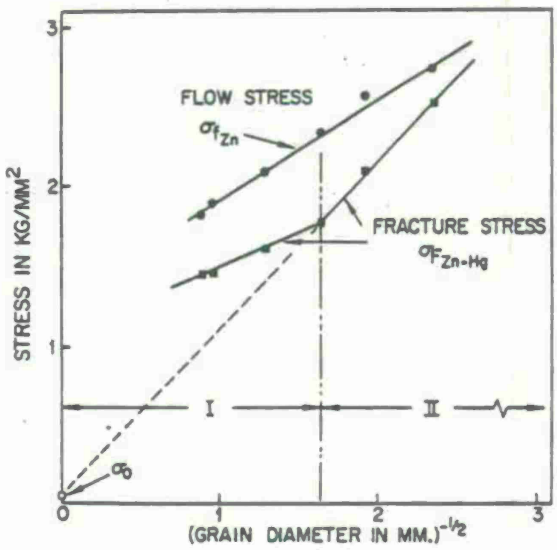

Figure 14. Variation of flow stress of zinc polycrystalline specimens, $\sigma_{f,Zn}$, and fracture stress of zinc specimens in liquid mercury, $\sigma_{F,Zn-Hg}$ with grain size at 298°K (from Westwood (ref 59)).

Effect of Temperature and Strain Rate

Temperature can affect LME through both the solid and the liquid. In the solid increase in temperature decreases the yield stress and increases the ductility thereby blunting the crack tip. This reduces stress concentrations at the tip or at the fracture nucleating sites. The effects of liquid on LME is related: (i) to the adsorption, dissolution, or diffusion of the liquid at

the crack tip, and (ii) to the rate of arrival or diffusion of liquid to the propagating crack tip. Item (i) has been discussed in the section on mechanisms of LME and (ii) in the section on the role of liquid in crack propagation. These processes are both temperature and time dependent. In some instances, temperature has virtually no effect on LME at least over a limited range as in zinc-mercury, Figure 6. Diffusion of liquid in the grain boundary can disintegrate the solid by separation of individual grains, e.g., aluminum-gallium, hot cracking of steel by liquid copper. Recently, Kamdar (ref 42) showed that liquid antimony embrittlement of steel increases with increasing temperature suggesting a temperature dependent liquid metal diffusion type of embrittlement. It is apparent that temperature dependence of LME is important in providing understanding of the mechanistic and transport related processes.

In most instances, temperature dependence of LME is similar to that in an inert environment and suggests adsorption induced and reduction in cohesion rather than diffusion or dissolution as the embrittling process. Thus, LME occurs at the melting temperature of the embrittler*, decreases with increase in temperature, and ceases at the so-called brittle-ductile transition temperature. The transition does not occur at a sharply defined temperature and its occurrence is not predictable from theoretical or other considerations. Generally, it is accepted that a synergistic effect of increased ductility with temperature counteracts the inherent severity of the

*In some solid-liquid metal couples, embrittlement occurs below the m.p. of the embrittler. Embrittlement increases with increase in temperature with a sharp increase in severity at the m.p. of the embrittling solid. The phenomena is called the solid metal induced embrittlement of metals (SMIE) (ref 87).

embrittling liquid metal. Transition temperature does vary with grain size, strain rate, and the type of test methods, etc (ref 1). Such transitions have been reported for titanium-cadmium (ref 29), zinc-mercury (ref 62), aluminum-mercury (refs 1,3,63), steel-lead (refs 64,65), and steel-lead-antimony solutions (refs 8,41). Grain size dependence of transition temperature has been reported for alpha-brass in mercury (ref 60) and strain rate effects for titanium-cadmium (ref 29). Upon transition, the fracture mode and the mechanical properties return to those in the inert environments.

Effects of strain rate on LME have been reported for cadmium-gallium (ref 28), zinc-mercury (refs 1,55), titanium-cadmium (ref 29), zinc-indium (ref 44), and brass-mercury (ref 60). The embrittlement susceptibility increases with increase in strain rate and is in agreement with similar behavior reported for metals tested in inert environments.

