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THE LIQUID METAL EMBRITTLEMENT OF ZINC AND ALUMINUM

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INTRODUCTION

Some otherwise ductile metals are known to fracture prematurely if stressed in the presence of certain low melting-point metals. This phenomenon of liquid-metal embrittlement (LME) is still not well understood, even though it has been extensively reviewed from time to time [1, 2]. Since the effect is clearly relevant to the use of liquid metal coolants in the fast reactor and the proposed fusion reactor, a fundamental programme is in progress at the U.K.A.E.A. Research Establishment at Harwell. This paper presents results obtained from preliminary studies on model systems.

One of the most serious aspects of LME is that its occurrence (or non-occurrence) cannot be confidently predicted for any previously uninvestigated combination of liquid and solid. There are, at present, rule-of-thumb guidelines based on phase relationships and electronegativity values, but such rules are at best empirical. The problem of assessing the behaviour of any particular system from literature reports is, with a few exceptions, rendered more difficult by the lack of reliable data for well-defined materials based on any simple and reproducible test. Indeed, LME is still widely reputed to be specific to individual systems, although this concept has recently been challenged [3].

THE MECHANISM OF LME

The most widely-held explanation is based upon a reduction in the bond strength of the solid metal at the crack tip by the presence of atoms of the embrittler. This approach was first advanced by Rostoker et al [1], who suggested that the explanation probably lay in the effect of the liquid metal on the interfacial energy and the role played by the latter in brittle fracture processes. In 1963, Westwood and Kamdar [4] and Stoloff and Johnston [5] further developed the argument and advanced the concept of an "adsorption induced reduction in cohesion". In effect, this argued that the presence of the liquid metal reduced the surface energy of the solid metal from that in its own vapour, γ_{SV}, to some new lower value γ_{SL}. Since the stress, σ, necessary to separate two adjacent planes of atoms during the propagation of a Griffith-type crack in an elastic material of surface energy γ is given by [6]

$$\sigma \ \alpha \left(\frac{E\gamma}{a_o}\right)^{1/2}$$

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where E is the Young's modulus, and a_0 is the lattice parameter, then the reduction of the interfacial energy from γ_{SV} to γ_{SL} should allow brittle fracture to occur at a lower stress. In 1967, Stoloff [7] argued more explicitly that the reduction in cohesive stress would promote brittle fracture by allowing local tensile failure at the tip of the crack before the shear stresses could build up to a point where local yielding and crack blunting could occur. More recently still, Kamdar has suggested [2] that provided the presence of the embrittling atoms has no effect on the plastic deformation processes inside the bulk of the solid metal, then a "coefficient of embrittlement", η, can be defined by the equation

$$\eta = \frac{\gamma_{SL}}{\gamma_{SV}} .$$

Hence, according to this theory, the embrittling efficiency of any liquid on any solid can be predicted from a knowledge of the interfacial energies. This approach implies that LME should display the characteristics normally associated with classical brittle fracture, i.e., a high crack propagation rate driven by the release of elastic strain energy, which has given rise to the term "catastrophic brittle fracture".

The experiments described in this paper were designed to test the validity of these concepts using model systems. Thus, the interfacial energies were determined for a number of low melting-point metals on zinc and compared with their reported embrittling behaviour. Similarly, the processes of crack initiation and propagation have been studied in aluminum wetted by gallium.

RESULTS AND DISCUSSION

The Embrittlement of Zinc

The interfacial energies were determined using the sessile drop technique which involves measuring the contact angles of a liquid drop on a solid surface at some given temperature. The experiments were carried out in a furnace, as shown in Figure 1, evacuated to ∿ 5 mNm^{-2} except when liquid metals with a high vapour pressure were used, in which case a cover gas of argon containing < 1 p.p.m. oxygen was used. To maintain the surfaces as clean as possible, pellets of the low melting point metal were prepared in an argon glove-box and transported to the furnace in an atmosphere of argon. The zinc plaques were polished down to 1 μm diamond before placing in the furnace and evacuating. After outgassing the plaque at 200° C for 30 mins., the temperature was adjusted to that required for the run and the pellet was dropped onto the plaque. Since LME is reputed to be at its most severe just above the melting point of the embrittler, the equilibration temperature was usually chosen to lie in that range. The shape of the drop was photographed at intervals, and the contact angles were subsequently measured from the film. Experiments were carried out for Hg, Ga, In, Sn and Pb, which are reported to embrittle zinc, and Na, Bi, and Cd, which do not. The highest purity materials obtainable were used; fuller details are given elsewhere [8].

