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Materials Report 102

THE MECHANISM OF
LIQUID-METAL EMBRITTLEMENT-CRACK
GROWTH IN ALUMINIUM SINGLE CRYSTALS
AND OTHER METALS IN
LIQUID-METAL ENVIRONMENTS

S. P. LYNCH

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by

10 S. P. LYNCH

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SUMMARY

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1. INTRODUCTION

The fracture behaviour of metals stressed in certain liquid-metal environments differs markedly from their behaviour in 'inert' environments (usually air). The reduction in ductility and fracture stress of specimens tested in liquid-metal environments (Fig. 1)⁽¹⁾, and sub-critical crack growth induced by liquid metals in loaded pre-cracked specimens, is generally known as liquid-metal embrittlement (LME). All degrees of embrittlement are observed (Fig. 1)—the severity of embrittlement depends on the composition of the liquid metal, composition and microstructure (and strength) of the solid metal, temperature and strain-rate. Embrittlement often occurs only over a certain range of temperature and a transition from ductile to brittle behaviour may occur with decreasing temperature (Fig. 2)⁽²⁾. Embrittlement can occur below the melting point of an embrittling metal, due to surface diffusion of embrittling atoms to crack tips⁽³⁾, and it can also occur in the presence of the vapour phase.

Fracture in liquid-metal environments is not only accompanied by less plastic deformation than fracture in air, but fracture paths and fracture modes may also depend on the environment. For example, Westwood *et al.*⁽⁴⁾ reported that aluminium single crystals failed by cleavage in liquid gallium and by ductile shear in air. Other examples are given in reviews of LME^(1, 5-7). While fracture characteristics are markedly influenced by liquid-metal environments, yield stress and strain-hardening rate are not significantly affected (Fig. 1).

The mechanism generally proposed for LME is essentially that chemisorption of liquid-metal atoms at crack tips, and other regions of stress concentration, lowers the tensile fracture stress, σ , of interatomic bonds sufficiently to cause rupture of bonds by a low applied stress; repeated adsorption and tensile separation of bonds A-A₀, A-A₁, etc. produces crack growth (Fig. 3)^(1, 4-7). It has been assumed that the shear stress, τ , required to move dislocations is unaffected by chemisorption^(1, 4-7). Dissolution and diffusion processes are not considered necessary for most cases of LME since mutual solubilities of solid and liquid metals are often negligible and suitably pre-stressed specimens will fail instantaneously on 'wetting' with an appropriate liquid metal. (In a few cases, diffusion of embrittling metal atoms into specimens along grain boundaries is important, but such cases are not considered in the present studies.)

In the present work, a new explanation for LME, involving adsorption-activated nucleation of dislocations, is proposed on the basis of metallographic and fractographic studies. The results are also considered to be relevant to others cases of environmentally-induced fracture and to ductile and brittle behaviour in general.

2. EXPERIMENTAL

Materials tested were aluminium and zinc single crystals, and polycrystalline aluminium, cadmium and tin. Aluminium, zinc and cadmium were high purity; tin was commercial purity and contained large second-phase particles. Notched specimens, in the annealed condition, were tested in cantilever bending (Fig. 4) and in tension. Tests were performed in air, liquid gallium (melts at $\sim 30^\circ\text{C}$), liquid mercury (melts at $\sim -39^\circ\text{C}$) and a liquid alloy (44.7% Bi, 22.6% Pb, 19.1% In, 8.3% Sn, 5.3% Cd—wt.-%) (melts at $\sim 47^\circ\text{C}$). Tests were performed at $\sim 20^\circ\text{C}$ in air and mercury, $\sim 35^\circ\text{C}$ in gallium, and $\sim 50^\circ\text{C}$ in the alloy. (The small differences in these testing temperatures should not, in themselves, significantly affect fracture behaviour.) Specimens for LME studies were notched, using a fine saw, in the presence of liquid metal to ensure wetting at the tips of notches, and then immediately tested. There was insufficient time for significant diffusion of liquid metal atoms into solids.

After fracture, liquid metal was removed immediately from fracture surfaces by a jet of hot water; fractures were cleaned further by stripping plastic replicas from the surface and, for aluminium specimens fractured in liquid alloy, also by immersion in concentrated nitric acid for 1 minute. Polished surfaces were also 'wet' with liquid metal, and then the liquid metal

removed, to demonstrate that this procedure did not affect surface topography. Standard metallographic and fractographic techniques were used for studying specimens.

3. RESULTS

3.1 Aluminium Single Crystals

In the liquid alloy†, crack initiation occurred from the root of the notch after bending only a few degrees; further bending (i.e. increasing crack-opening displacement, COD) produced crack growth and complete fracture occurred after bending $\sim 20\text{--}30^\circ$. Rates of COD were controlled to give crack-growth rates ~ 1 mm/sec; crack growth stopped if the COD was kept constant. In air, bending (up to 90°) produced blunting at the notch root without initiation or growth of cracks. Tensile tests of specimens in liquid alloy resulted in very rapid unstable fracture with near-zero reduction of area. Fracture in air, in tension, occurred by ductile shear—specimens elongated considerably and necked down to a chisel edge (reduction of area $\sim 100\%$).

Fracture surfaces produced by LME were macroscopically flat except for steps (river lines) approximately parallel to the direction of crack growth (Figs 5, 6). These steps resulted mainly from coalescence of adjacent cracks nucleated at different levels at the root of the notch. X-ray back-reflection studies and the configuration of slip traces on fracture surfaces (Fig. 6) showed that, *macroscopically*, fractures were approximately parallel to $\{100\}$ planes, even if these planes were at angles considerably less than 90° to the axes of specimens. The orientation of specimens described in detail below was such that $\{100\}$ planes and fracture were normal to the specimen axis and crack growth was approximately in a $\langle 110 \rangle$ direction (Fig. 4).

These results are consistent with previous observations⁽⁴⁾ of LME in aluminium single crystals; however, in this previous study, no detailed metallography or fractography was reported. In the present work, taper sections showed that, on a *microscopic* scale, fracture surfaces were quite rough (Fig. 7) and transmission-electron microscopy of secondary-carbon replicas revealed that both fracture surfaces were completely covered by shallow, slightly elongated dimples—slip traces were also evident (Figs 8–10)††. (The dimples are similar to those often observed after fracture of high-strength aluminium alloys in air (Fig. 9, inset).) Wetting flat electropolished aluminium surfaces with liquid alloy (oxide films were removed in NaOH solution), and then removing liquid alloy, produced surfaces with the same (slightly pitted) appearance as those just immersed in NaOH solution (Fig. 10, inset). Thus, it is concluded that fracture-surface topography is not significantly affected by the presence of liquid alloy after fracture (or by its removal) and that the dimples observed on fracture surfaces are produced by the fracture process.

Polishing the sides of specimens partially cracked in liquid alloy, and then increasing the crack-opening displacement to produce an increment of crack growth in liquid alloy, showed that considerable slip emanated from the crack-tip region (at $\sim 50\text{--}60^\circ$ to the sides of the crack) during crack growth; except for the first $10\text{--}20\ \mu\text{m}$, little slip occurred *directly* ahead of the crack (Fig. 11). Crack-growth increments were about three times crack-opening displacements. Since crack fronts were fairly straight and fracture surfaces appeared the same at the edges and the centre of specimens, slip at the surface is probably reasonably indicative of the deformation occurring in the centre of specimens during crack growth. (Some slip at the surface is probably associated with through-the-thickness flow).

After liquid alloy had been removed from the crack, the specimen was re-polished and then the crack-opening displacement increased in air (at 20°C , any remaining traces of liquid alloy will be solid.) This procedure resulted mainly in blunting of the crack tip (without appreciable crack growth) with considerable slip ahead of and around the crack tip (Figs 12, 13).

† Liquid gallium and liquid mercury produced similar results—fractures produced in liquid alloy were studied in detail since use of the liquid alloy eased experimental problems.

†† Fracture surfaces were examined mainly in the central regions of the fracture surface; regions near the back surface (Fig. 5) were considerably rougher. Mating areas of opposing fracture surfaces were not examined—Beacham⁽⁸⁾ has shown that dimples are not necessarily exact mirror images on opposing fracture surfaces.

3.2 Polycrystalline Aluminium

Crack growth in polycrystalline aluminium in liquid alloy was intercrystalline but in other respects was very similar to crack growth in the single crystals. Extensive slip originated from the crack-tip region during crack growth (Fig. 14) and shallow dimples and slip traces were observed on fracture surfaces (Fig. 14, inset). Removing liquid alloy and stressing in air at 20°C produced somewhat different behaviour from that in the single crystals. Intercrystalline cracks continued to grow, with little crack-tip blunting, for some distance before extensive blunting occurred. This effect was not studied in detail but was probably associated with diffusion of 'embrittling' atoms along grain boundaries ahead of the crack tip, from the liquid-metal environment; such diffusion is probably significant only when the crack is stationary for some time in the presence of liquid metal.

