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Fracture behaviour of statically loaded metals in liquid metal solutions

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Summary

A study has been made of the fracture behaviour of polycrystalline aluminium, cadmium and silver specimens statically loaded in liquid mercury, gallium, or various mercury solutions at room temperature. In all embrittling environments, specimens either failed in < 1 sec at some critical stress $\sigma(1)$, or did not fail in > 2000 sec at some slightly lower stress. Such behaviour is considered to indicate that failure in these environments is controlled by the crack initiation process. Estimates of the fracture energies of polycrystalline crack initiation process. Estimates of the fracture energies of polycrystalline silver in liquid mercury or gallium ($\phi_{Ag-Hg} \simeq 270$ ergs/cm^2; $\phi_{Ag-Ha} \simeq 50$ ergs/cm^2) derived via the analysis of Smith and Barnby are in accord with this view. It is concluded that liquid metal solutions can be used to control, sometimes over a wide range, the stress to produce catastrophic failure in otherwise ductile solid metals.

Introduction

When a ductile solid is subjected to a tensile stress σ in an inert environment, the relationship observed between time to failure, t_F, and σ is of the general form

$$t_F = t_0 \exp\,[(U_0 - \Gamma\sigma)/kT], \tag{1}$$

where t_0 is a constant of order 10^{-13} sec, U_0 is a term related to the binding energy of the solid and approximately equal to its heat of sublimation, Γ is a structure dependent coefficient, k is Boltzmann's constant, and T is the absolute temperature [1]. This relationship has been demonstrated to be appropriate for the failure in air under static loading conditions of many polycrystalline metals, including aluminium [1], zinc and cadmium [2]. Under such conditions, the failure process is considered to be controlled by the rate of propagation of a particular crack, rather than by those factors which determine the initiation of such a crack.

Bruyukhanova *et al.* [2] have shown, on the other hand, that when polycrystalline zinc is statically loaded in pure liquid mercury, failure either occurs in less than 1 sec, or does not occur in times of more than 10^6 secs, depending on whether or not some critical stress, $\sigma(1)$, is exceeded. Noting that the magnitude of $\sigma(1)$ was not significantly affected by temperature over the range 20–100 °C, they concluded that failure in the presence of an embrittling liquid metal is not thermally activated. Similar behaviour was observed for the solid cadmium-liquid gallium couple. The catastrophic nature of the embrittlement of statically loaded solid metals by pure, surface-active liquid metals suggests that fracture in this case may be controlled by crack initiation rather than crack propagation [3].

Embrittlement can also be induced by the presence in an otherwise "inert" liquid metal environment of relatively low concentrations (< 10 a/o) of some surface-active metallic species [4]. For example, liquid mercury does not embrittle solid cadmium, but mercury-indium solutions containing more than ~7 a/o indium cause significant reductions in its strength and ductility [4]. At present, little is known about the relationship between severity of embrittlement and chemical composition of the environment. In particular, there do not appear to have been any studies of the influence of liquid metal solutions on the behaviour of statically loaded metals. However, one would anticipate that the stress to nucleate a crack would be dependent on the surface concentration of the active species in the environment, and that the rate of propagation of a nucleated crack would be controlled by the rate of arrival of the active species at its tip. To examine these and other possibilities, a study has been made of the fracture behaviour under static loading conditions of polycrystalline aluminium, cadmium and silver exposed to solutions of cadmium, gallium, indium, thallium and zinc in mercury at room temperature.

Experimental

Tensile specimens, approximately 42 mm × 12 mm in size and having gauge dimensions of 6·5 mm × 3 mm, were stamped from 1 mm thick sheets of polycrystalline aluminium, cadmium or silver, heat-treated as indicated in Table 1, and then chemically polished or etched immediately prior to coating the gauge length with the appropriate liquid metal. After coating, specimens were tested to failure in a conventional constant load machine, the time taken between coating and stressing being held to less than 1 min to minimize any contribution of intergranular penetration effects to the failure process.

The liquid metal environments used were gallium, mercury, and mercury solutions containing 0-4 a/o gallium, 0-10 a/o cadmium, 0-70 a/o indium, 0-15 a/o thallium, and 0-5 a/o zinc. To prevent the rapid oxidation of amalgamated aluminium specimens which occurs on exposure to air, all tests involving aluminium and mercury environments were conducted under water-free hexadecane.

