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THE EFFECTS OF MICROSTRUCTURE ON CRACK INITIATION IN LIQUID-METAL ENVIRONMENTS

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Abstract—Liquid-metal-induced embrittlement under tensile test conditions is identified by the existence of a characteristic ductility trough. In this study, the effect of molten gallium on the behaviour of two brass alloys with different microstructures is studied. The role of plastic slip behaviour in the generation of high localized stresses and, consequently, on crack initiation is examined, Furthermore, the effects of various parameters such as strain rate, temperature and grain size on the degree of embrittlement are explained in terms of their effect on the dislocation mobility. © 1997 Published by Elsevier Science Ltd

Keywords: Cracks, liquid metal embrittlement, fractography.

1. INTRODUCTION

The liquid-metal-induced embrittlement (LMIE) literature frequently makes reference to the *specificity* of LMIE, i.e. the observation that certain liquid-metal–solid-metal couples are susceptible to embrittlement while others appear to be immune. While a number of theories have been developed to explain these observations [1, 2], all of the models developed to date have been unable to correctly predict embrittlement for all liquid-metal–solid-metal combinations. This, together with the fact that most of the specificity data arises from studies which have employed simple tensile testing techniques in which, at best, only a very narrow range of conditions are examined, have led many researchers to question the validity of specificity in general.

In a recent study by Fernandes and Jones [3], it was shown that specificity is not generally true in the case of the brass–gallium system, in spite of tensile results indicating the contrary. In this study, the results of the tensile tests carried out on the two different brasses will be re-examined and explained in terms of the effects of microstructure on crack initiation and, consequently, on the observation of embrittlement.

2. EXPERIMENTAL PROCEDURE

Tensile tests were used to study the embrittlement of two brass alloys by molten gallium ($T_m = 29.8\,^\circ C$). The alloys used were CZ106, a 70/30 alpha brass, and CZ109, a 60/40 alpha–beta brass. The microstructures of these alloys are shown in Figs 1 and 2. The alpha phase has a face-centred cubic (fcc) structure, while the beta phase has a body-centred cubic (bcc) structure. Both alloys were tested in the annealed condition, and various annealing times were used to obtain a range in grain size.

The tests were carried out on smooth, unnotched specimens with a gauge length of 30 mm and a diameter of 5 mm. In all cases, the specimens were polished to a 1 μm finish before testing. Specimens tested in gallium were heated to over 30 °C, and the gallium was applied to the centre of the gauge length. No problems were experienced with the wetting of the brass by the molten gallium. The tests were carried out at various temperatures, and in each case adequate time was allowed for temperature stabilization. The temperature was controlled to $\pm 2\,^\circ C$.

Various initial strain rates were used, and the specimens were tested to failure. The percentage