3.3 Polycrystalline Cadmium

The behaviour of cadmium was similar to that of aluminium in that, in air, specimens tested in tension failed by ductile shear with ~100% reduction of area while, in liquid gallium, the reduction of area was near zero. Crack growth in cadmium polycrystals was mainly transcrystalline (predominantly along basal planes); a small amount of cracking along other planes and along grain boundaries also occurred. Compared with aluminium, only a small amount of deformation accompanying crack growth was observed on the polished sides of specimens; however, as with aluminium specimens, extensive deformation and crack-tip blunting occurred in air (Fig. 15). (Similar observations have been reported previously⁽⁷⁾.)

Optical and scanning-electron microscopy showed 'flat' transcrystalline (cleavage) facets (Figs 16, 17). Replica techniques, however, revealed shallow, elongated dimples on many of these 'flat' facets (Figs 18–20), although some regions still appeared to be fairly flat except for river lines (Figs 20, 21). Wetting polished cadmium surfaces with liquid gallium (oxide films were removed by dilute HCl), and then removing the gallium produced surfaces with the same (etched) appearance as those immersed only in HCl. The presence of flat areas on replicas of fracture surfaces is also a good indication that gallium does not affect surface topography—etching effects, such as occur in HCl, are uniformly distributed. The perturbations on fracture surfaces around large second-phase particles also suggested that fracture-surface details were 'real' and that dimples were produced during the process of fracture.

3.4 Polycrystalline Tin

Fracture of tin in air occurred in a manner similar to aluminium and cadmium, i.e. tensile specimens elongated considerably and necked down to a chisel edge. When deformation was highly constrained, as in specimens consisting of a thin (~500 μm) sheet of tin sandwiched between, and bonded to, harder regions, fracture (of tin) in air occurred by coalescence of microvoids and very large, deep dimples were observed on fracture surfaces (Fig. 22). Fracture of tin in liquid gallium (reduction of area is near zero in tension tests) was generally intercrystalline (Fig. 22) and very little slip was observed adjacent to cracks, on the polished sides of specimens, after fracture. Replicas revealed small, shallow dimples on most grain facets (Figs 23–25). As with aluminium and cadmium specimens, observations indicated that fracture-surface topography was not significantly affected by the presence of liquid gallium after fracture or by its removal.

3.5 Zinc Single Crystals

Fracture of zinc single crystals in *both* air and liquid gallium produced cleavage fractures parallel to basal planes with very little deformation apparently associated with fracture. There were 'suggestions' of extremely shallow dimples on fracture surfaces produced in air (the resolution of replicas was insufficient to determine their presence with certainty); LME fracture surfaces appeared somewhat flatter than those produced in air (Fig. 26).

4. DISCUSSION

4.1 Mechanism of LME

LME has previously been considered^(4, 5) as a special case of a general criterion⁽⁹⁾ that the σ/τ ratio governs ductile versus brittle behaviour. It has been assumed that chemisorption of liquid-metal atoms lowers the tensile strength, σ , of atomic bonds at crack tips (but does not significantly affect the shear stress, τ , required to move dislocations) so that crack growth occurs by repeated adsorption and breaking of bonds at low applied stress (Fig. 3). It is implicit that if some dislocations do move in the stress fields of such cracks, then these dislocations do not generally intersect crack tips or cause blunting at crack tips. Fracture surfaces produced by such a 'bond-rupture' process would be flat and very little deformation would be associated with fracture.

The present studies of LME in aluminium single crystals and polycrystals show slip densities and distributions which suggest that dislocations do interest crack tips. Moreover, dimpled fracture surfaces (aluminium, cadmium and tin specimens) indicate that crack growth involves nucleation of voids ahead of crack tips followed by necking of material between cracks and voids until coalescence occurs; this process involves nucleation and/or egress of dislocations at tips of cracks (and voids) producing crack growth, with general dislocation activity around cracks resulting in some blunting at crack tips. (Voids nucleate by fracture of brittle second-phase particles or by separation of particle/matrix interfaces as a result of plastic strain ahead of cracks.) Dimples on LME fractures were often elongated in the direction of crack growth on both fracture surfaces, indicating that cracks grew preferentially towards voids.

These observations suggest that crack growth in embrittling liquid-metal environments occurs by alternate shear on slip planes intersecting crack tips with sufficient general strain accompanying crack growth to produce some blunting at crack tips and growth of microvoids ahead of cracks. In aluminium single crystals, crack growth involving alternate shear on $\{111\}$ slip planes would produce fracture surfaces macroscopically parallel to $\{100\}$ planes (Fig. 27). Other workers⁽¹⁰⁻¹²⁾ have also proposed that, under certain conditions, cracks can grow by alternate shear with the production of cleavage-like $\{100\}$ fracture surfaces. In cadmium (HCP structure), alternate shear on pyramidal planes would produce fracture surfaces parallel to basal planes. In the case of intercrystalline fractures, details of the slip processes would depend on the orientation of adjacent grains. Crack growth by alternate shear at crack tips with *insufficient* general strain to produce voids ahead of cracks would produce flat fracture surfaces; fracture of zinc single crystals, and 'flat' areas of cadmium and tin fractures could have resulted from such a process. Alternatively, these flat areas may be regions where dimples are too small and/or too shallow to be resolved—the formation of dimples below the limit of resolution of replicas is quite probable. Thus, it is concluded that fracture in embrittling liquid-metal environments generally occurs by plastic flow (shear movement of atoms) rather than by tensile separation of atoms at crack tips.

Fracture in embrittling liquid-metal environments (by plastic flow) can be explained on the basis that chemisorption of liquid metal atoms facilitates nucleation (and/or egress) of dislocations at crack tips. Such a process is consistent with theoretical considerations of the effect of chemisorption on metal surfaces, would not influence 'bulk' flow characteristics, but would produce sub-critical crack growth and fractures with reduced ductility; these aspects are discussed in detail below.

4.2 Adsorption Activation of Dislocations

There is evidence⁽¹³⁾ that since atoms at surfaces (in vacuum) have fewer neighbours than atoms in the interior, the lattice spacings in the first few atomic layers differ from those in the interior (Fig. 28(a)). In addition, the strength of bonds between surface atoms may be stronger than those in the interior.⁽¹⁴⁾ Such surface-lattice perturbations should hinder the nucleation and egress of dislocations at surfaces since dislocations moving in the first few layers would be associated with larger-than-normal lattice distortions⁽¹⁵⁾ and stronger surface bonds would be more difficult to shear. Since chemisorption of liquid-metal atoms at surfaces effectively increases the number of neighbours around surface atoms, 'surface-lattice distortion' (and bond strength of surface atoms) should be decreased⁽¹⁴⁾ (Fig. 28(b)) and, hence, dislocation nucleation and egress

facilitated in liquid-metal environments. (The resistance to shear of liquid-metal atoms themselves will be negligible.)

An adsorption-induced reduction in 'surface-lattice distortion' could facilitate (a) nucleation of dislocations from surface (crack-tip) sources, (b) movement of screw dislocations intersecting surfaces, and (c) egress of dislocations at surfaces and, hence, operation of near-surface dislocation sources. Crack growth probably mainly occurs by nucleation (and subsequent movement) of dislocations from surface sources at crack tips—near-surface sources and screw dislocations would probably not always be present on planes intersecting crack tips.

The high concentration of mobile conduction electrons in metals† screens out any influence of adsorbed species within a few atomic diameters of the surface so that adsorbates should not affect the stress required to move dislocations on slip planes **not** intersecting surfaces (crack tips). Thus, for oxide-free metals, the volume of material affected by adsorption-activated dislocation movement should generally be very small and, hence, it is not surprising that yield stresses and strain-hardening rates of specimens with small surface-to-volume ratios are the same in liquid-metal environments as in air. The flow characteristics of single crystals are sometimes affected by surface conditions, (the size of crystals, their orientation, strain rate, and other factors determine the importance of surfaces^(16, 18) and hence chemisorption could affect their flow behaviour in some cases. However, wetting surfaces with liquid metal would not only produce chemisorption but would also involve removal of oxide films and, if time of pre-exposure is sufficient, diffusion of atoms into crystals; the latter two processes are known to influence plastic flow of single crystals and, hence, results of such experiments would be difficult to interpret. Environmentally—induced reductions in flow stress, creep strength, hardness, etc. ('Rebinder effects') have been observed in other environments^(16, 18) but can usually (but not always?^(19, 20)) be attributed to effects other than chemisorption on clean metal surfaces⁽¹⁶⁾. Rapid crack growth (by shear) induced by liquid-metal environments, however, can only be attributed to an effect of chemisorption on dislocation activity.

