

Mechanisms and Kinetics of Environmentally Assisted Cracking: Current Status, Issues, and Suggestions for Further Work

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Mechanisms and kinetics of metal-induced embrittlement, hydrogen-embrittlement, and stress-corrosion cracking are discussed, and long-standing controversies are addressed by reviewing critical observations. Recommendations are also made regarding further work (including repetition of previous work using more advanced measurement and characterisation techniques) that should be carried out in order to resolve some of the contentious issues. The evidence to date suggests that adsorption-based mechanisms, involving weakening of substrate interatomic bonds so that dislocation emission or decohesion is facilitated, accounts for embrittlement in many systems. Embrittling adsorbed species include some metal atoms, hydrogen, and complex ions produced by de-alloying. Other viable mechanisms of embrittlement include those based on (1) dissolution of anodic grain-boundary regions, and (2) decohesion at grain boundaries owing to segregated hydrogen and impurities. The hydrogen-enhanced localised-plasticity mechanism, based on solute hydrogen facilitating dislocation activity in the plastic zone ahead of cracks, makes a contribution in some cases, but is relatively unimportant compared with these other mechanisms for most fracture modes. The film-induced cleavage mechanism, proposed especially for stress-corrosion cracking in systems involving de-alloying at crack tips, is questionable on numerous grounds, and is probably not viable. Rate-controlling processes for environmentally assisted cracking are not well established, except for solid-metal induced embrittlement where surface self-diffusion of embrittling atoms to crack tips controls cracking kinetics. In some systems, adsorption kinetics are probably rate-controlling for liquid-metal embrittlement, hydrogen-environment embrittlement, and stress-corrosion cracking. In other cases, rate-controlling processes could include the rate of anodic or cathodic reactions at and behind crack tips (responsible for producing embrittling species such as hydrogen) and rates of hydrogen diffusion ahead of cracks.

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I. INTRODUCTION

THE mechanistic and rate-controlling processes for environmentally assisted cracking (EAC) are difficult to establish because: (1) crack tips cannot be directly observed on the atomic scale in the bulk of the material, (2) fracture surfaces are often corroded thereby precluding 'reconstruction' of crack-tip events, and (3) numerous material-environment interactions can occur, especially in aqueous environments. For example, slip-induced rupture of (semi-) protective films at crack tips in aqueous environments can lead to anodic dissolution/de-alloying (producing metal ions), while cathodic reactions at and behind crack tips can produce hydrogen and hydroxyl ions. Adsorption of hydrogen and other ions, involving charge-transfer with substrate atoms, could be critically important in weakening

interatomic bonding at crack tips so that decohesion or dislocation emission is facilitated. Hydrogen can also diffuse ahead of crack tips and affect interatomic bonding and deformation processes in the plastic zone. Vacancies can also be generated by dissolution and de-alloying, and can diffuse ahead of crack tips, with synergistic interactions between vacancies and hydrogen possibly affecting deformation and fracture.

There is a widespread view that different mechanisms of EAC are applicable in different material:environment systems, but it is not surprising (given the above) that there is considerable controversy regarding the processes responsible for EAC in particular systems. For example, one of the earliest known cases of EAC (α -brass in aqueous ammonia environments) has been 'explained' by at least six different mechanisms, *viz.* (1) localised dissolution, (2) adsorption of specific ions (produced by de-alloying) leading to dislocation emission or decohesion, (3) film-induced cleavage, (4) corrosion-induced cleavage, (5) vacancy injection and embrittlement, and (6) environmentally enhanced surface-mobility. There are numerous reviews (*e.g.*, [1–5]) which describe and discuss these and other mechanisms (and cite original references), and these reviews should be consulted for more detail than provided in the present paper.