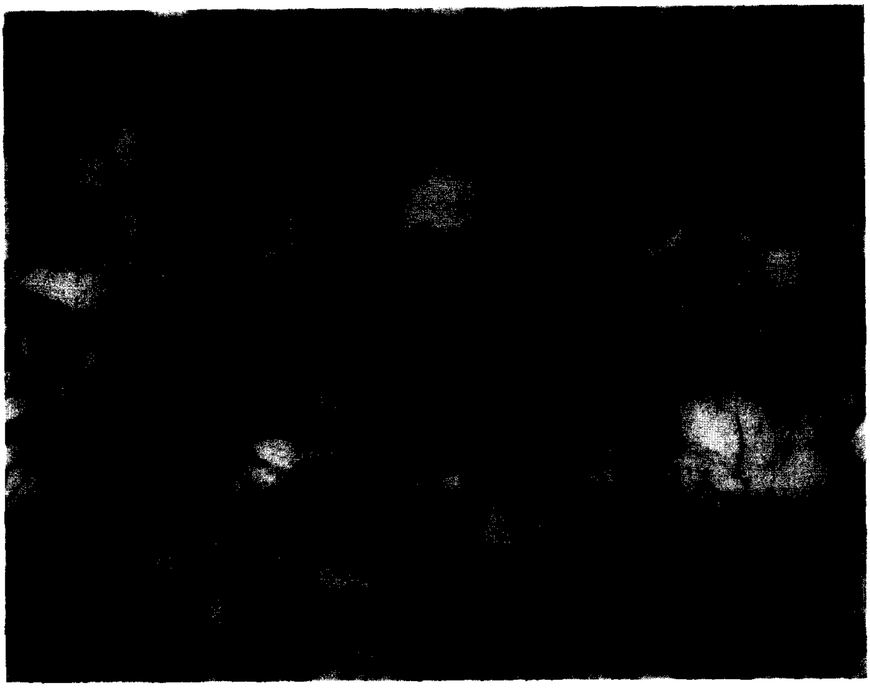

Fig. 1. Microstructure of CZ106, alpha brass (× 200).

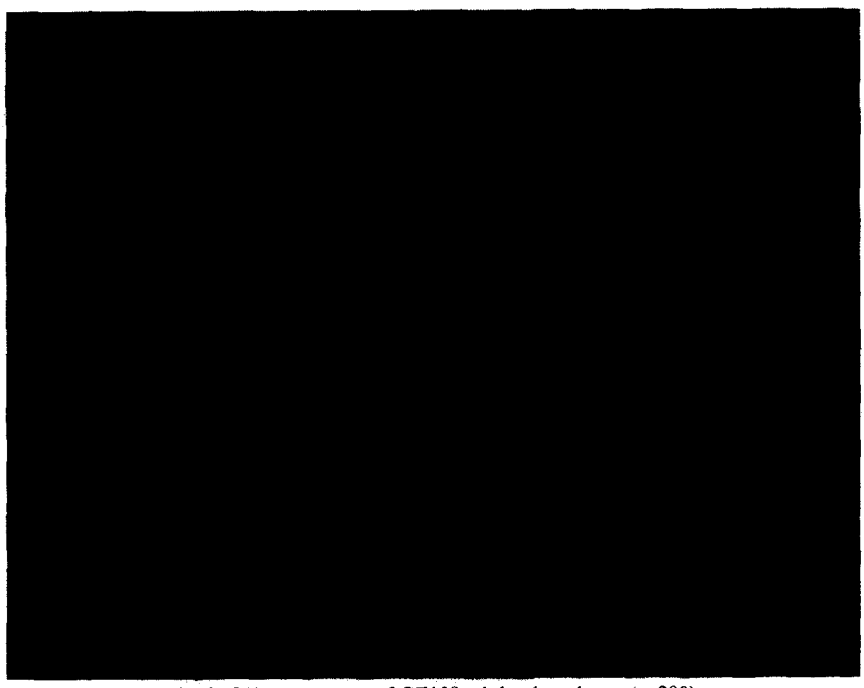

Fig. 2. Microstructure of CZ109, alpha–beta brass (× 200).

elongation, percentage reduction in cross-sectional area (%RA), and the true fracture stress were calculated in each case. The range of variables used were as follows.

(1) Grain size: 24 μm, 72 μm and 148 μm
(2) Temperature: 20–200 °C
(3) Strain rates: $3.33 \times 10^{-4}\,s^{-1}$, $3.33 \times 10^{-3}\,s^{-1}$, $3.33 \times 10^{-2}\,s^{-1}$

After completion of the tensile tests, all samples were examined in a scanning electron microscope (SEM). Attention was given to the fracture surfaces as well as to the surface of the specimen in the vicinity of the fracture.

3. RESULTS

3.1. *Tensile testing*

The results of the tests on CZ109 brass are shown in Fig. 3, where the %RA is plotted as a function of temperature for various initial strain rates. Similar results were obtained for the percentage elongation and true fracture stress. The specimens tested without gallium show a gradual decrease in %RA with increasing temperature. Furthermore, the %RA is independent of the strain rate. In the case of specimens tested with gallium, a significant decrease in %RA is observed over a finite temperature range. This is referred to as a *ductility trough*, and its occurrence in LMIE under tensile testing conditions is well documented [4]. Moreover, the severity of embrittlement, as measured by the "depth" of the ductility trough, as well as the temperature range over which embrittlement persists, i.e. the "width" of the ductility trough, increases with increased strain rate.