Adsorption-activated dislocation nucleation/movement on slip planes intersecting crack tips would produce sub-critical crack growth (by shear) and also result in fractures with reduced ductility (less crack-tip blunting). Extensive blunting at tips of cracks in specimens below general yield requires a general strain in the plastic zone ahead of cracks, and hence necessitates slip on at least five independent systems which freely interpenetrate and cross-slip⁽²¹⁾; crack growth by alternate shear requires slip on only two slip planes intersecting crack tips. The balance between crack growth and crack-tip blunting (both relax elastic strain energy around cracks) should therefore be determined by the relative proportions of slip on planes intersecting crack tips compared to 'general' slip ahead of cracks; larger proportions of the former, which is promoted by chemisorption, favour crack growth. In other words, in embrittling liquid-metal environments, dislocations on planes intersecting crack tips are activated at lower stresses than in air (and produce crack growth), dislocations on other planes are not activated to the same extent at these lower stresses, and only a small amount of blunting occurs at crack tips (Fig. 11). In air (for ductile materials), considerable dislocation activity occurs on many slip planes around cracks at about the same stress so that extensive blunting occurs at crack tips (Fig. 12).

Crack initiation in liquid-metal environments at lower stresses (and strains) than in air can also be explained by adsorption-activation of dislocations. Slip on planes intersecting smooth surfaces will produce steps and notches which will behave similarly to crack tips. In air, sharper-than-average notches will blunt during stressing, producing local work-hardening beneath them, so that surface slip becomes fairly evenly distributed over the surface. In liquid-metal environments, a sharper-than-average notch will deepen by alternate shear and initiate

† Chemisorption at surfaces of non-metals, where there is a much lower concentration and mobility of charge carriers than in metals, can affect general dislocation activity up to several μm from surfaces and therefore often affects flow behaviour as well as fracture.⁽¹⁶⁾ Although metals and non-metals differ in this way, environmentally induced crack growth in both could involve adsorption-activated dislocation nucleation at crack tips—slow crack growth in soda-lime glass in non-corrosive environments has been attributed to adsorption-induced plastic flow.⁽¹⁷⁾

crack growth; hence, elongation at fracture is much lower in liquid-metal environments than in air. The most severe surface notches (and hence crack initiation) occur where slip bands intersecting surfaces are blocked by obstacles such as grain boundaries, twin boundaries and slip bands on intersecting slip systems.

4.3 Environmental Factors (Hydrogen Embrittlement, SCC)

The degree of LME should, on the basis of the proposed mechanism, be greater for larger reductions in 'surface-lattice distortion'; increased coverage of the surface by chemisorbed atoms should also increase embrittlement since longer dislocation sources, probably requiring lower activation stresses, may then be nucleated. (Preferential chemisorption along grain-boundary/surface intersections could account for the propensity for intercrystalline fracture in liquid-metal environments.) Embrittlement should therefore be promoted by high affinities of the liquid metal for the solid metal, accompanied by high activation energies for any reaction such as dissolution or compound formation—the activation energy determining the relative life of adsorbates on metal surfaces and, hence, the surface coverage at a particular instant. Although experimental data are limited,⁽²²⁾ this prediction is consistent with general trends⁽⁵⁾: LME is unlikely if the two metals involved readily form high-melting-point compounds or show significant mutual solubility, and large interaction energies between solid and liquid metal are conducive to embrittlement.⁽²³⁾

In some cases, LME can involve an 'internal' source of embrittling metal atoms, e.g. embrittlement of steel by lead can result from the transport† of lead atoms from (lead-rich) inclusions to tips of internal microcracks.⁽²⁴⁾ Embrittlement of steels by solute elements⁽²⁵⁾ (e.g. Sn, Te, Sb, Ar, S, P) which segregate at grain boundaries and induce brittle intercrystalline fracture may involve a similar process (steels are embrittled by liquid and solid tin, and liquid tellurium).

Chemisorption of non-metallic species could reduce 'surface-lattice distortion' and facilitate crack growth (although probably not to the same extent as liquid metals); hence, the mechanism proposed for LME could be applicable to many cases†† of hydrogen embrittlement and stress-corrosion cracking (SCC). The many similarities between hydrogen embrittlement and LME⁽²⁶⁾ support this suggestion, as do observations⁽²⁷⁾ of iron-alloy surfaces in the presence of hydrogen, using field-ion microscopy, which suggest that nucleation of dislocations is catalysed by adsorption of hydrogen. Analogies between SCC and LME⁽²⁸⁾ have prompted other workers to suggest that similar mechanisms are involved in both cases. Recent studies, by the present author,⁽²⁹⁾ of crack growth in high-strength Al-Zn-Mg alloys in liquid-metal and aqueous environments support the case for a common mechanism for LME, SCC and also corrosion-fatigue. (Previous objections⁽³⁰⁾ to a common mechanism for LME and SCC (and, implicitly, to SCC associated with chemisorption) are considered not to be valid since they were based mainly on assumptions that (a) LME occurred by a 'bond-rupture' process, and (b) 'bond-rupture' was unlikely during SCC.)

4.4 Ductile versus Brittle Behaviour in General

Previous analyses of ductile and brittle behaviour have usually been based on considerations of the σ/τ ratio⁽⁹⁾ described earlier. This criterion provides a basis for differentiating materials which fracture by tensile separation of atoms from those which fracture by shear movement of atoms at crack tips. The metallographic and fractographic studies of LME discussed above indicate that such a criterion is not applicable to LME and that one based on the distribution of slip around crack tips is more appropriate. There is an increasingly held view⁽³¹⁻³⁴⁾ that brittle (cleavage) fracture in inert environments occurs by plastic flow in many materials.††† Detailed

† Transport at temperatures above the melting point probably occurs by capillary flow since crack tips are not 'atomically' sharp; at temperatures below the melting point, second-monolayer diffusion probably occurs⁽⁵⁾.

†† Some cases of SCC and hydrogen embrittlement clearly involve other processes, e.g. dissolution, oxide-film formation, hydride precipitation, besides chemisorption.

††† 'Absolute' brittle fracture (i.e. by bond-rupture) probably occurs in a few materials, e.g. mica, diamond at low temperature⁽³²⁾.

fractography^(31, 34) generally shows evidence of plastic flow on cleavage fracture surfaces (Fig. 26), and indirect evidence,⁽³³⁾ e.g. the temperature dependence of the fracture stress, suggests that brittle fracture (in alumina) occurs by plastic flow. Thus, a criterion based on the distribution of slip around crack tips could be applicable to ductile and brittle behaviour in general—illustrated schematically in Fig. 29. In other words, ductile versus brittle behaviour depends on τ_s and ϵ_g , where τ_s is the stress required to produce rapid crack growth by extensive nucleation (or egress) of dislocations at crack tips and ϵ_g is the general strain (proportional to the elongation, δl) in an element of material ahead of cracks at a stress of τ_s ; ϵ_g will depend on the number of slip systems operating and the ease of slip on each system, and on slip flexibility (i.e. ease of cross-slip and interpenetration of dislocations) in this element (Fig. 29). The effects of crystal structure, strength (microstructure), temperature, stress intensity, as well as environment, on ductile versus brittle behaviour could possibly be explained in these terms.

5. CONCLUSIONS

1. Metallographic and fractographic studies of LME of aluminium single crystals and polycrystals show that extensive slip occurs at crack tips and that dimpled fracture surfaces are produced during crack growth in embrittling liquid-metal environments. LME of other materials (cadmium, tin) also results in shallow elongated dimples on fracture surfaces. These observations suggest that crack growth in embrittling liquid-metal environments occurs by plastic flow and not, as previously proposed, by tensile separation of interatomic bonds at crack tips.

2. LME can be explained on the basis that chemisorption of liquid-metal atoms facilitates nucleation of dislocations at crack tips. This effect probably occurs because chemisorption, by effectively increasing the number of 'neighbours' around surface atoms, reduces the 'distortion' of the lattice at the surface; in inert environments, this distortion hinders the nucleation and egress of dislocations at surfaces. Thus, crack growth in liquid-metal environments occurs by nucleation/movement of dislocations on slip planes intersecting crack tips at lower stresses than in air so that dislocations ahead of cracks (unaffected by chemisorption) are not activated to the same extent and less blunting occurs at crack tips.