Effects of Alloying Additions to the Solid

Alloying additions usually have strengthening effects and hence increase the yield and fracture stress of the solid. Alloying can also change stacking fault energy, and alter the slip character from wavy or cross slip to planer besides producing other effects. All these factors affect the embrittlement of the solid. The dilute additions of copper or gold (0.1%) to zinc (ref 27), additions of 4 to 16 percent of aluminum to steel (ref 25) (Figure 2), additions of 1 to 8 percent nickel to iron (ref 66), and beryllium and other additions to copper increase the susceptibility of zinc, iron, and copper by mercury. Many such examples of embrittlement of metals and alloys by various liquid metals are documented in other reviews (refs 1,3,6,8,9). Additions of various elements to copper decrease the stacking fault energy of copper and

increase its susceptibility to embrittlement by mercury (ref 7). Stoloff et al (refs 7,25) have shown that a change in slip character from wavy to planer increases LME of metals. These investigations indicate that any or all of these effects of alloying prevent relaxation of stress concentrations at a barrier and increase the propensity for fracture. This is generally the reason for increased severity to embrittlement by alloying the solid. Besides these effects, the chemical composition and the nature of the grain boundary, i.e., sub-boundary, coinsidence boundary, etc., have significant effects on the severity of embrittlement. Funkenbusch et al (ref 67) have shown that intergranular embrittlement of monel 400 in both mercury and hydrogen environments is decreased with increase in the segregation of phosphorus at the grain boundary. A strong interaction between the segregating element and the embrittling atoms appears to account for the decreased susceptibility to embrittlement. The structure of the grain boundary on crack propagation has been investigated by Watanabe et al (ref 68) in brass-gallium couple. They investigated crack initiation and propagation in scanning electron micrograph (SEM) with a specimen in which all the grain boundaries were characterized using electron channelling patterns. It was found that cracks nucleated preferentially and propagated at random boundaries. The fracture mode change from intergranular to transgranular or vice versa occurred when grain boundaries were low angle or or coincidence type, which are more resistant to intergranular failure. The frequency of random and coincidence grain boundary was ~ 70 and 20 percent respectively. In other studies, Watanabe et al (ref 69) investigated the misorientation dependence of LME induced intergranular fracture in zinc bicrystals in liquid gallium. The fracture stress and strain

depends strongly on the misorientation angle, having a maximum effect at 55° in <1010> tilt and twist boundaries. They observed that ledges produced by deformation act as capillary tubes for the penetration of liquid gallium and as a notch for a propagating crack in the grain boundary.

Static and Cyclic Fatigue in LME

LME may occur by the penetration or diffusion of the liquid in the grain boundaries under applied stress. Diffusion is also time and temperature dependent. Static fatigue tests thus provide means for evaluating such embrittlement mechanisms. Very few such investigations have been reported in the literature. However, it has been reported that delayed failure could not be induced in notch-sensitive metals such as zinc (ref 70), cadmium, and iron-aluminum alloys in appropriate liquid metal environments (refs 5,71). For zinc single crystals and polycrystals tested in mercury, it was shown that fracture was critically stress sensitive and initiated instantaneously at a specific threshold stress, Figure 3. This indicates that diffusion is not a possible mechanism in this embrittlement couple. Delayed failure has been reported for notch-sensitive aluminum-copper and copper-beryllium alloys in liquid mercury (ref 72). Penetration of liquid in the grain boundaries was observed accompanied by embrittlement. However, the depth of penetration of liquid itself could not be related directly to grain size or Griffith crack size-controlled embrittlement process.

Gordon and An (ref 45) have investigated delayed failures in 4140 steel in indium as a function of stress, time, and temperature. They found that an incubation period exists which is related to stress induced dissolution and diffusion of liquid in the grain boundaries. The activation energy derived