Results

Cadmium in (Hg-In) solutions

Cadmium is not embrittled by pure mercury, and failure in this environment occurs by ductile shear [4]. The relationship between t_F and σ for mercury-coated specimens was exponential and identical to that for specimens stressed in air, Fig. 1. Additions of < 5 a/o indium to the mercury did not significantly alter this relationship or the fracture mode. For mercury solutions containing > 5 a/o indium, however, significant embrittlement occurred, the fracture mode changed to mixed inter- and trans-crystalline cleavage, and failure occurred in a catastrophic manner ($t_F \leq 1$ sec) at some critical stress, $\sigma(1)$. The variation of $\sigma(1)$ with indium content of the (Hg-In) environments is shown in Fig. 2(b).

Silver in (Hg-In) solutions and gallium.

Polycrystalline silver specimens, coated with mercury and statically loaded, fractured in a brittle, intercrystalline, and catastrophic manner at a stress approximately half of the ultimate tensile stress in air. As noted with the cadmium-(Hg-In) couple, minor additions (5-10 a/o) of indium to the mercury had little effect on the embrittling influence of this environment on silver. However, in contrast to behaviour in the former system, additions of $>$ 5-10 a/o indium to mercury *reduced* the severity of embrittlement in silver, Figs. 2(a) and 3.

A limited number of tests were also performed with gallium-coated specimens, and it was observed that gallium markedly embrittles silver, $\sigma(1)$ being about 3·4 Kg/mm^2 compared with 7·9 Kg/mm^2 for similar specimens coated with mercury. The possibility was considered that such severe embrittlement might be the consequence of intergranular penetration by the gallium. However, the value of $\sigma(1)$ for specimens exposed to liquid gallium for two hours prior to testing was identical with that for freshly coated specimens. Thus, intergranular penetration does not seem to be a significant factor in the embrittlement of silver by liquid gallium at room temperature.

Aluminium in mercury solutions and gallium.

Aluminium is embrittled by both mercury and gallium and, as noted earlier [3,5], additions of 0-3 a/o gallium to mercury testing solutions cause a marked increase in the severity of embrittlement, Fig. 4. $\sigma(1)$ was found to decrease linearly with gallium content of the mercury environment, Fig. 5. For (Hg-3 a/o Ga) solutions, some indication of a variation in t_F with σ was observed, but for (Hg-4 a/o Ga) environments the scatter of data was such that no conclusive trend could be determined.

The embrittlement of high-purity aluminium by pure gallium is so severe that specimens occasionally fractured while being mounted in the testing rig. Other work [6] has shown that the dynamic fracture stress of aluminium specimens exposed to environments containing free gallium is dependent on the time of exposure to the environment (at 30 °C) prior to testing, indicating that intergranular penetration is involved in embrittlement by such environments. Since the solubility of gallium in mercury at 25 °C is ~3·5 a/o, and the two elements are immiscible at higher concentrations [7], (Hg-4 a/o Ga) environments contain free gallium at this temperature. Thus, the embrittlement of aluminium by this environment may involve two mechanisms—gallium adsorption and bond weakening [8, 9] and intergranular penetration (absorption).

Additions of small amounts (< 3 a/o) indium to mercury had no significant influence on the embrittlement of aluminium by mercury, but additions of between 3 and 35 a/o indium caused a gradual increase in severity of embrittlement. Greater additions produced the opposite effect, and for 70 a/o indium solutions $\sigma(1)$ was identical with that for pure mercury.

The influences of additions of cadmium, thallium and zinc to mercury on the embrittlement of aluminium also were examined, and the results of this work are summarized in Fig. 5. Additions of up to 8 a/o cadmium increased embrittlement, but greater additions reversed this trend (the solubility limit of cadmium in mercury is ~10 a/o at 25 °C (10)). A similar minimum in the $\sigma(1)$ versus solute concentration plot for (Hg-Tl) was observed at σ 10 a/o thallium, but for this system there was no variation in $\sigma(1)$ for concentrations of < 8 a/o thallium. Additions of up to 5 a/o zinc to mercury increased the embrittlement of aluminium.

Possible relationship between embrittlement and surface diffusion rate.

On the basis of their studies with zinc, Summ *et al.* [11] have suggested that a correlation may exist between the rate of surface diffusion of a liquid metal or solution over the surface of a metal and its embrittling capacity for that metal. To determine the applicability of this correlation to the present work, drops of mercury and (Hg-50 a/o In) of similar volume (~0·05 ml) were placed on freshly polished silver and cadmium surfaces, and their rates of diametral growth determined using an optical microscope. It was noted that for cadmium over a period of 5 hours, the (Hg-50 a/o In) drop expanded three times more rapidly than the mercury drop. For silver, on the other hand, exactly the opposite behaviour occurred, the mercury drop expanded several times more rapidly than the (Hg-50 a/o In) drop. These results are, therefore, in accord with Summ's correlation, in that a (Hg-50 a/o In) solution produces greater embrittlement in cadmium than does mercury, while the converse is true for silver, Figs. 2(a) and 2(b).