3. Adsorption-induced slip at crack tips could occur in other environments besides liquid metals and is probably relevant to hydrogen-embrittlement, stress-corrosion cracking and corrosion-fatigue.

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FIGURES

EM — Electron-micrographs of secondary-carbon replicas

SEM — Scanning electron micrographs

Arrows on micrographs indicate direction of crack growth.

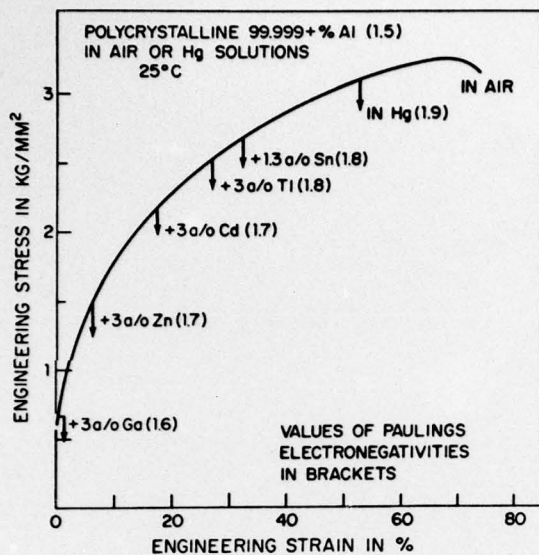


Fig.1. Stress-Strain curves for polycrystalline pure aluminium in air and in various mercury solutions (after Westwood et al. (ref. 1.)).

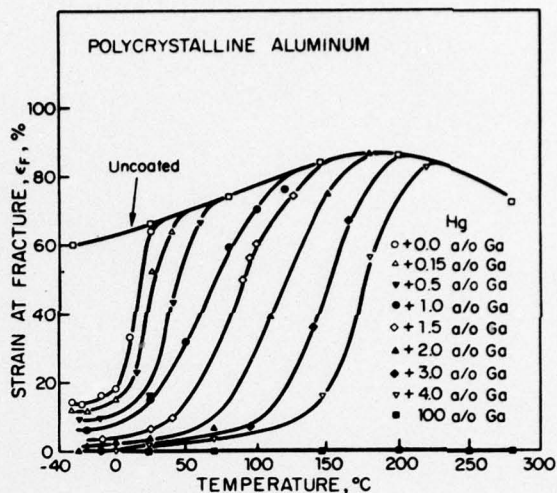


Fig.2. Temperature dependence of strain at fracture for polycrystalline aluminium specimens in mercury, gallium and mercury-gallium solutions (after Preece and Westwood (ref.2)).

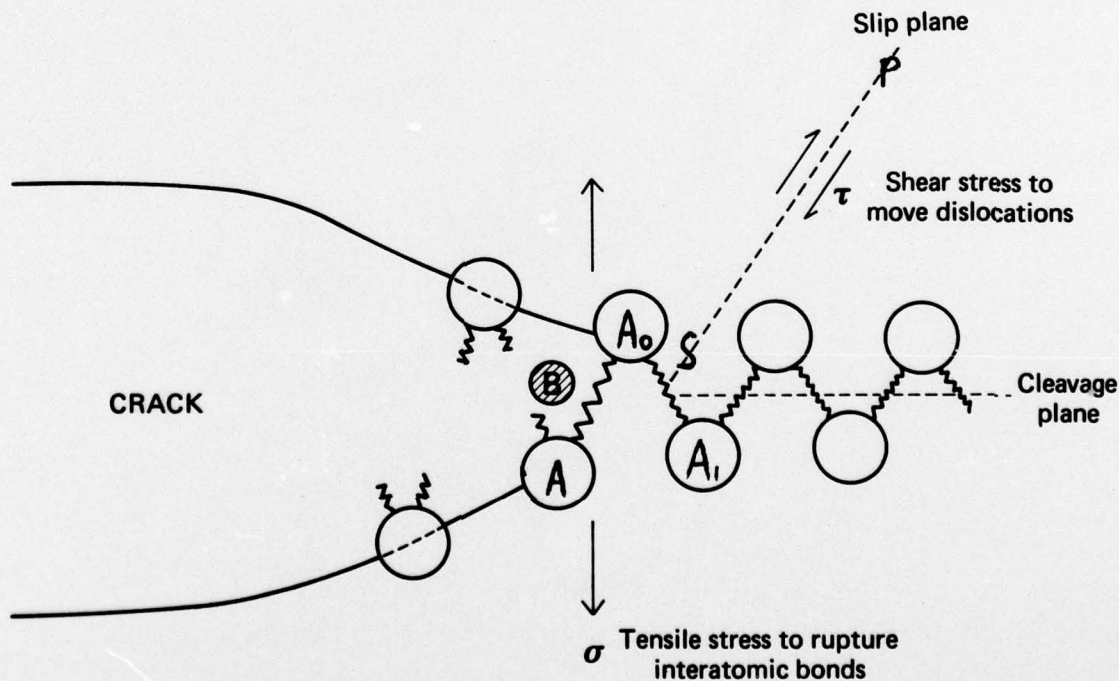


Fig.3. Schematic diagram illustrating commonly proposed mechanism of LME; adsorption of liquid-metal atom, B, at crack tip lowers the tensile stress, σ , required to rupture interatomic bond, A-A₀, but does not influence the shear stress, τ , necessary to move dislocations on slip plane (S-P).

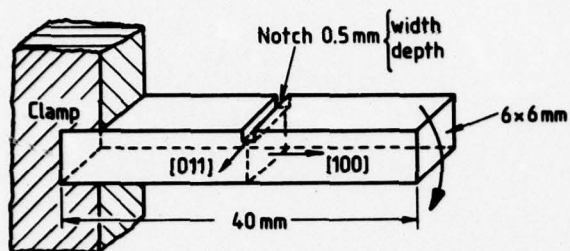


Fig.4. Configuration of specimens tested in cantilever bending; approximate orientation of aluminium single crystals is shown.

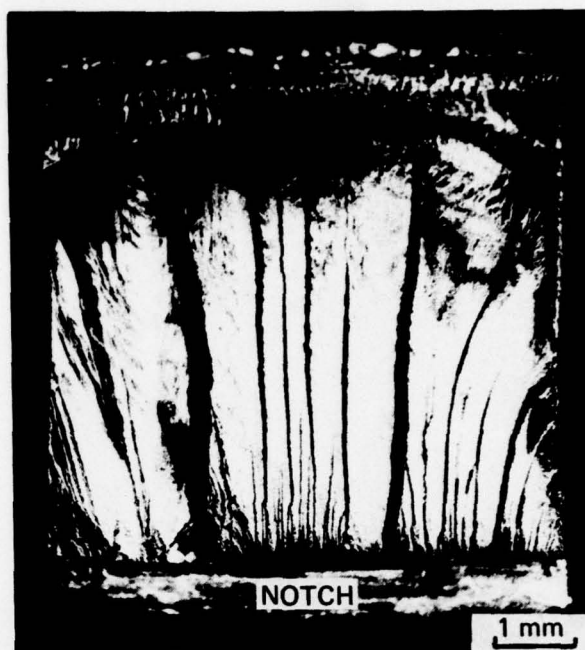


Fig.5. Optical fractograph of aluminium single crystal after fracture in liquid gallium.

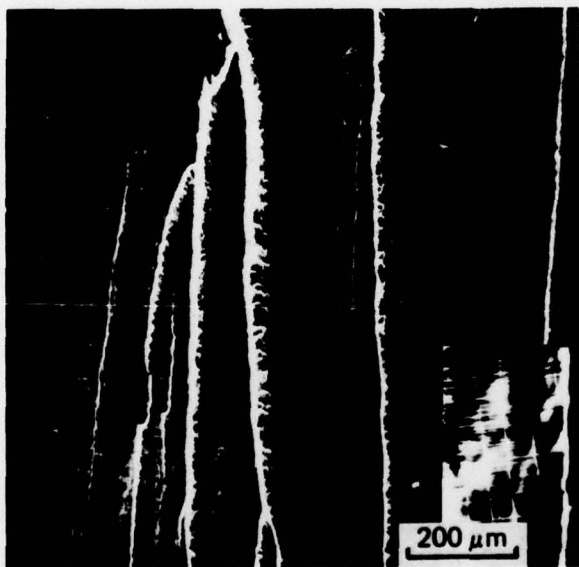


Fig.6. Fractograph (SEM) of aluminium single crystal cracked in liquid alloy. Inset (optical micrograph) shows fracture surface after electropolishing and straining slightly; orthogonal network of slip traces indicates that the surface is macroscopically parallel to $\{100\}$.