For any particular liquid metal to cause embrittlement, η must be <1 and hence $\gamma_{SL} < \gamma_{SV}$. Now according to the Young-Dupre equation for the equilibrium of a sessile drop on a flat surface,

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$$

where γ_{LV} is the surface energy of the liquid and θ is the contact angle measured through the liquid. For η < 1, θ must be <90° and the drop is said to be "wetting". It follows, therefore, that any liquid which embrittles a solid must also wet that solid. (This condition is, of course, also necessary to allow the transport of the embrittling atoms to the crack tip.) The converse is not necessarily true, however, because there may be a certain minimum reduction in interfacial energy which must be achieved before embrittlement will occur. On the other hand, the embrittling efficiencies of any liquid metals known to embrittle a particular solid metal should be proportional to their ability to reduce the interfacial energy; i.e., the most efficient embrittler would be expected to have a high γ_{LV} and low θ.

Table 1 shows the values of η which were obtained. Values for γ_{LV} [9] and γ_{SV} [10] were taken from the literature. It is seen that the embrittlers tend to have interfacial energies less than about 400 mJm^{-2}, while the non-embrittlers tend to give higher values. Too much attention should not be given to the absolute values, however, because there were strong indications that surface contamination played a significant part in the ease with which wetting was achieved. The actual values of γ_{SV} and γ_{LV} would therefore be expected to be lower than the values used in the calculations.

The coefficients of embrittlement calculated from the interfacial energies should relate directly to the work of fracture of the embrittled specimen during a conventional mechanical test. Westwood and Kamdar [4] report values of η_{Hg} = 0.61 and η_{Ga} = 0.48 for the fracture of zinc single crystals. Neither of these values compare well with those obtained in the present work, but this might be explained by the theoretical analysis [11] used by these workers, which gives a fracture surface energy for zinc of 90 mJm^{-2} compared with a surface energy of 830 mJm^{-2} from zero-creep experiments. It is likely, however, that the ratio of the embrittling efficiencies is more accurate and it may be more appropriate to compare the ratios of the coefficients derived from fracture energy and surface energy measurements. This gives η_{Ga}/η_{Hg} = 0.79 and 0.66 respectively, which are in fair agreement. Unfortunately, Hg and Ga are the only two embrittlers for which fracture energy values exist at present, so a more detailed comparison is not possible. However, these results are consistent with the surface energy approach and predict that the embrittling efficiencies in descending order are Ga, In, Sn, Hg and Pb.

Crack Propagation in Aluminum Wetted by Gallium

The action of gallium on aluminum is quite complex and there are some inconsistencies in the literature. Thus, samples of polycrystalline alluminum are reported to fail by grain boundary penetration at low strains [1], but single crystals were observed to fail in a ductile manner, even when fracture began by cleavage cracking [12].

These findings were re-examined during the present work using both polycrystalline and single crystal flat-sheet specimens wetted on one edge with gallium. The tests were carried out in air at approximately 30° C, i.e., just above the melting point of Ga, in a conventional tensile testing machine. The progress of the crack was recorded on cine-film.

The results from the polycrystalline specimens were consistent with previous reports. Specimens of commercially pure aluminum with a UTS of 75-90 MNm^{-2} and elongation of ∿ 35% failed at 44-51 MNm^{-2} when wetted with gallium. The reduction in plastic ductility was much more severe, and all specimens appeared to fail at the limit of proportionality. Close observation of the specimen surface during testing showed that the gallium was absorbed as soon as stress was applied, and at the same time, the grain-boundaries opened up (Figure 2). Fracture was by intergranular separation, and was "catastrophic" in that the crack propagated at a rate > 10 mm s^{-1} and could not be arrested by unloading the specimen. However, it was noted that in some cases the gallium supply was inadequate and this resulted in a transition from brittle to ductile failure.

In contrast, the single crystals showed a different mode of behaviour which is in conflict with some previous reports. Experiments were carried out with randomly oriented specimens grown by the critical strain method from commercially pure aluminum and also with specimens grown from the liquid with <001> parallel to the tensile axis.