The effect of grain size on the degree of embrittlement is shown in Fig. 4 for an initial strain rate of $3.33 \times 10^{-3}\,s^{-1}$. As the grain size increases, the severity of embrittlement, as defined by the depth and width of the ductility trough, also increases. In the case of the specimens tested without gallium,

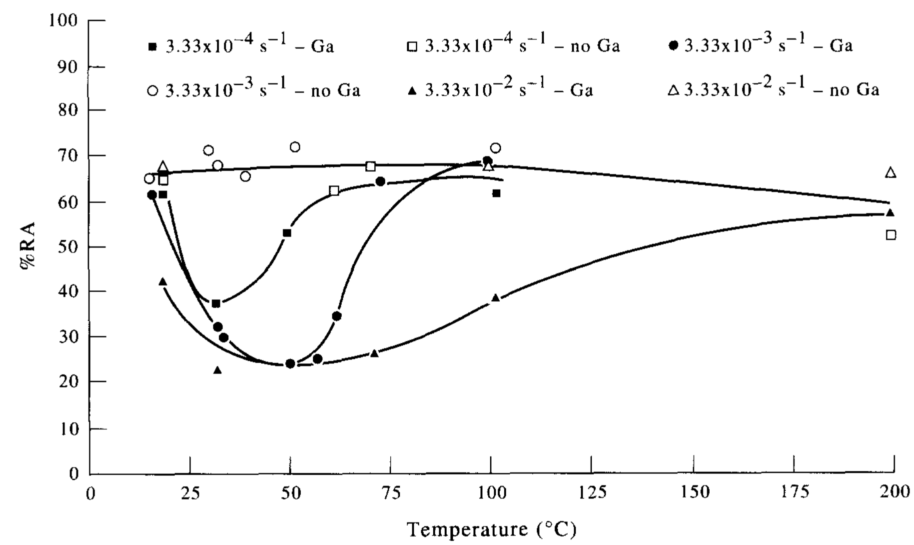

Fig. 3. Plot of %RA as a function of temperature at various initial strain rates for CZ109 brass.

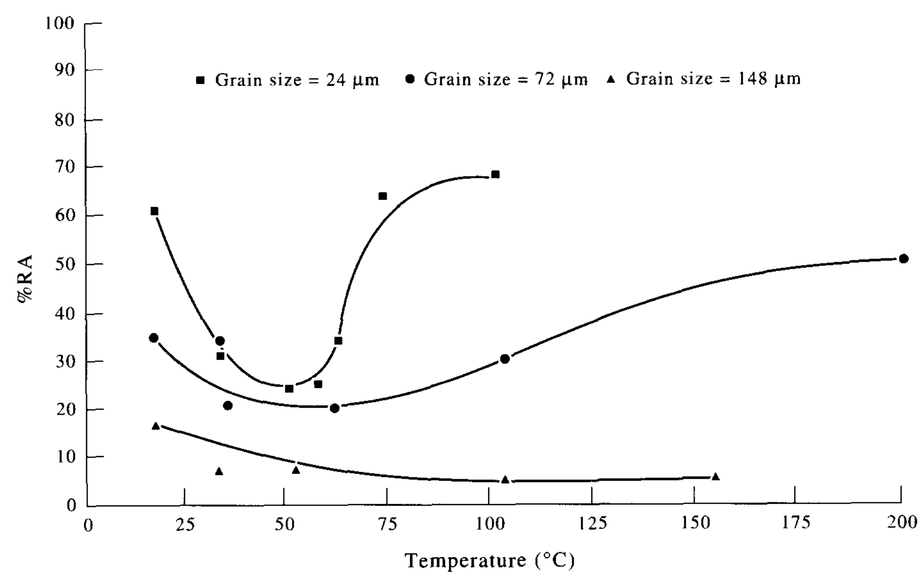

Fig. 4. Plot of %RA as a function of temperature for various grain sizes for CZ109 brass (initial strain rate: $3.33 \times 10^{-3}\,s^{-1}$).