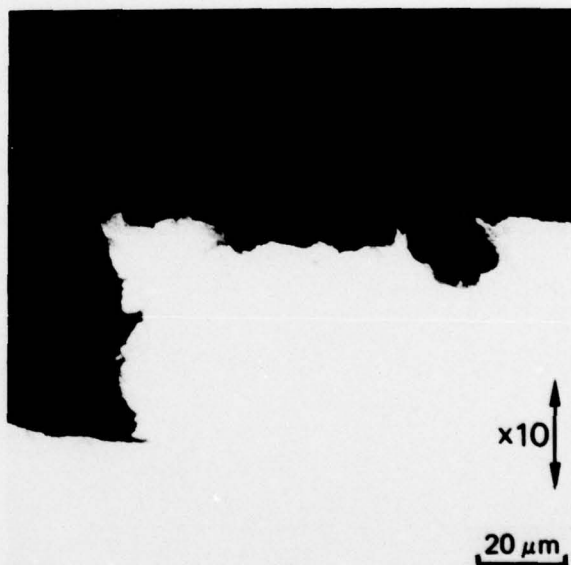


Fig.7. Optical micrograph of taper section through fracture surface shown in Fig.5.



Fig.8.

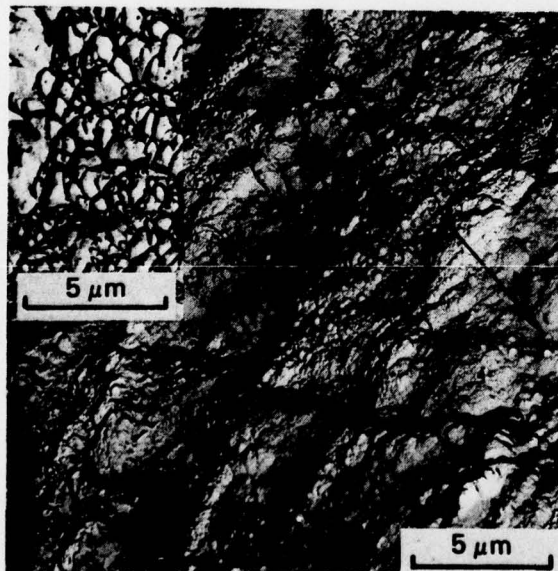


Fig.9.

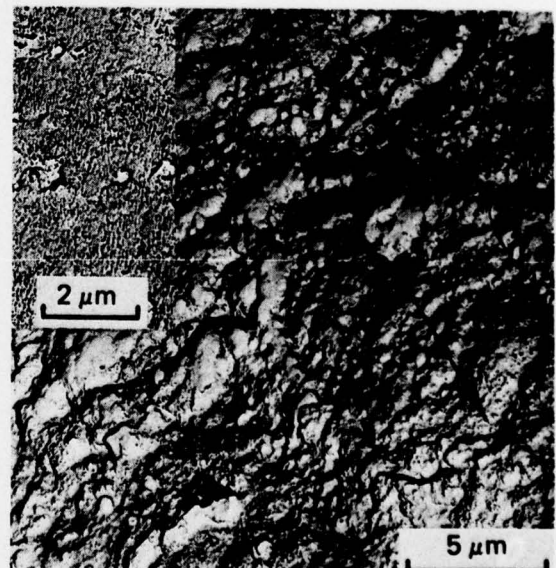


Fig.10.

Figs.8 -10. Fractographs (EM) of aluminium single crystal cracked in liquid alloy showing dimples and slip traces. Inset (Fig.9) shows similar dimples on fracture surface of a high-strength Al-Zn-Mg alloy fractured in air. Inset (Fig.10) shows electropolished aluminium surface after 'fluxing' in NaOH solution, 'wetting' with liquid alloy, and removing liquid alloy; the surface is flat except for pitting produced by the NaOH solution.

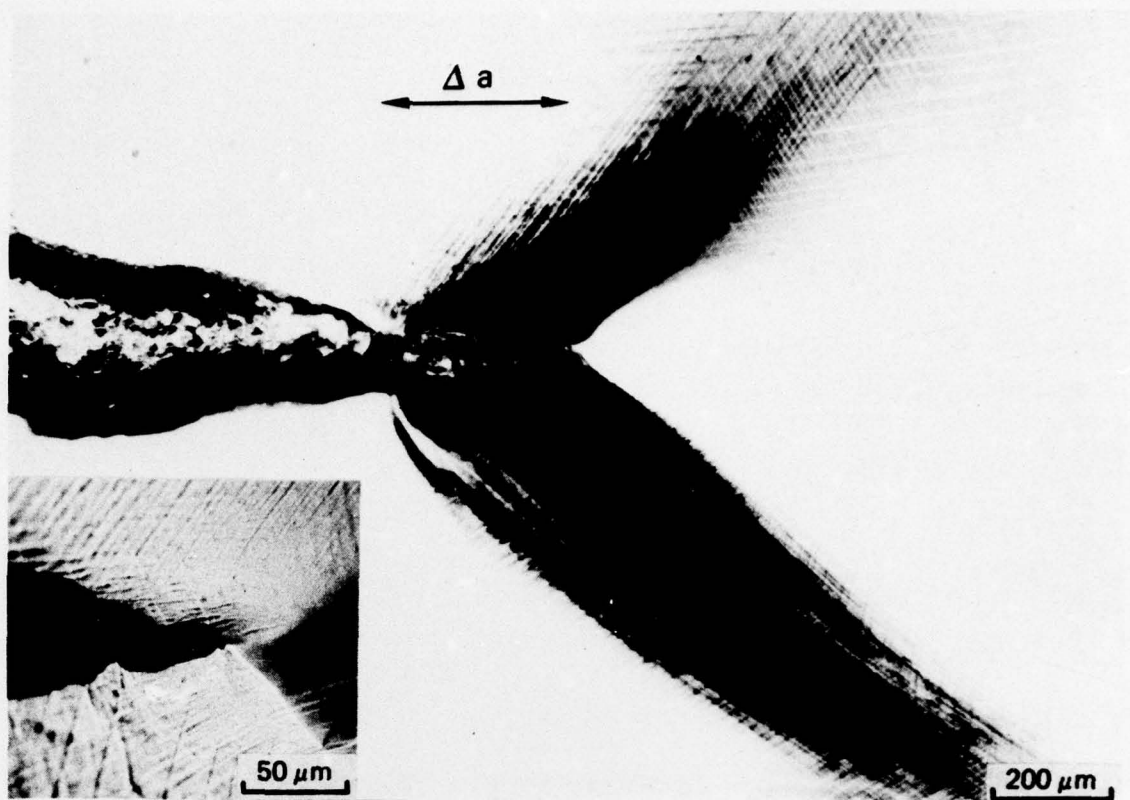


Fig.11. Optical micrographs showing slip associated with a crack-growth increment, Δa , in aluminium single crystal cracked in liquid alloy (crack is filled with alloy). Inset shows crack-tip region at a higher magnification; however, profile of crack tip is not very clear since liquid alloy has 'stained' the surface adjacent to the crack.