Both types of specimens failed by cleavage cracking, but the cracks were not initiated until strains of 10 - 20% had been reached. Crack velocities were slow compared with the polycrystalline specimens and were constant for a given orientation and extension rate, as shown in Figure 3. Moreover, growth rates were found to be linearly dependent on the extension rate, (Figure 4). Those specimens which were oriented with respect to the tensile axis all tended to fracture perpendicular to the axis, i.e., along the (001) plane. Crack directions varied in the randomly oriented specimens and no preferred plane was detected.

The amount of plastic deformation associated with the failure was somewhat surprising in view of the cleavage nature of the fracture. The work of fracture has been calculated from the stress-strain curves and although it falls around the value 10^7 mJm^{-2} for all the oriented specimens, Figure 5 shows that energy absorption tends to be higher at higher rates of extension. This is probably due to the variation in yield stress with strain rate. Typical fracture faces have been examined by SEM and show both plastic and cleavage features as in Figure 6. The cleavage crack clearly tends to branch at the tip and the misalignment produced is then subsequently accommodated by ductile shear parallel to the tensile axis.

CONCLUSIONS

The results from the two sets of experiments described in this paper indicate that while surface energies and elastic fracture are probably fundamental to LME, other processes such as plastic deformation play an important part. The work on the zinc suggests that a low solid/liquid interfacial energy is associated with embrittlement. In the case of gallium and mercury, the interfacial energies can correctly predict the order of embrittlment, thus tending to support an explanation based on elastic fracture. In contrast, the embrittlement of aluminum by gallium only shows "catastrophic brittle fracture" in polycrystals. Although single crystals also suffer a brittle cleavage-type failure, it is preceded by extensive ductility. While the occurrence of LME in any given system might therefore be predicted from a study of the surface energies, the macroscopic, and indeed engineering, aspects of the fracture such as total strain and energy absorption depend heavily on metallurgical features. It is quite possible that this dependence is responsible for some of the uncertainty and conflicts in reports on the occurrence of LME.

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Table 1 Interfacial Energies and Coefficients of Embrittlement Calculated from Sessile Drop Experiments

Embrittling Metals	Temperature °C	θ (degrees)	Energies (mJm^{-2}) γ_{LV}	γ_{SL}	$\eta = \frac{\gamma_{SL}}{\gamma_{SV}}$
Hg	13	10	498	340	0.41
Ga	104	33	718	228	0.27
In	250	15	544	293	0.35
Sn	256	15	544	305	0.37
Pb	370	24	468	402	0.48
Non-Embrittling Metals					
Na	232	123	191	967	1.16
Bi	295	32	378	509	0.61
Cd	362	43	570	413	0.50

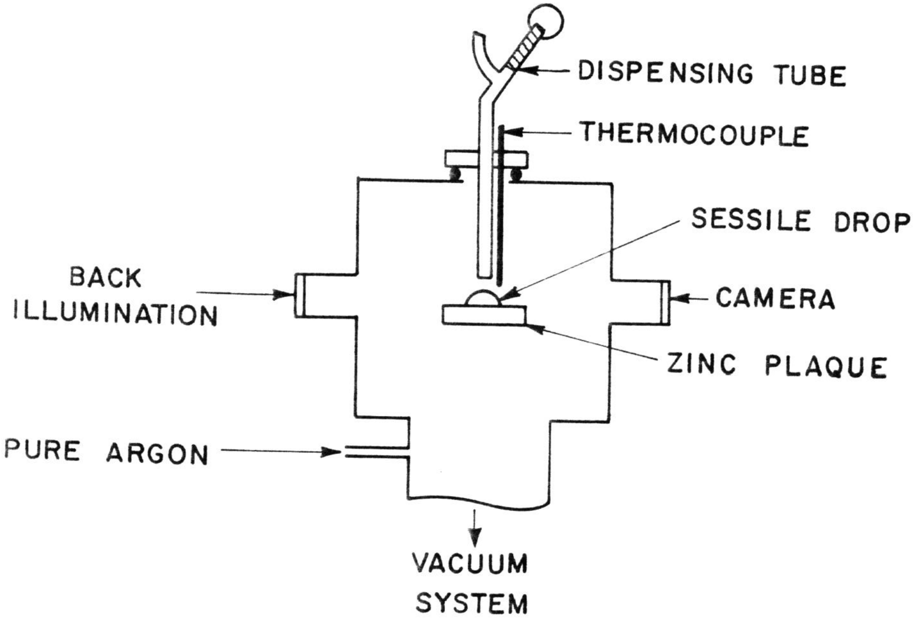

Figure 1 Schematic Diagram of Furnace

Figure 2 Grain Boundaries Opened up by Stress in the Presence of Liquid Gallium X 700