The significance of this correlation may be that both the ease with which a liquid spreads over a surface and the effort required to initiate a crack at that surface in the presence of the liquid are related to the surface free energy of the solid-liquid interface.

Discussion

This work has shown that additions of metallic solutes to liquid metal environments can be used to control, sometimes over a wide range, the stress to induce catastrophic failure in polycrystalline metals under static loading conditions. Additions can be used either to enhance or inhibit embrittlement. Figs. 2(a) and 2(b).

With the exception of dilute (Hg-In) and (Hg-Tl) solutions, which will be discussed below, the influence of solute additions of less than ~10 a/o on $\sigma(1)$ is in proportion to their concentrations, C_S. This is an important observation because it indicates that, in most cases, neither solvent nor solute elements are preferentially adsorbed at the metal surface. If preferential adsorption were involved, then since additions of < 1 a/o solute to the environment would be sufficient to provide many monolayers of solute on the metal surface, $\sigma(1)$ would not be expected to vary significantly with C_S. That $\sigma(1)$ does vary with C_S indicates instead that a dynamic equilibrium exists between metallic surfaces and liquid metal solution environments.

In all embrittling environments, specimens failed either in < 1 sec or not in > 2000 sec. This is considered to indicate that failure under experimental conditions employed is controlled by the crack initiation process, and that the rate of arrival of the most active species at the crack tip is at all times sufficient to maintain the crack propagating in a brittle manner, even in intrinsically notch-insensitive solids such as pure aluminium or silver. Theoretical analyses [12, 13] indicate that such behaviour may be expected if the effective fracture surface energy, ϕ, is at all times equal to or less than the true surface free energy γ (or, for intercrystalline failure, $\phi \leq (2\gamma - \gamma_b)2$, where γ_b is the grain boundary energy [14]).

To examine the likelihood of this possibility, an estimate of the fracture surface energies of polycrystalline silver in mercury and gallium environments was made utilizing the criterion proposed recently by Smith and Barnby [13] and data from the present work and a concurrent investigation [6]. The Smith-Barnby criterion removes several objections to the earlier and widely-quoted Stroh criterion [12], and relates to the nucleation of a crack at an arbitrary angle to a group of one sign piled up against a stable obstacle. The criterion is

$$\tau_E = [G\pi\phi/2(1-\nu)d]^{1/2}[1/F(\theta)^{1/2}] \qquad (2)$$

where $$F(\theta) = (5 + 2\cos\theta - 3\cos^2\theta)/4 \qquad (3)$$

and τ_E is the effective shear stress acting on the dislocations, G is the shear modulus, ν is Poisson's ratio, d is the distance between the dislocation source and the obstacle, and θ is the angle between the slip plane and the fracture plane.

In this work, we have assumed that a crack is nucleated in a grain boundary lying perpendicular to the tensile axis by a dislocation pile-up on a slip plane lying at 45° to this axis ($\theta = 45°$). Then τ_E can be taken as $[(\sigma(1) - \sigma_0)/2]$, where σ_0 is the intercept at $d^{-1/2} = 0$ of a plot of the fracture stress of polycrystalline silver in mercury at room temperature versus $d^{-1/2}$. Taking G as $2{\cdot}92 \times 10^{11}$ dynes/cm² [15], ν as 0·37 [15], d as the grain diam., 0·15 mm, $\sigma(1)$ as 7·9 Kg/mm² (Fig. 3), and $\sigma_{0\,\text{Ag-Hg}}$ as 5·8 Kg/mm² [6], $\phi_{\text{Ag-Hg}}$ is computed to be $\simeq 270$ ergs/cm². A similar calculation for silver in liquid gallium, taking $\sigma(1)$ as 3·4 Kg/mm² and $\sigma_{0\,\text{Ag-Ga}}$ as 2·5 Kg/mm² [6], gives $\phi_{\text{Ag-Ga}} \simeq 50$ ergs/cm². These values appear to be sufficiently below the surface free energy of silver, $\gamma \simeq 1140$ ergs/cm² [16] or, assuming $\gamma_b = \gamma/3$, $(2\gamma - \gamma_b)/2 \simeq 950$ ergs/cm², to support the view that the failure of polycrystalline silver in mercury or gallium environments is crack-initiation controlled. Then, since the fracture behaviour of aluminium and cadmium in other embrittling environments is similar to that of silver in mercury or gallium, it may be inferred that failure in these systems also is crack-initiation controlled.