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In the present paper, the author's views (and evidence supporting these views) regarding mechanisms and kinetics of embrittlement by liquid-metal, hydrogen, and aqueous environments, are outlined. Unresolved issues are then discussed, with an emphasis on what further work (and repetition of previous work using more advanced measurement and characterisation techniques^[6]) should be carried out to resolve these issues. Liquid-metal embrittlement (LME), solid-metal induced embrittlement (SMIE), and metal-vapor induced embrittlement (MVIE) are considered first since these phenomena are relatively simple compared with hydrogen-embrittlement (HE) and stress-corrosion cracking (SCC), and provide a basis for understanding these more complex phenomena. Crack-initiation stages are not considered—just the mechanisms and kinetics of crack growth.

II. METAL-INDUCED EMBRITTLEMENT

A. Mechanistic Aspects

LME in systems such as Al, Ni, Ti and Fe alloys in mercury where (1) rates of sub-critical cracking are high (10 to 100 mm/s), (2) mutual solubilities of substrate and liquid metals are low, and (3) there is no tendency to form intermetallic compounds, is generally attributed to adsorption-induced weakening of interatomic bonds at crack tips since there is neither time nor tendency for other reactions to occur.^[7–10] An adsorption mechanism

for such systems is also consistent with surface-science observations that show that adsorbed metal atoms have substantial effects on substrate interatomic bonding at surfaces.^[1] There are other liquid-metal:substrate-metal systems, *e.g.*, Al-Ga, Ni-Bi, Cu-Bi, Cu-Hg, where diffusion of embrittling metal can occur along grain boundaries to produce a thin (nanometre-scale) liquid film or grain-boundary phase (one to three atomic layers thick), which results in intergranular fracture at low stresses,^[9–14] but such systems are less common than those involving adsorption, and they will not be considered further in the present paper. It is worth noting that thin films of embrittling metal between grains, observed in partially cracked specimens (or in secondary cracks), are not necessarily evidence that embrittling metals have diffused along grain boundaries prior to crack growth. Such films are observed within cracks after adsorption-induced intergranular LME since liquid is drawn into cracks by capillary flow. For some systems, *e.g.*, Al-Ga, Cu-Hg, LME can be associated with either adsorption or grain-boundary diffusion, depending on the testing conditions.

The idea that stress-assisted dissolution at crack tips contributes to crack growth in liquid-metal environments (with re-condensation occurring behind crack tips) has recently been 'resurrected' and modified to account for plasticity/void-formation ahead of cracks.^[15] However, detailed fractographic observations show that the characteristics of LME are the same as those for SMIE and MVIE in many systems, *e.g.*,