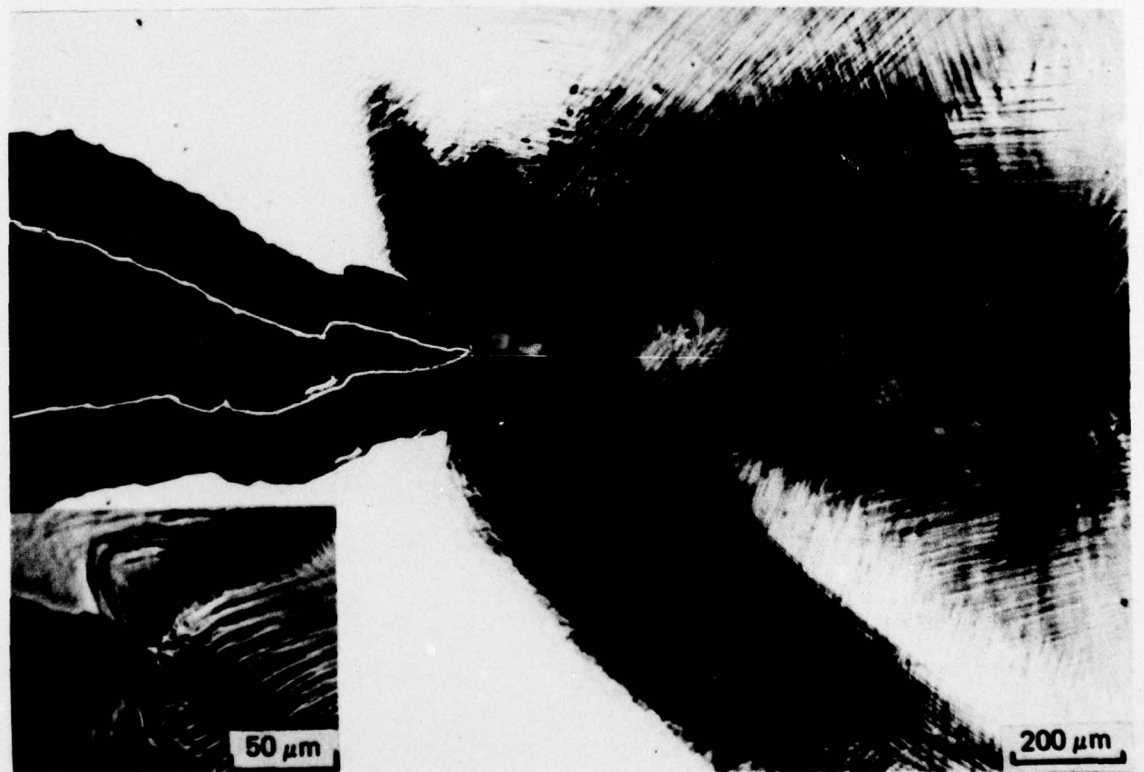


Fig.12. Optical micrograph of crack shown in Fig.11 after removing liquid alloy, repolishing, and increasing COD in air; the crack tip has blunted and considerable slip has occurred ahead of the crack. The crack profile before blunting has been superimposed. Inset shows crack-tip region after only a small amount of blunting.



Fig.13. Optical micrograph (dark-field illumination) of crack shown in Fig.12 after repolishing and again increasing COD in air, producing more crack-tip blunting.

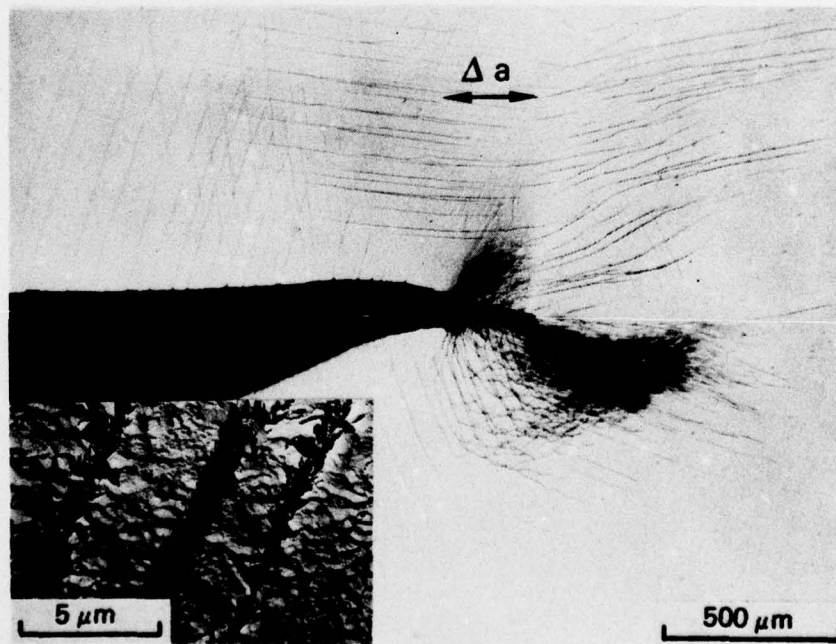


Fig.14. Optical micrograph showing slip associated with a crack-growth increment, Δa , along a grain boundary of an aluminium polycrystal cracked in liquid alloy. Inset is a fractograph (EM) from this specimen showing dimples and slip traces.

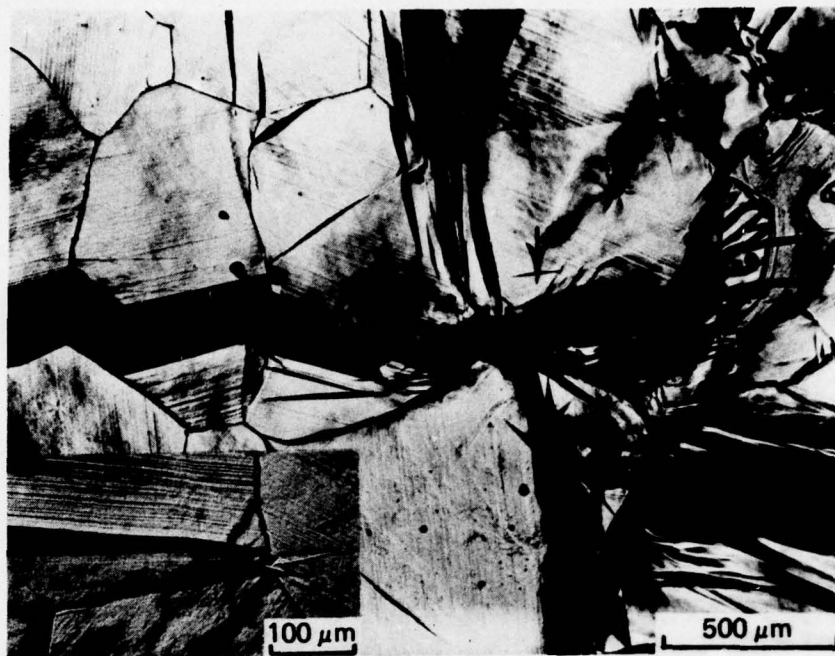


Fig.15. Optical micrographs of cadmium specimen partially fractured in liquid gallium showing intercrystalline and transcrystalline crack growth; the supply of gallium became exhausted at arrows and crack-tip blunting, with considerable slip and twinning around the crack tip, occurred in air. Inset shows small amount of mainly basal slip around the tip of a secondary crack in the liquid-gallium environment.



Fig.16. Fractograph (SEM) after fracture of cadmium specimen in liquid gallium showing cleavage facets.



Fig.17. Fractograph (optical) after fracture of cadmium in liquid gallium showing river lines on a cleavage facet.



Fig.18.



Fig.19

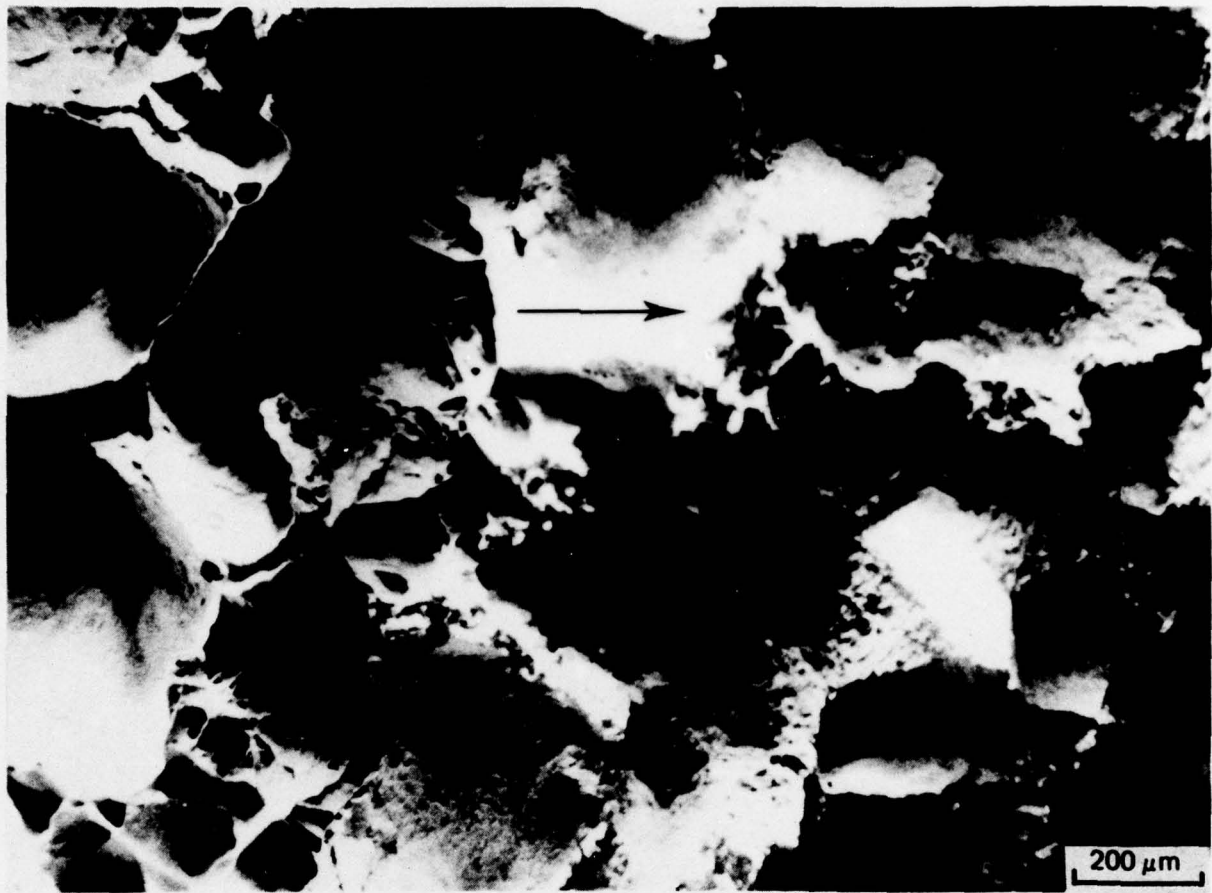


Fig.20.