from static fatigue data was used to support this mechanism. Actual penetration of the liquid was not observed because it was considered too small to be detected by available techniques. The role of liquid metal penetration on embrittlement is not yet clearly understood. Delayed failure in notched fatigue precracked specimens as a function of stress, time, and temperature may provide further understanding concerning diffusion-controlled embrittlement. Rather than static fatigue tests, in situ investigations of crack initiation and propagation in SEM, such as those reported by Watanabe et al (refs 68,69), should be performed in a high vacuum chamber with Auger, Sims, and other surface sensitive techniques to determine whether the liquid is at or near the crack tip or has diffused in the grain boundary. Also, in this manner, one can observe in the grain boundaries the effects of impurities on the susceptibility embrittlement and determine the effects of the structure of the grain boundaries on the crack path. In situ investigations of crack propagation in single crystals of iron-2% silicon and nickel in gaseous hydrogen environment has been reported by Vehoff and Rothe (ref 73). In addition to providing a new model for crack propagation, they concluded that embrittlement is caused by adsorption of hydrogen at the crack tip. It is clear that the mechanisms of environmentally induced embrittlement, specifically LME, can be better understood by performing investigations in situ in a microscope such as those reported by Watanabe (ref 68) and by Vehoff and Rothe (ref 73).

Investigations of LME in cyclic fatigue are few and have been summarized by Stoloff (ref 71). Brass, aluminum, and steel are severely embrittled in mercury (ref 9). In steel-mercury, however, such effects disappear at high

stress levels. Kamdar (ref 8) has suggested that fatigue crack propagation in LME should be investigated using fracture mechanics techniques (crack growth vs. stress intensity) as has been used in numerous SCC investigations. Such studies should provide activation energy for processes which control various stages of crack growth and indicate the role of liquid such as adsorption, surface or volume diffusion in grain boundaries, penetration, etc. on LME. Accordingly, Kamdar (ref 8) and Kapp (ref 74) have used fracture mechanics type tests and investigated the role of liquid on crack propagation which was discussed earlier. Their results are given in Figures 10 through 13. Such investigations with other embrittlement couples are needed to provide greater understanding of the role of liquid on LME.

Kamdar (ref 42) has investigated embrittlement of notched 4340 type specimens in cyclic fatigue in lead, lead-antimony solution, and liquid antimony as a function of temperature. In lead and lead-25% antimony solutions, embrittlement decreases with temperature, whereas in lead-35 to 75%, antimony and liquid antimony embrittlement increases with temperature. This suggests that in lead and lead containing low concentrations of antimony, embrittlement is due to lead and occurs by the reduction in cohesion mechanism. However, in lead containing higher concentrations of antimony, embrittlement is due to antimony and is controlled by temperature dependent grain boundary diffusion type process (ref 75).

EFFECT OF LIQUID METAL ENVIRONMENTS

Solute Addition to the Liquid

Solute additions which are in solution in the embrittling liquid or in nonembrittling "inert carrier" liquid metals have significant effects on the embrittling susceptibility of the solid. Rostoker et al (ref 3) have reported intriguing effects of small additions of solution dissolved in the embrittling liquid metal in varying the embrittlement susceptibility of many metals and alloys. It is not clear whether all these effects are due only to the solute additions, or are caused by factors such as metallurgical, mechanical, or others which have been discussed earlier. Recently, however, Breyer (ref 64) and his co-workers have reported systematic and extensive investigations of the effects of small additions of antimony and tin and other metals to lead on the lead embrittlement of smooth specimens of 4140 steel tested in tension. It was shown that additions of 0.004 to 2.0 w/o antimony to lead significantly degrade the mechanical properties of steel. The brittle to ductile transition temperature varies with the concentration of antimony and increases by ~ 300°F when antimony content is maximum. However, in a later publication it was reported that such linear correlation did not occur when some specimens were tested in tin containing antimony. Nevertheless, these significant effects are attributed to increased concentrations of antimony atoms at the crack tip where antimony is more severely embrittling of steel than is lead. It is not apparent how such small concentrations of solute will preferentially segregate at the crack tip in sufficient amounts to increase embrittlement, nor is it clear how the solute will preferentially keep up with the propagating tip to complete the fracture process.