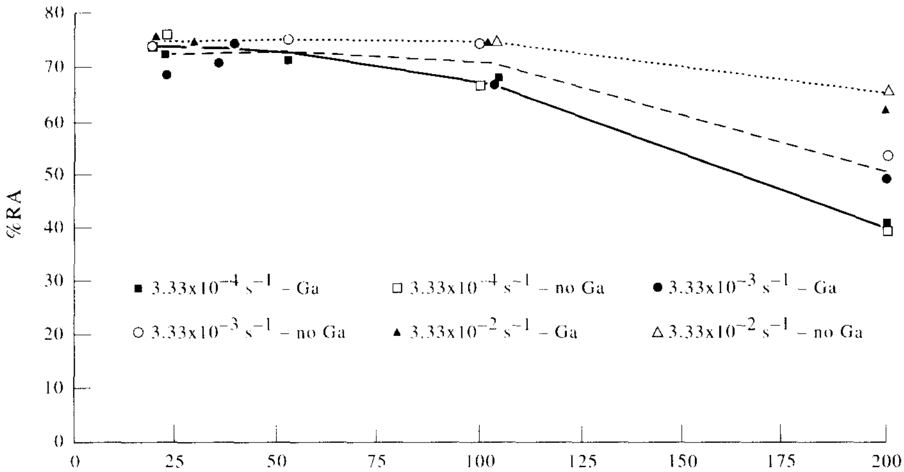

Fig. 5. Plot of %RA as a function of temperature at various initial strain rates for CZ106 brass.

the %RA decreases gradually as the temperature increases, and no significant grain size effect is observed.

The results of the tests on CZ106 brass are given in Fig. 5, where again the %RA is plotted as a function of temperature for various strain rates. In this case, the %RA decreases gradually with increasing temperature for specimens tested both with and without molten gallium. A noticeable strain rate dependence is observed at high temperatures, where the %RA decreases as the strain rate decreases. However, the ductility trough observed in the case of the CZ109 brass is absent, and there is no evidence of embrittlement. This was confirmed by SEM studies of all the specimens tested, and failure was in all cases by ductile microvoid coalescence. Similarly, the results of the tests for the various grain sizes show that the %RA decreases gradually as the temperature increases with no significant grain size effect (Fig. 6). Once again, no ductility trough is observed.

The failure to detect embrittlement under any of the test conditions studied in the CZ106 brass using smooth tensile specimens prompted the use of notched specimens. A sharp, shallow notch approximately 0.25 mm in depth was made at the centre of the gauge length of two CZ106 brass specimens, and these were subsequently tested with and without gallium. In the latter, no significant difference was observed in the load–elongation plot, and final failure was ductile. This can be expected since alpha brass is not notch-sensitive. However, in the case of the specimen tested in gallium, significant embrittlement was detected. This was evident from the reduced plastic defor-

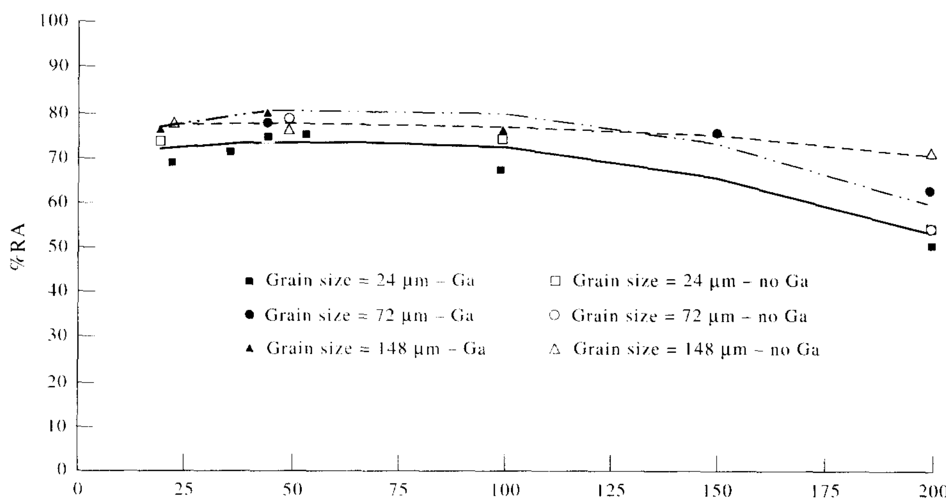

Fig. 6. Plot of %RA as a function of temperature for various grain sizes for CZ106 brass (initial strain rate: 3.33×10^{-3} s^{-1}).