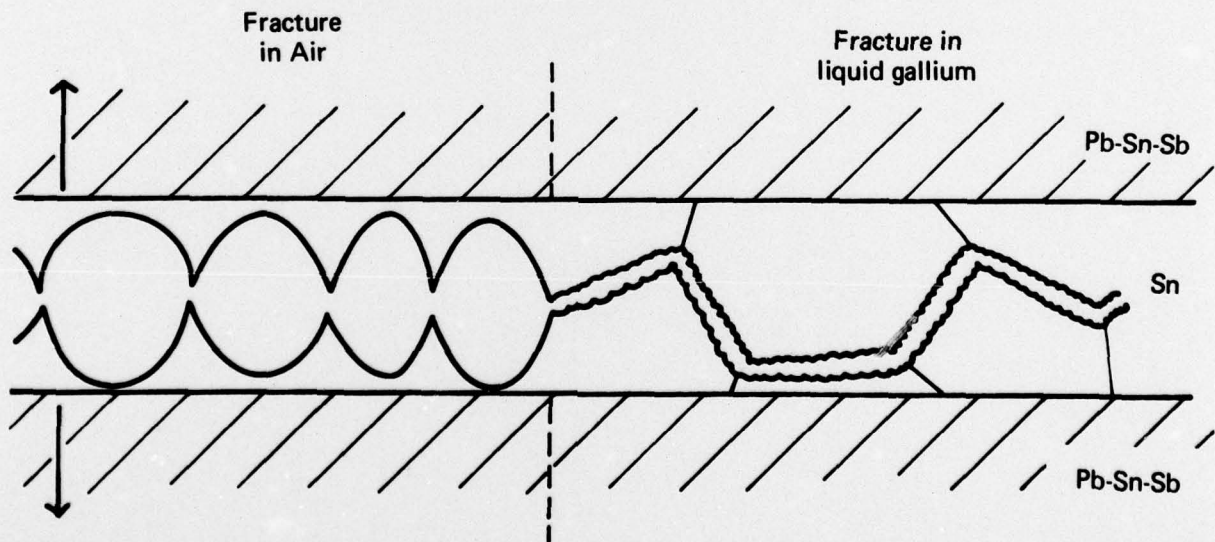


Fig.21.

Figs.18-21. Fractographs (EM) after fracture of cadmium in liquid gallium showing shallow elongated dimples and (Figs. 20, 21) also fairly flat regions on facets similar to those shown in Figs. 16, 17. Note (Fig.18) the perturbations on the fracture surface associated with large second-phase particles (A) and twins (B,C); twin (B) was probably formed after fracture and twin (C) was probably present ahead of the crack tip.



(a)



(b)

Fig.22(a) Fractograph (SEM) of a specimen consisting of a thin sheet of tin sandwiched between and bonded to harder blocks of Pb-Sn-Sb. The specimen was partially cracked in air, producing large, deep dimples, then in liquid gallium resulting in intercrystalline fracture facets; fracture occurred within the soft layer of tin, shown schematically in Fig.22(b).

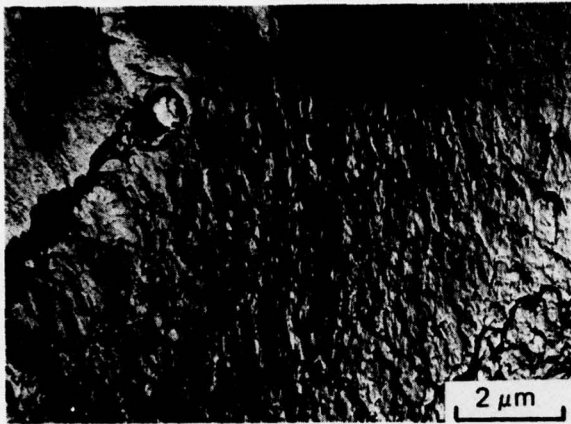


Fig.23.



Fig.24.

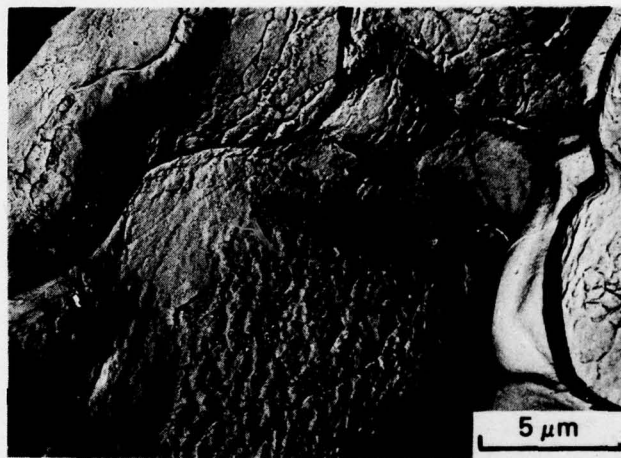


Fig.25

Figs. 23–25 Fractographs (EM) of tin cracked in liquid gallium showing shallow dimples on intercrystalline facets similar to those shown in Fig.22(a). The large perturbations on some facets are associated with large second-phase particles.

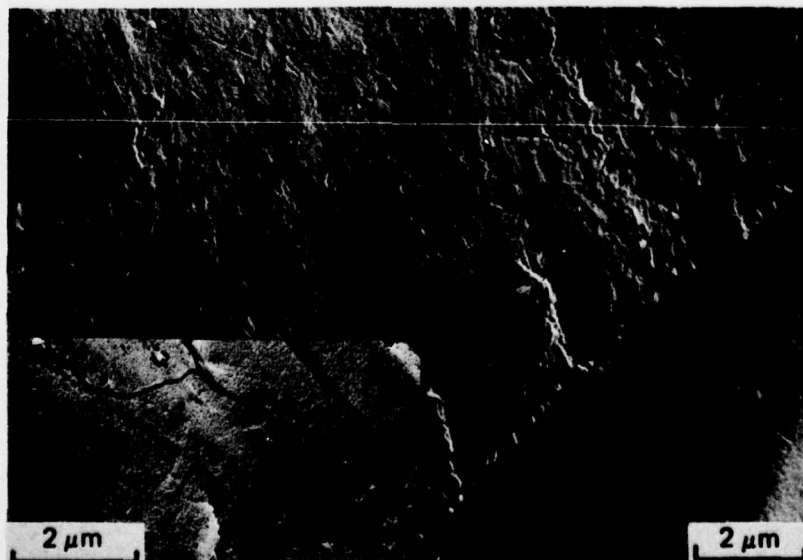


Fig.26. Fractographs (EM) of zinc single crystal after crack growth in air and (inset) liquid gallium showing cleavage facets and river lines.