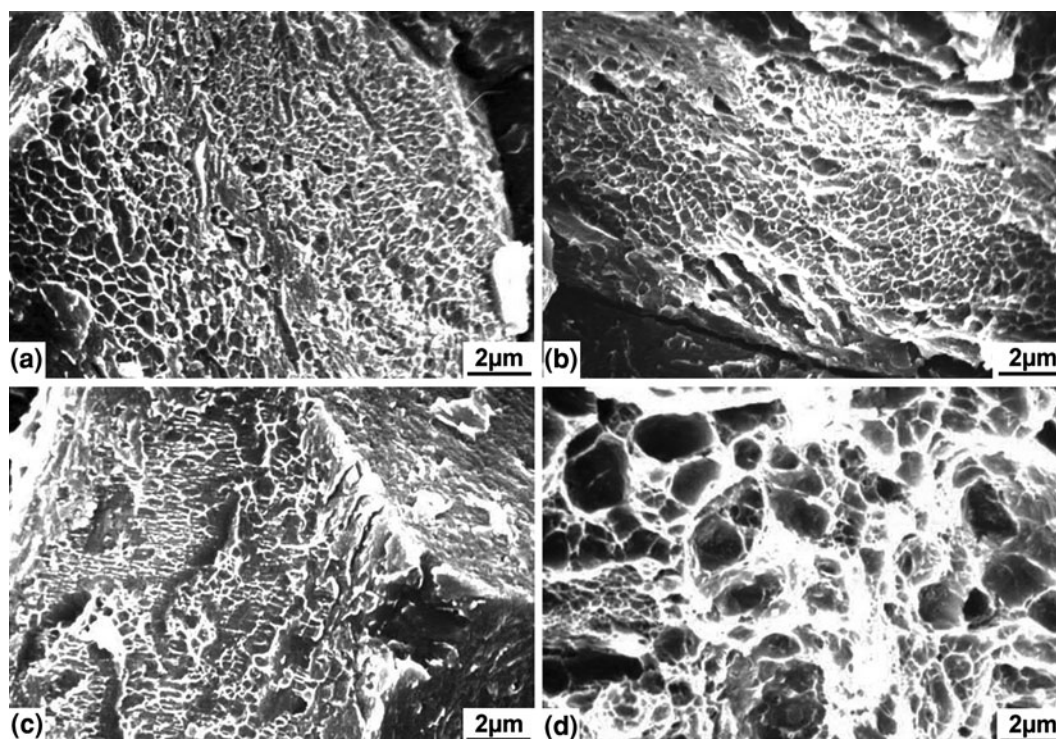


Fig. 1—SEM of fracture surfaces of an ultra-high-strength D6aC steel [tempered at 923 K (650 °C)] ($VH \sim 400$) tested in (a) liquid Hg at 293 K (20 °C) ($v \sim 5$ mm/s) (b) mercury vapor (+ argon) at 423 K (150 °C) ($v \sim 10^{-2}$ mm/s), (c) solid In at 413 K (140 °C) ($v \sim 10^{-5}$ mm/s), and (d) air at 293 K (20 °C), showing shallow dimples on intergranular facets produced by sub-critical sustained-load cracking in these various types of metal environments, and larger/deeper dimples after fast (transgranular) fracture in air.^[16,21,24]

steels in Hg (liquid and vapor) and solid indium (Figure 1),^[7-9,16-18] suggesting that the mechanism of all these phenomena is the same. If this is the case, then any role of dissolution can be discounted for LME since it cannot occur in solid-metal and metal-vapor environments. Mechanisms of LME, SMIE, and MVIE in such systems are probably all associated with adsorption at crack tips.

The metallographic and fractographic observations for adsorption-induced embrittlement depend on the material, environment, and other variables. In some cases, the features observed include: (1) shallow dimples on fracture surfaces (compared with deep dimples after fast fracture in inert environment), (2) extensive slip localised on planes intersecting crack tips (with dislocation cell structures just beneath fracture surfaces), and (3) crack fronts parallel to the line of intersection of crack planes and slip planes^[19-24] (Figures 1 and 2). More commonly, fracture surfaces are relatively featureless (using scanning-electron microscopy (SEM) at up to ~20,000 times magnification) (Figure 3) and there are little or no signs of plasticity around cracks on this scale.^[8,18,21,24] An adsorption-induced dislocation-emission (AIDE)/void-coalescence mechanism (Figure 4), described in detail elsewhere,^[1,24] best accounts for the first category. When fracture surfaces appear featureless, it has been generally *assumed* that an adsorption-induced decohesion process (Figure 5) is applicable.^[7,8]

Concluding that an atomically brittle decohesion process occurs when fracture surfaces are featureless (when examined by SEM) is unjustified since the imaging capabilities of most instruments are probably insufficient to detect features such as very shallow dimples. Indeed, comparison of SEM with transmission-electron microscopy (TEM) of replicas, appropriately shadowed and examined under optimum conditions, has shown that very shallow dimples on

brittle intergranular and cleavage-like fracture surfaces are sometimes not resolved by SEM^[24] (even when using an SEM with a field-emission gun (FEG)) (Figure 6).^[26] Thus, the AIDE mechanism may be more widely applicable than SEM observations suggest. Comparisons of the *same areas* of fracture surfaces with shallow features using a state-of-the-art FEG-SEM and replica-TEM techniques have not been carried out as far as the author is aware, and would be worthwhile since this issue is relevant not only for understanding LME but is a more general one. Comparisons of SEM/TEM images with those obtained by atomic-force microscopy and scanning-tunnelling microscopy would also be interesting.