Recently, Kamdar (refs 42,75) investigated the effects of 5 to 75% antimony additions to lead on the liquid lead embrittlement of single-edge notched specimens of 4340 type steel tested in cyclic fatigue. Lead embrittlement of steel decreases with increasing temperature and the brittle-ductile transition temperature is ~ 1200°F. Small additions of antimony (5 to 25%) to lead do not have significant effects on lead embrittlement of steel. Embrittlement increases with additions of antimony as the temperature increases and becomes maximum at 1200°F, the brittle-ductile transition temperature in lead. However, embrittlement is most severe in liquid antimony. The variation in the susceptibility with temperature suggests that lead embrittlement of steel or lead containing small additions of antimony is consistent with the reduction in cohesion mechanism, whereas antimony induced embrittlement by lead-antimony solutions, as well as embrittlement by liquid antimony, is consistent with temperature dependent diffusion-controlled grain boundary embrittlement of steel. Since LME is a prerequisite for the occurrence of solid metal induced embrittlement (refs 8,17,18), LME of steel by antimony may be used to study solid metal induced embrittlement (SMIE) in order to better understand the temper embrittlement of steel by antimony.

The Concept of "Inert Carriers"

In some instances, direct investigation of the embrittlement behavior of a potentially interesting solid metal-liquid metal couple is not feasible. The reason is that the solid metal at temperatures just above the melting temperature of the liquid metal is either too ductile to maintain the stress concentrations necessary to initiate and propagate a brittle crack, or it is excessively soluble in the liquid metal, thus allowing crack blunting. It is

possible, however, that the embrittlement of a given solid metal by a potentially embrittling liquid metal might be achieved at temperatures much below the melting point of the liquid metal if one incorporates it in solution in an inert carrier liquid metal of lower melting point (refs 76,77). In this way, the active element can be present effectively in the liquid state, though at some temperature far below its melting point. Besides providing a possible means for inducing embrittlement in a potentially interesting system, this approach has been used by Kamdar to investigate the variation in the degree of embrittlement induced in many solid metals as a function of the chemical nature of several active liquid-metal species dissolved separately in a common inert carrier liquid metal (ref 76).

To examine the validity of the proposition, experiments were performed with the solid cadmium-liquid (mercury + indium) system (ref 77). Mercury is inert in that it is known not to embrittle cadmium (ref 1) and it dissolves up to 70 at. percent of indium (m.p. 156°) at 25°C. Thus, indium is effective in liquid state at 25°C in mercury-indium solutions. The embrittlement of cadmium by indium-mercury solutions is shown in Figure 15. It is significant to note that cadmium monocrystals which fail by shear at liquid helium temperature can be cleaved in mercury-indium solutions at 25°C (Figure 1). This indicates that diffusion is not the controlling mechanism. Such embrittlement behavior has been observed in the nuclear industry where zirconium tubes which contain nuclear fuel rods are embrittled by the fission product cadmium dissolved in the liquid cesium. Cesium is used as a coolant and does not embrittle zirconium (refs 9,14,78-80).

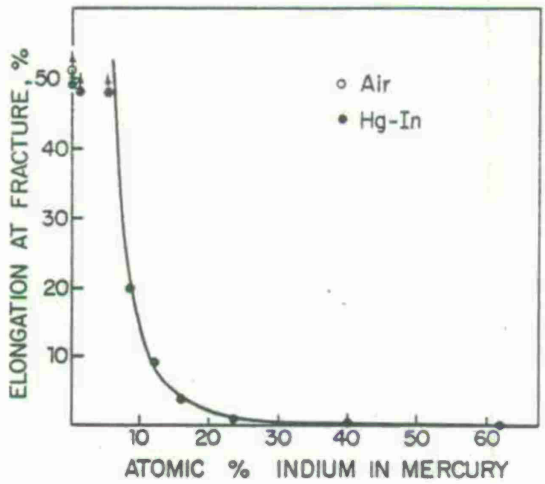

Figure 15. Variation in ductility of polycrystalline cadmium with indium content of mercury-indium coatings at 298°K. The filled circles are for test in Hg-In and open circle for that in air (from Kamdar (ref 76) and Kamdar and Westwood (ref 77)).