Fig. 7. Brittle cleavage fracture in embrittled samples of CZ109 brass.

mation accompanying failure, and the large decrease in the true fracture stress from 950 MPa for the specimen tested without gallium to 300 MPa for the specimen tested in gallium.

3.2. *SEM analysis*

Examination of the fracture surfaces of CZ109 brass by SEM showed that, in the case of specimens tested in gallium and within the conditions defined by the ductility trough, fracture was by brittle cleavage (Fig. 7). Since only a small amount of gallium was applied to the surface of the specimens before testing, there were specimens in which the gallium became depleted during brittle crack growth. In such cases, a transition from the gallium-induced brittle cleavage to ductile microvoid coalescence normally expected for this material was clearly evident on the fracture surface (Fig. 8). Those specimens tested without gallium, and those tested with gallium but under conditions outside that defined by the ductility trough, failed by ductile microvoid coalescence, and exhibited a classical cup-cone-type failure. The surfaces of both brittle and ductile specimens showed that deformation at and near the fracture surface was predominantly by planar glide (Fig. 9). Moreover, numerous surface cracks were evident in the stressed region, these being in most cases grain boundary cracks (Fig. 10). The number and size of the grain boundary cracks generally increased as the grain size increased. However, no quantifiable correlation was found between the number and size of the cracks and the degree of embrittlement.

SEM examination of the fracture surfaces of all smooth specimens of CZ106 brass indicated that failure was by ductile microvoid coalescence. This was observed on specimens tested both with and without gallium, and over the entire grain size range considered. These results are consistent with the %RA results given in Figs 5 and 6. In contrast, the notched specimen tested in gallium showed clear evidence of brittle intergranular cracking (Fig. 11). The deformation in the necked region of the gauge length showed extensive surface rumpling and clear evidence of cross slip (Fig. 12). Moreover, the grain boundary cracks observed in the CZ109 brass were completely absent in the case of the CZ106 alloy.

4. DISCUSSION

The results of the tensile tests carried out on smooth specimens suggest that CZ106 alpha brass is immune to embrittlement by molten gallium, while CZ109 alpha–beta brass is susceptible to it.

Fig. 8. Transition between liquid-metal-induced cleavage cracking and ductile microvoid coalescence.

This is an example of the type of observation referred to in the literature as specificity. However, the result of the test carried out on the notched alpha brass clearly indicates that under certain conditions severe embrittlement of this material can occur. Similar observations have been made on the same material using precracked fracture mechanics type specimens [5]. The effect of the notch in the alpha brass is therefore to act as a stress concentration site, and to increase the localized stresses to a level at which brittle cracking is favoured over plastic deformation.

During plastic deformation, movement of dislocation occurs along favourably orientated planes. If dislocation motion is impeded, say by a grain boundary, kink or twin band, or second-phase particle; the resulting dislocation pile-up leads to the formation of a stress concentration at the

Fig. 9. Evidence of planar glide on the surface of CZ109 brass.

Fig. 10. Grain boundary cracking on the surface of CZ109 brass.

point where the leading dislocation is obstructed. In polycrystalline materials, these localized stresses can be relieved in a number of ways, namely by activating dislocation sources in neighbouring grains, by dislocation climb, or by crack nucleation. The latter is favoured only when dislocation climb or cross slip is inhibited, or when dislocation sources in neighbouring grains are locked.

The ease with which cross-slip occurs is related to the stacking fault energy (SFE). This, in turn, defines the distance between partial dislocations in a stacking fault. The higher the SFE, the closer the partial dislocations remain, and, therefore, the easier it is for cross-slip to occur. Cross-slip acts to relieve the stresses due to dislocation pile-ups, and hence inhibits crack nucleation. In the case of

Fig. 11. Fracture surface of the notched CZ106 brass specimen tested in gallium, showing severe brittle intergranular cracking.