The influence of various mercury solutions on the dynamic fracture stress, σ_F, of polycrystalline zinc has been studied by Summ *et al.* [17], and they noted that σ_F at first decreased with solute concentration, and then, for the more highly soluble solutes cadmium, indium and thallium, increased. A similar variation in the values of $\sigma(1)$ for aluminium may be seen in Fig. 5. The cause of the reversal at higher solute concentrations is not known, but may be related to the fact that both aluminium and zinc show little affinity for either cadmium, indium or thallium, exhibiting extremely limited solid solubilities, and sometimes immiscibility in the liquid state, with these elements [10].

The observation that additions of < 3 a/o indium and < 8 a/o thallium do not influence the embrittling action of mercury environments on aluminium, Fig. 5, is of particular interest, since anomalous effects have also been noted in the thermopower [18-20] and Knight shift [21] behaviour of these solutions. To illustrate this point, the inset to Fig. 5 presents thermopower data from Cusak *et al.* [18] and Fielder [20] for (Hg-In), (Hg-Tl) and (Hg-Cd) solutions. Note that thermopower, S, first decreases with increasing solute concentration for both (Hg-In) and (Hg-Tl) solutions, before increasing in the conventional manner. (Hg-Cd) solutions, on the other hand, do not exhibit this anomalous decrease. Comparison of this data with the variation of $\sigma(1)$ with solute concentration, Fig. 5, reveals evident similarities, and suggests that the factor(s) causing anomalous thermopower and other physical property behaviour in dilute (Hg-In) and (Hg-Tl) solutions might also be responsible for the lack of activity of minor additions of indium and thallium in mercury environments as far as embrittlement phenomena are concerned.

A tentative explanation for such behaviour has been offered by Mott [22] in terms of the existence of a minimum in the density of states curve for mercury near to the Fermi energy level, E_F. Solute additions are considered to influence the position of E_F with respect to this minimum, and also to eventually blunt and cause the disappearance of the minimum. While Mott's hypothesis remains the subject of vigorous debate in the scientific literature, there seems little doubt that strong solvent-solute interactions do occur in (Hg-In) and (Hg-Tl) solutions, and that these serve in some way to reduce the surface activity of the solute species—perhaps by providing a solvation sheath of mercury atoms around them. The significance of the present observations is that they demonstrate that solvent-solute interactions can play an important role in determining the embrittlement behaviour of solids in liquid metal solutions.

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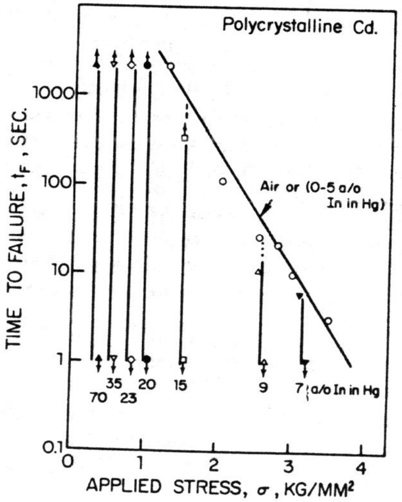

Fig. 1. Effects of applied stress and (Hg-In) environments on the time to failure of statically loaded polycrystalline cadmium at room temperature. (Grain diam. = 0·7-1·0 mm.) Note that for indium concentrations of more than ~7 a/o, severity of embrittlement increases with indium concentration.

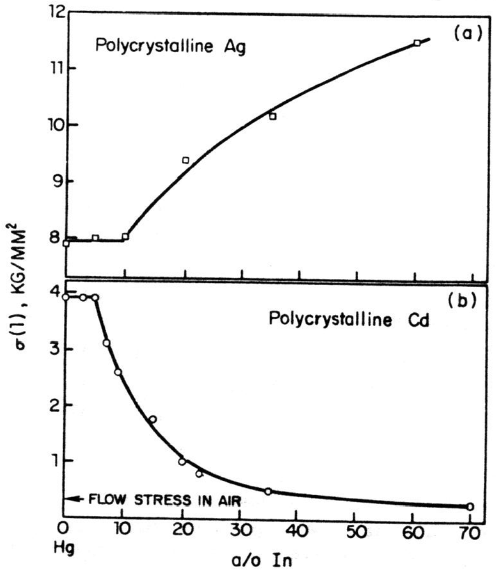

Fig. 2. Variation of stress to cause brittle failure in 1 sec., (1), with indium concentration of (Hg-In) environments for (a) polycrystalline silver (grain diam. = 0·15 mm), and (b) polycrystalline cadmium (grain diam. = 0·7-1·0 mm). Room temperature. Note opposite influences of indium concentration on severity of embrittlement for these two metals.