It would be surprising if crack tips were atomically sharp during crack growth in liquid-metal environments since embrittling metal atoms (up to twice the size of substrate atoms in some cases) need to be able to reach crack tips by capillary flow to keep up with rapidly growing cracks, and this probably needs a crack-tip radius of at least several nanometres. Further insights into crack-tip geometries and processes during LME would probably be obtained from thin-foil TEM studies using ion-beam-thinning preparation techniques to examine dislocation structures around crack tips, as has been done for SCC and HE in a few systems.^[27-31] For LME, it would be beneficial to allow the liquid metal to solidify after cracking (without unloading) so that the crack-tip radius and dislocation arrangements around crack tips would not be changed by unloading. (The presence of solidified metal within cracks might also facilitate 'edge-retention' around crack tips during foil preparation.) It would be worthwhile carrying out these TEM studies for both cleavage-like fractures (along various crystallographic planes) and intergranular fractures to determine how dislocation arrangements depend on the fracture path. Using embrittling metals

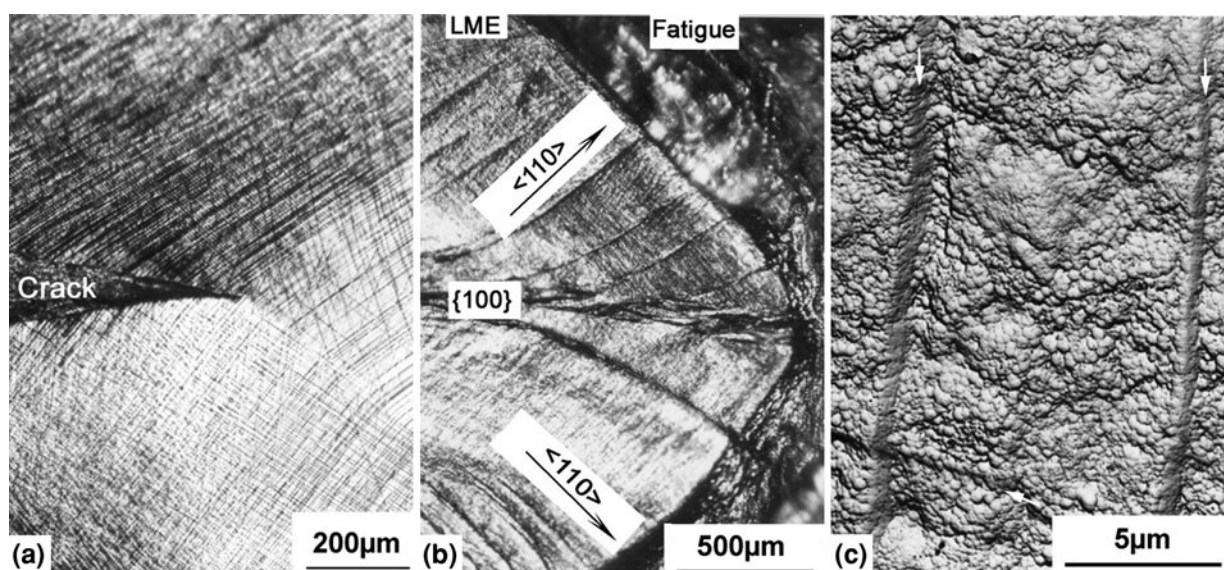


Fig. 2—(a), (b) Optical micrographs for pure Al single crystals tested in a liquid Bi-Pb-Sn-In-Cd alloy at 333 K (60 °C), showing (a) slip localised on {111} planes intersecting {100} crack on the side surface of a specimen, (b) {100} fracture surface with V-shaped crack front (delineated by a transition from LME to fatigue in air) running in two different $\langle 110 \rangle$ directions such that slip planes intersect crack fronts, and (c) TEM of replica showing small, shallow dimples and slip lines (arrowed) on fracture surfaces.^[20]