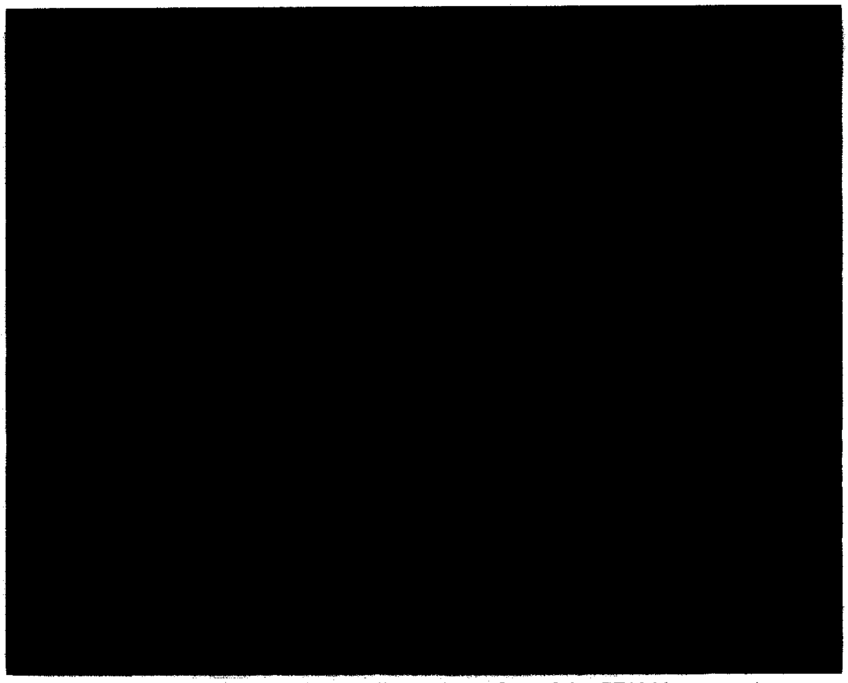

Fig. 12. Surface rumpling and cross-slip on the surface of the CZ106 brass specimens.

the CZ106 alpha brass, the wavy glide observed on the specimen surface is clear evidence that cross-slip does occur. The localized stresses created at dislocation pile-ups are relieved by dislocation climb, and, therefore, do not increase to levels sufficient to cause crack initiation. In contrast to the alpha brass, the slip behaviour of the CZ109 alpha–beta brass is found to be predominantly by planar glide with little evidence of cross-slip. The dislocation pile-ups under such conditions can be expected to result in higher stresses, and hence facilitate crack initiation. The effect of cross-slip on crack initiation in liquid metals has been previously considered by Stoloff *et al.* [6] and Johnston *et al.* [7]. These researchers studied the behaviour of various copper-based solid solution alloys in liquid mercury, and found that the degree of embrittlement is linearly related to the SFE.

Note that numerous workers have considered the effects of slip behaviour on the degree of embrittlement in liquid metals. Shea and Stoloff [8] considered the behaviour of beta brass alloyed with nickel and manganese in various liquid-metal solutions. Nickel is known to increase the critical temperature for long-range order in brass, and, therefore, increases the ease with which cross-slip occurs. Manganese, however, has the opposite effect. They found that manganese increases the severity of embrittlement (increases the width of the ductility trough), and changes the slip behaviour from wavy glide to planar slip. Hayden and Floreen [9] studied the effects of alloying iron with nickel, and found that additions of 7–8% nickel have no effect on the properties of iron in liquid mercury compared to that of iron in air. Additions of more than 8% nickel result in the transformation of ferrite to martensite, and brought about the onset of embrittlement. This was coincident with an increase in the heterogeneity of slip and the formation of high stress concentrations at dislocation pile-ups.

The effects of microstructure on the flow behaviour of solid metals are also known to affect LMIE. Nichols and Rostoker [10] compared the behaviour of chill cast and wrought copper in molten bismuth, and found the latter to be more susceptible to LMIE. This was explained by considering the orientation differences between neighbouring grains. In the chill cast material, the orientation differences in the columnar grain structure are likely to be small, thus making grain boundaries inadequate barriers to dislocation motion. A similar behaviour can be expected from cold worked microstructures where the texture is orientated in the direction of working [10]. The effect of second-phase particles on embrittlement has also been considered. Lynch [11, 12] and Reynolds and Stoner [13] found that precipitate-hardened aluminium alloys heat treated to form a fine, homogeneous distribution of precipitates are less susceptible to LMIE by mercury than those with a coarser precipitate distribution. This was attributed to strain localization and the formation of stress concentrations in the latter condition.