Specificity of Embrittlement

It was stated in the beginning of this report that only certain liquid metals embrittle certain solid metals, implying that LME is a specific phenomena. This idea of specificity has been questioned by Shunk and Warke (ref 54). Their tabulation of embrittling and non-embrittling couples differentiated between tests with pure metals, laboratory alloys, and commercial alloys. The report of nonsusceptibility for an LME couple was valid for specific test conditions, whereas under different conditions the same couple became susceptible. They concluded that specificity of LME is questionable. This view has been supported by the dependence of embrittlement

on strain rate, test temperature, grain size, alloying, presence or absence of stress raiser such as a notch, type of test, i.e., tensile vs. cyclic fatigue, etc., and is discussed in detail by Kamdar (refs 1,8,9) and by others in various reviews (ref 9). In addition, the concept of "inert carrier" discussed above can also be used to induce embrittlement in very ductile solid metals.

Recent reports of many new embrittlement couples, e.g., cadmium-indium (ref 1), zinc-indium (refs 1,6), pure copper-mercury (ref 5), iron-nickel alloys - mercury (ref 66), iron-3% silicon-mercury, gallium, indium (ref 1), steel-lead, zinc, tin, tellurium, bismuth (ref 3), aluminum containing lead, bismuth or cadmium as inclusions (ref 81), and iron-copper (ref 82) indicate the possibility of discovering other unknown or apparently nonsusceptible embrittlement couples. The combinations of the effects of the solid, liquid, and test conditions described above and other factors discussed in this report, strongly suggest that specificity, in fact, may not exist. However, the author believes that this may not necessarily be the case. In fact, extensive investigations concerning the possibility of embrittlement of zirconium alloy by some 35 chemical liquid metals and liquid metal solutions revealed that only a couple of metals embrittle zirconium (ref 78). It seems that the interactions between the solid and the liquid that results in embrittlement should be specific and that the susceptibility should be related to the magnitude or the strength of the interaction. Furthermore, the underlying assumption here is that most LME occurs by a mechanism such as reduction in cohesion. However, diffusion penetration induced weakening of the grain boundaries is also a likely possibility. Some examples are the

degradation of aluminum in gallium, steel in liquid antimony, and the hot shortness of steel in copper. It is suggested, therefore, that the question of specificity be investigated in a general manner by considering only those embrittlement couples which have been well characterized under conditions discussed earlier, with the possibility that other mechanisms may also operate individually, or in combination in other systems. In any event, we will take a brief look at some of the attempts to explain specificity that are presented in the literature. These are electronegativity differences between solid and liquid, solid-liquid interfacial energies, heat of mixing, heat of solution, formation of eutectics, and solubility and bond interaction model of Kelly and Stoloff (ref 83). The last appears to be the most viable approach to specificity.

It was shown that embrittlement or otherwise in many solid liquid metal couples can be related to the relative magnitudes of the solubility parameter, i.e., solubility of the solid in the liquid and the solid-liquid interaction energy, or the reduction in the fracture energy as shown in Figure 16. Kelly and Stoloff used the thermodynamics approach in their calculations. However, Clyde and Messmer (refs 84,85) have made quantum-mechanical calculations to understand the specificity of embrittlement. They found that it was the ability of the embrittling atoms to draw electrons to itself from the solid metal or the electronegativity of the embrittling elements that determined the relative susceptiblity of these element to cause embrittlement of the solid. These studies provide some support for the empirical correlation reported by Kamdar (ref 76) between the electronegativities of the solid and the liquid and of embrittlement susceptibility noted in many

solid-liquid metal couples. Specificity is indeed a very important but difficult problem and its resolution is a very important challenge.

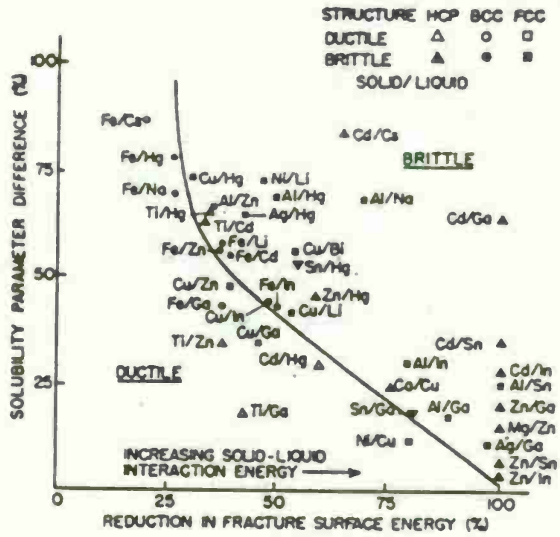

Figure 16. Calculated reductions in the fracture surface energy relating to the solubility parameter for various solid-liquid metal couples. The curve separates embrittled couples from unembrittled couples (from Kelly and Stoloff (ref 83)).