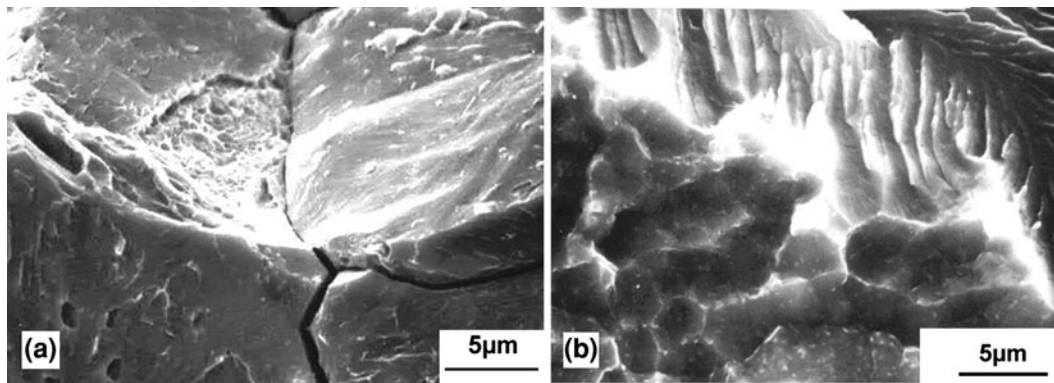


Fig. 3—SEM of fracture surfaces produced by sustained-load cracking of (a) an ultra-high-strength (D6aC) steel [tempered at 673 K (400 °C)] ($VH \sim 540$) in liquid mercury at 293 K (20 °C), showing 'brittle' intergranular facets with flat areas except for tear ridges, and an isolated area of dimples where crack growth appears to have occurred just adjacent to the boundary,^[21] and (b) 7075 Al alloy tested in solid indium at 413 K (140 °C) showing no evidence of dimples on intergranular or cleavage-like areas at this magnification.^[18]

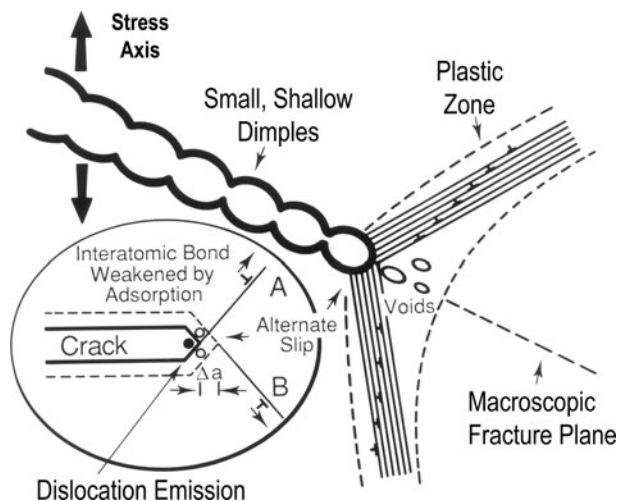


Fig. 4—Schematic diagram illustrating mechanism of metal-induced embrittlement involving adsorption-induced weakening of interatomic bonds at crack tips, resulting in adsorption-induced dislocation emission (AIDE) (facilitating the linking of cracks with voids ahead of cracks). For transgranular cracking, alternate-slip occurs to minimise back-stresses from emitted dislocations so that fracture planes bisect the angle between slip planes, such that nano-dimpled cleavage-like fractures, *e.g.*, on {100} planes in $\langle 110 \rangle$ directions, are produced.^[24] Second-phase particles are favoured sites for initiation of voids, but if they are few and far between, other sites such as dislocation-cell boundaries or slip-band intersections nucleate voids when strains are high.

(or alloys) with low-melting-points would facilitate experimental procedures and minimise thermal rearrangement of dislocations during cooling.