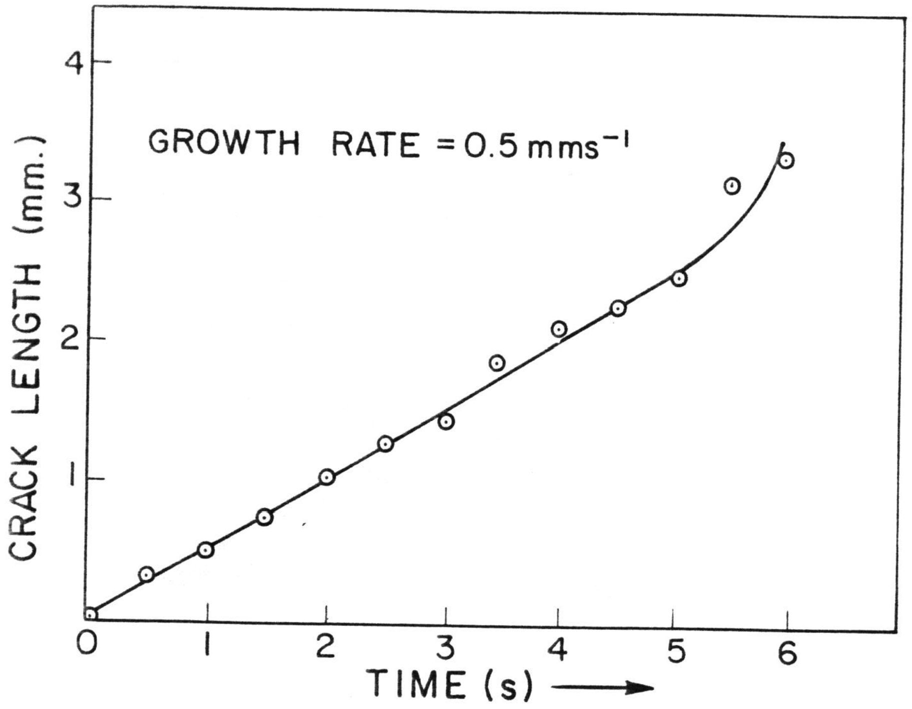

Figure 3 Crack Growth at a Strain Rate of 3.8×10^{-3} s^{-1}

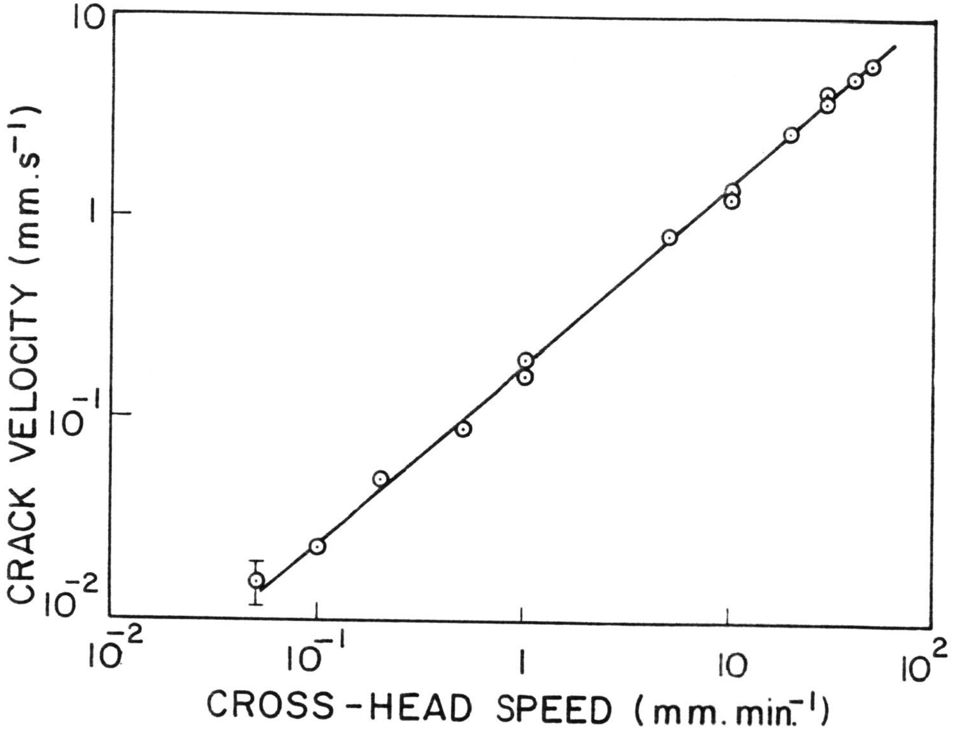

Figure 4 Crack Growth Rate vs. Extension Rate