SUMMARY AND SUGGESTIONS FOR FUTURE RESEARCH

Chemical or electronic interactions at the solid-liquid metal interface or at the crack tip which promote good wetting is a necessary condition for the occurrence of liquid metal embrittlement. In addition, the other prerequisites that also must be fulfilled are the same as those for brittle fracture in an inert environment. Even then, whether embrittlement will or will not occur in a specific solid-liquid metal couple will depend upon the metallurgical, mechanical, physical parameters, and on the chemical nature of

the liquid and that of the solute dissolved in the liquid metal. All the factors which promote brittleness in a solid will also induce embrittlement and will enhance the severity of embrittlement.

It is generally accepted that LME occurs by "Adsorption Induced Reductions" in the tensile or shear cohesion of the atomic bonds at the crack tip. The conditions that lead to embrittlement by brittle failure due to tensile stress or dimpled rupture failure due to shear processes at the crack tip are not yet understood. It is likely that solids which are inherently brittle or are ductile at low temperatures will be embrittled and fail by brittle or dimpled rupture mode, respectively. The relative strength of the solid-liquid metal interaction energies is also an important consideration. In either case, it is considered that the arrival of the liquid at the propagating crack tip by surface diffusion of liquid by either liquid over liquid or liquid over crack surface is the rate controlling step in LME. It is possible that once nucleated a brittle crack of critical size may propagate to failure in the absence of liquid at the crack tip. Besides this mechanism, other mechanisms of embrittlement should be considered, in particular diffusion-controlled penetration of liquid in the grain boundaries. It is believed that LME is a specific phenomena, however, evidence for non-specificity of embrittlement is quite considerable.

It is significant that chemical species dissolved in inert-carrier or non-embrittling liquid metals can induce embrittlement in a solid. The importance of the "inert carrier" concept is well illustrated by the cracking of nuclear fuel cladding metal zircoloy-2 by the fission product cadmium dissolved in inert carrier - non-embrittling coolant liquid cesium. There is

considerable evidence of LME in steel and other industries as well as industrial processing such as welding, steel processing, etc. Thus, failure analysis of industrial components should include LME besides considerations of other environmentally induced failures. More investigations of the effects of static and cyclic fatigue on LME are needed, specifically crack growth rate as a function of stress intensity at the crack tip and temperature should provide better understanding of the adsorption, diffusion, or penetration of liquid on LME.

New and significant developments in LME are the in situ investigations of LME of polycrystals and bicrystals by Watanabe et al (refs 68,69). It was shown that correlation exists between crack path and the embrittlement susceptibility, both of which are related to the structure of the grain boundaries. Also, in situ investigations at high magnification in SEM of crack propagation in iron-2% silicon and nickel single crystals by Vehoff and Rothe (ref 73), have provided further understanding of the role of hydrogen on adsorption, diffusion, etc. in the hydrogen embrittlement of metals. The fracture surfaces have provided support for a model proposed by these investigators. Similar investigations in SEM with surface sensitive chemical and structural capability such as scanning Auger, ESCA, Sims, and others which allow observations of processes of adsorption, diffusion, liquid penetration, and chemical and structural changes occurring at the crack tip should provide significant insights into atomistic aspects of LME.

Thermodynamic calculations of bond-interaction-solubility parameter of Kelly and Stoloff (ref 83) have provided some understanding concerning the difficult problem of specificity of LME. Clyde and Messmer (refs 84,85) have

shown that the electronegativity of embrittling species are related to the severity of embrittlement. In future years, such experimental and theoretical investigations should improve our understanding of LME as well as other environmental induced embrittling processes. LME type fracture processes occur in industry and industrial processes and it is hoped that technologies and engineers become aware of this phenomena of environmental induced failure.

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