The degree of cross-slip depends on the ease with which dislocation climb occurs. This, in turn, depends on such factors as temperature and strain rate. At higher temperatures, the rate of dislocation climb increases, and the stresses generated at dislocation pile-ups are rapidly relieved. It is therefore feasible to expect that there exists a temperature above which sufficient stress relieving by cross-slip occurs so that crack nucleation is effectively suppressed. Below this temperature, however, the rate of dislocation climb is too low, and stresses can increase to a level at which crack initiation can occur. It appears that in a liquid-metal environment the temperature at which this transition from crack initiation to cross-slip occurs is the brittle-to-ductile transition temperature. As such, the width of the ductility trough is determined by the melting temperature of the low melting point metal at the lower temperature end, and the cross-slip–crack initiation transition temperature at the higher temperature end.

Previous work on LMIE offers support to the above hypothesis. Thus, Perovic *et al.* [14] studied the embrittlement of aluminium alloys by molten bismuth, and found that, at temperatures within the ductility trough, grain boundary sliding and grain boundary cavitation occurs, and embrittlement was observed. At higher temperatures, grain boundary migration inhibits the formation of cavities, and, although grain boundary sliding occurs, no embrittlement is observed. Similarly, Wolley and Fox [15] found that the brittle-to-ductile transition temperature for 70/30 alpha brass coincides with the onset of rapid recrystallization and grain boundary migration. Shea and Stoloff [8] used alloying additions to decrease the ease with which cross-slip occurs in the solid metal, and found that the transition temperature in this case increases significantly.

Since dislocation climb is a time-dependent process, the brittle-to-ductile transition temperature can be expected to depend on the strain rate. At high strain rates, less time is available for effective stress relieving through dislocation climb, and hence crack initiation will be favoured. The brittle-to-ductile transition temperature will therefore be moved to higher temperatures where the dislocation climb is faster. This hypothesis is consistent with the results of the tensile tests carried out at different strain rates on the CZ109 brass (Fig. 3), and with previously published literature [2, 14]. Old and Trevena [16, 17] also studied the embrittlement of polycrystaline zinc by various liquid metals, and found that, by controlling the strain rate, the brittle-to-ductile transition temperature could be reduced so as to restrict the ductility trough temperature range to a few degrees. The temperature for the onset of embrittlement, however, was independent of the strain rate.

Finally, the magnitude of the stress concentration at a dislocation pile-up depends on the length of the pile-up, which, in turn, depends on the maximum length of the slip plane. To a first approximation, this is equal to the grain size of the material, and, as such, grain size is expected to affect the severity of embrittlement observed in LMIE. This again is consistent with the results of the effects of grain size on the degree of embrittlement in the case of CZ109 brass. As the grain size increases, the severity of embrittlement increases significantly, as shown in Fig. 4. Similar results have also been reported by other researchers [18–20]. Nichols and Rostoker [18] tested fcc 70/30 alpha brass in mercury and found that this material exhibits a brittle-to-ductile transition temperature similar to that normally observed in bcc materials. Furthermore, it was found that the transition temperature varied with grain size according to a relation based on a dislocation model for crack nucleation proposed by Stroh [21] for bcc materials.

5. SUMMARY

The magnitude of the localized stresses formed at dislocation pile-ups depends on the type of slip behaviour. Under conditions of planar slip, the stresses generated are sufficiently high to promote brittle crack initiation in normally ductile materials when stressed—whilst in intimate contact with a molten metal. These conditions are satisfied in the case of CZ109 brass. The effect of temperature, strain rate and grain size on the degree of embrittlement can be explained in terms of the effect of these parameters on dislocation mobility. The wavy slip behaviour observed in the case of the CZ106 brass effectively relieves the stresses at dislocation pile-ups, and inhibits crack nucleation. Plastic deformation is therefore favoured and no embrittlement is observed. However, if sufficiently high localized stresses can be generated by other means, e.g. by the introduction of a notch, while inhibiting plastic deformation, even this material is found to fail by LMIE.

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