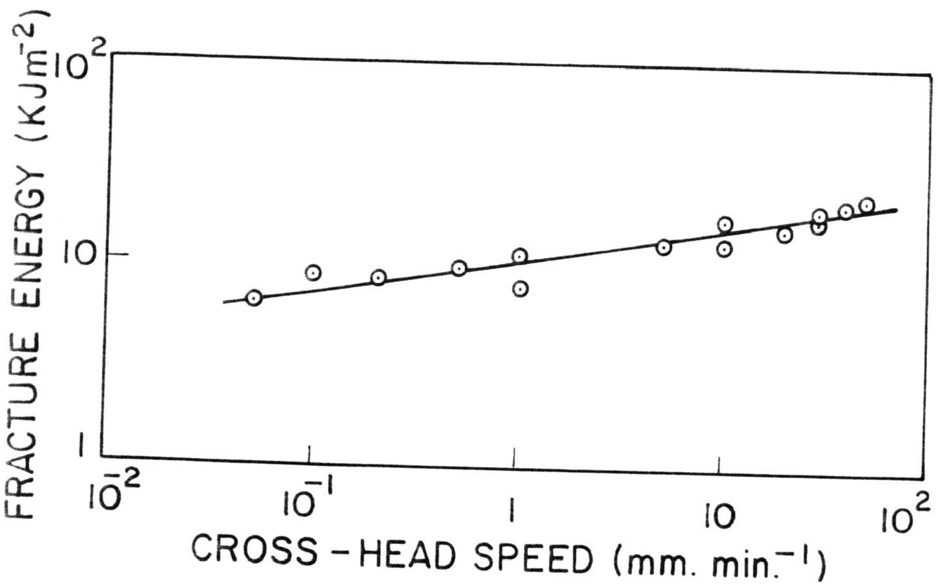

Figure 5 Work to Fracture vs. Extension Rate

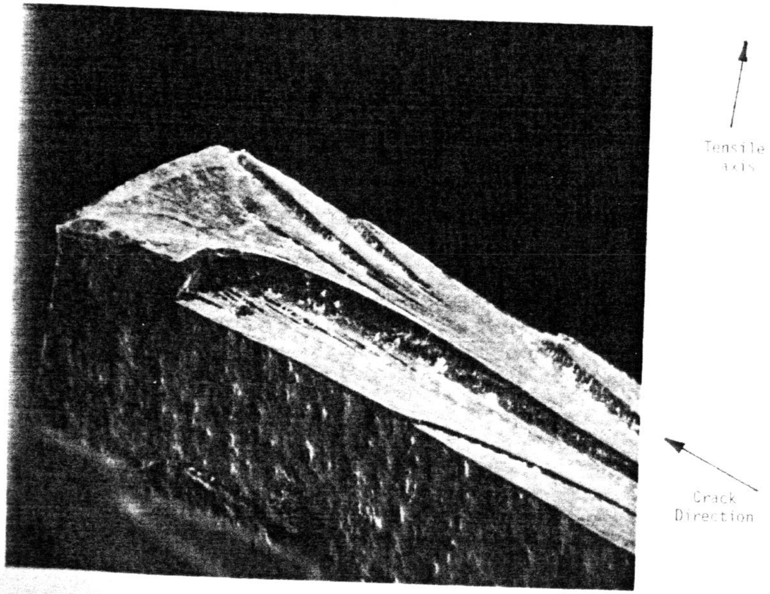

Figure 6 Plastic Tearing Near End of Fracture X 35