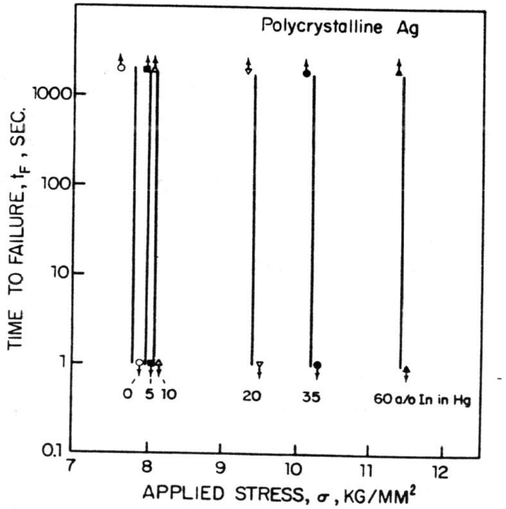

Fig. 3. Effects of applied stress and (Hg-In) environments on the time to failure of statically loaded polycrystalline silver at room temperature. (Grain diam. 0·15 mm.) Note that severity of embrittlement decreases with increasing indium content of the environment.

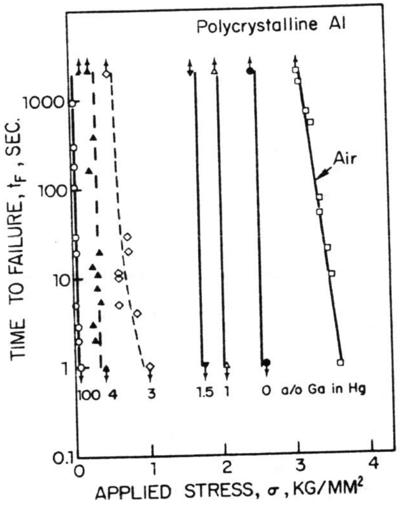

Fig. 4. Effects of applied stress and (Hg-Ga) environments on the time to failure of statically loaded polycrystalline aluminium at 30°C. (Grain diam. 0·7-1·0 mm.)

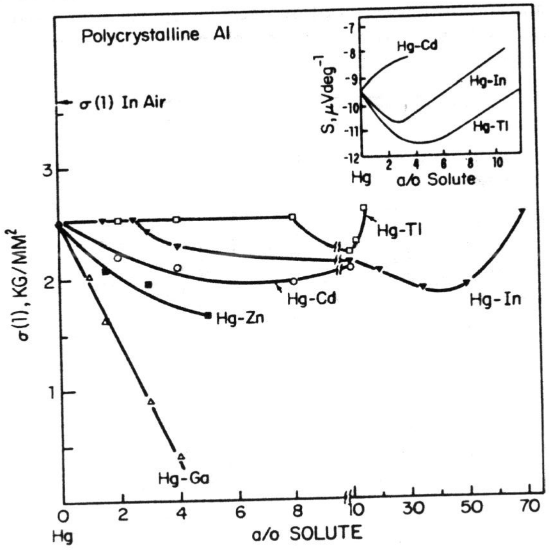

Fig. 5. Effect of solute concentration of mercury environment on the stress to produce failure in 1 sec in statically loaded polycrystalline aluminium. Grain diam. = 0·7-1·0 mm. Room temperature. Inset illustrates variation in absolute thermopower, *S*, for several mercury solutions. Data from refs. 18 and 20. Note anomalous behaviour of dilute (Hg-In) and (Hg-Tl) solutions in both thermopower and embrittlement studies.

Table 1

Material (purity)	*Heat-treatment*	*Av. grain diam.*	*Surface preparation prior to coating*
Al (99·999%)	550°C for 1 hr Air cool.	0·7-1 mm	Chem. pol. in 80% H_3PO_4-20% HNO_3 for 3-4 min at 70-90°C. Coat under conc. HF.
Cd (99·99%)	300°C for 1·5 hr Air cool.	0·7-1 mm	Chem. pol. in 1:1:1:: C_2H_5OH:HNO_3:H_2O_2 at 25°C.
Ag(99·9%)	900°C for 1 hr Air cool.	0·15 mm	Etch in HNO_3 immed. prior to coating.