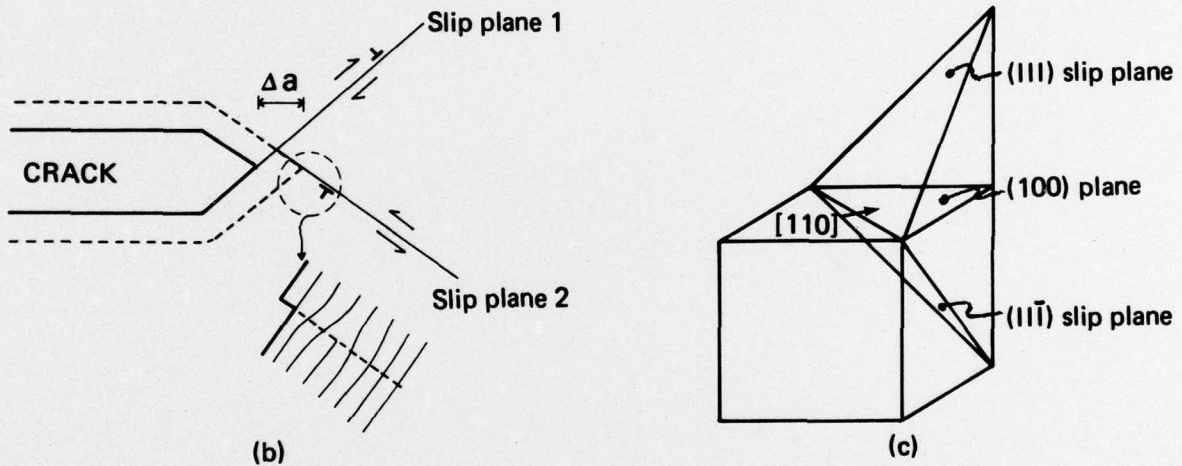
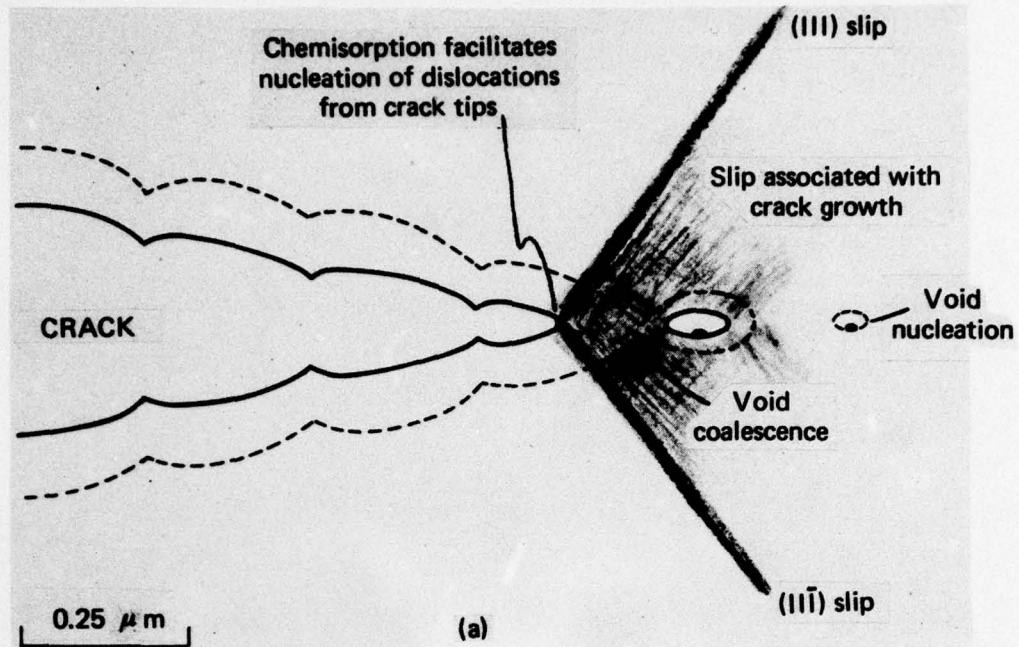


Fig. 27. Diagrams illustrating (a) crack growth in aluminium single crystal in liquid-metal environment. Full lines show initial position of crack and void ahead of crack tip; dashed lines show position of crack and void nucleation ahead of crack tip after an increase in COD. Distribution of slip around crack tip on initially increasing COD is also shown. (b) crack-growth increment, Δa , produced by nucleation and movement of dislocations on slip plane 1 then 2. (c) orientation of $\{III\}$ slip planes with respect to $\{100\}$ planes and $\langle 110 \rangle$ directions for FCC materials.

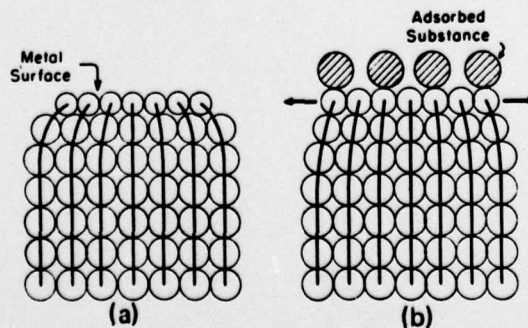


Fig. 28. Diagram illustrating (a) the distortion of the lattice at surfaces in vacuum and (b) the reduction of 'surface-lattice distortion' produced by chemisorption of environmental species (after Uhlig (ref. 14)).

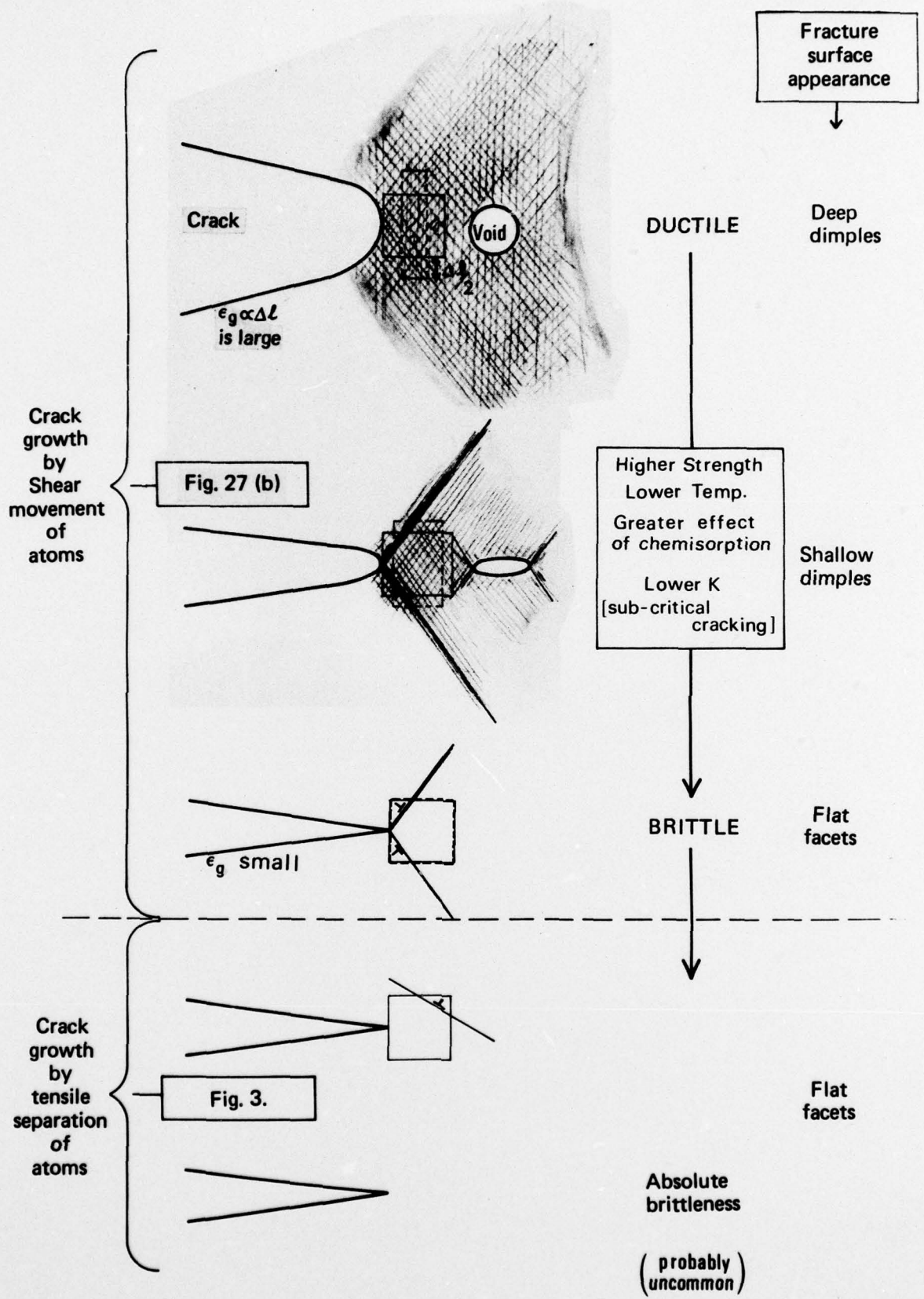


Fig.29. Diagram illustrating transition from ductile to brittle behaviour with decreasing amounts of 'general' slip ahead of cracks.

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