If such TEM sections showed significant crack-tip radii and high strains localised around crack tips—as previous optical metallographic and SEM/TEM observations in some systems suggest—this would provide further evidence for the AIDE mechanism. If crack-tip radii approached atomic dimensions, and strains ahead of crack tips and beneath fracture surfaces were small, then this would support a decohesion mechanism. Limited dislocation activity can accompany decohesion, but such activity should not be so extensive that crack

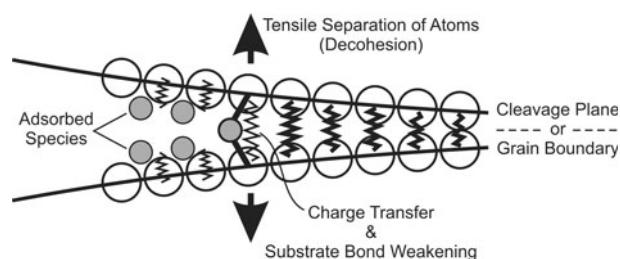


Fig. 5—Schematic diagram illustrating the adsorption-induced decohesion model of metal-induced embrittlement, involving tensile separation of atoms at atomically sharp crack tips.^[1] Observations of cubic arrays of 'atoms' on cleavage fracture surfaces of Cr by scanning tunnelling microscopy^[25] suggest that such atomically brittle fractures can occur in metals.

tips are continually blunted—otherwise crack growth would occur by localised plasticity (probably involving a void-coalescence process). Intermittent blunting could, of course, occur during decohesion, so that the suggested TEM experiments may not be completely definitive, but should still provide worthwhile data.

Directly observing dislocation activity around crack tips during crack growth in the presence of liquid metals, as was attempted many years ago,^[32] may now be more enlightening using the latest high-voltage TEM straining-stage techniques, such that thicker (electron-transparent) specimens can be used. Perhaps the best system to study (for adsorption-induced embrittlement) in the first instance would be an Al-Li alloy containing Na and K impurities since (1) these impurities are present as small discrete Na-K phases that are liquid at room temperature, and (2) fractographic observations on bulk specimens have shown that cleavage-like and brittle intergranular crack growth emanate from intragranular and intergranular liquid phases, respectively.^[33] It should, of course, be recognised that the behaviour of thin specimens would not be representative of bulk specimens/plane-strain conditions in many respects, *e.g.*, void nucleation and growth ahead of cracks may not occur to the same extent under conditions of low constraint in thin foils.

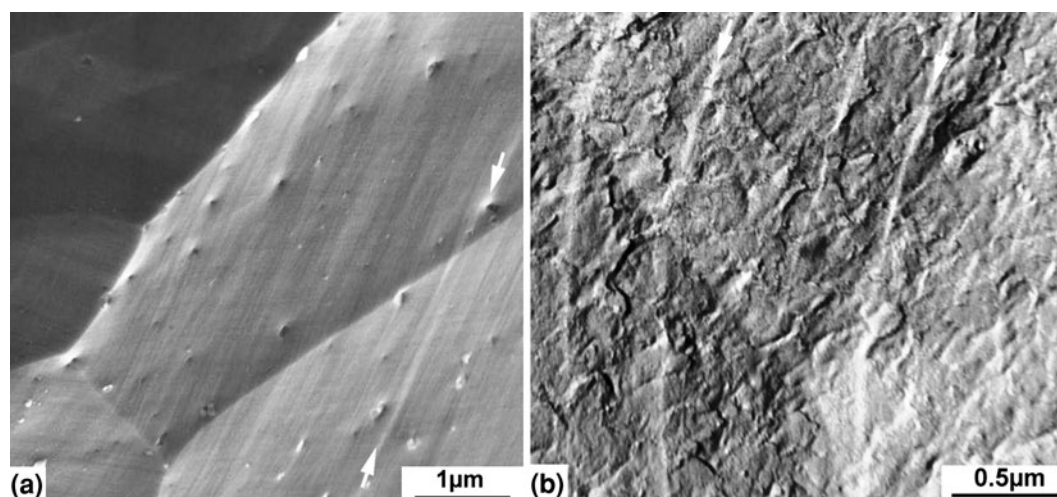


Fig. 6—Intergranular overload fracture surface of an underaged 8090 Al-Li alloy tested at 77 K (−196 °C): (a) FEGSEM operated at low kV and with a short working distance (3 kV and 4 mm, respectively) to enhance surface features, showing smooth facets except for isolated particles and fine slip lines (arrowed) (which are produced by slip behind crack tips), and (b) TEM of replica shadowed with Ge at a low angle (10 to 15°) from two orthogonal directions, examined at 60 kV using a small objective aperture, with the replica tilted 30 to 40°, to enhance contrast, showing shallow dimples (not resolved by FEGSEM) as well as slip lines (arrowed).^[26]

B. Specificity Issues

A long-standing question regarding adsorption-induced LME is why only some liquid metals embrittle particular substrate metals. There are general guidelines for embrittlement couples, *viz.* low mutual solubilities and no tendency to form intermetallic compounds,^[8,9,34] which seem reasonable given that (1) not only do adsorbates need to weaken substrate-substrate bonds, but (2) adsorbate-substrate bonds also need to be weak, so that dislocation emission (which involves shearing of all these bonds) is facilitated. There are, however, numerous exceptions to the general guidelines. For example, Ni is severely embrittled by liquid Li, moderately embrittled by liquid Na, but apparently not embrittled by other alkali metals (K, Rb, Cs) (Figure 7),^[22] even though similar interactions might be expected. Steels embrittled by liquid Zn are another exception since intermetallic compounds can form in this system.^[8,34] It is also puzzling why Cu polycrystals are embrittled by adsorption of liquid Hg (exclusively along intergranular crack paths) but copper single crystals are not embrittled.^[35] In contrast, most other systems exhibit both intergranular LME and transgranular LME, although intergranular crack paths are often favoured unless single crystals are used.

Insights into these ‘specificity’ issues could possibly be obtained from quantum-mechanical-based modelling techniques,^[36–39] which have become more powerful in recent years, although they are arguably still some way from ‘reality’ in terms of modelling EAC. In the first instance, {100}<110> cracks (as experimentally observed for Ni in Na and Hg) under mode-I loading should be modelled to determine if the simulations indeed show that dislocation emission (or decohesion) is facilitated in embrittling-metal environments but not in non-embrittling-metal environments. Models of atomistic zones (coupled to the surrounding plastic and elastic regions)

should have sufficient thickness that emission of dislocation loops along crack fronts is possible. Ideally, simulations should also be carried out at temperatures where thermally activated processes can occur. The interatomic potentials used should not only predict elastic moduli, surface energies, *etc.*, but should also predict the effects of adsorption on surfaces, *e.g.*, on surface-lattice relaxations/reconstructions, which have been (or can be) experimentally observed using surface-science techniques.

C. Rate-Controlling Steps

For SMIE, it is well established that transport of embrittling metal atoms to crack tips (by surface self-diffusion) is the rate-controlling step. This conclusion is based on (1) the effects of temperature on crack-growth kinetics (and activation energies for crack growth), (2) comparisons of these data with surface-diffusion data, and (3) the decreasing rate of crack growth with increasing crack length (*i.e.*, an increasing distance from the source of embrittling metal to the crack tip).^[18,40] For MVIE, vapor-transport of embrittling metal to crack tips presumably controls the rate of crack growth (which is orders of magnitude slower compared with LME in the steel:Hg system). For LME, it has been proposed that transport of liquid metal to crack tips by capillary flow sometimes controls crack-growth rates, but there are doubts that this is generally the case for various reasons.^[41]

For LME, plots of crack velocities (*v*) versus stress-intensity factor (*K*) sometimes show stage-II velocities that are constant over a wide range of *K* or exhibit several plateaux (Figure 8).^[41–46] Capillary flow would be expected to be faster at higher *K* levels since flow should be easier when crack-tip-opening displacements (which should increase smoothly with increasing *K*) are larger.^[41] Stage-II crack velocities (for Al alloys) vary by one or two orders of

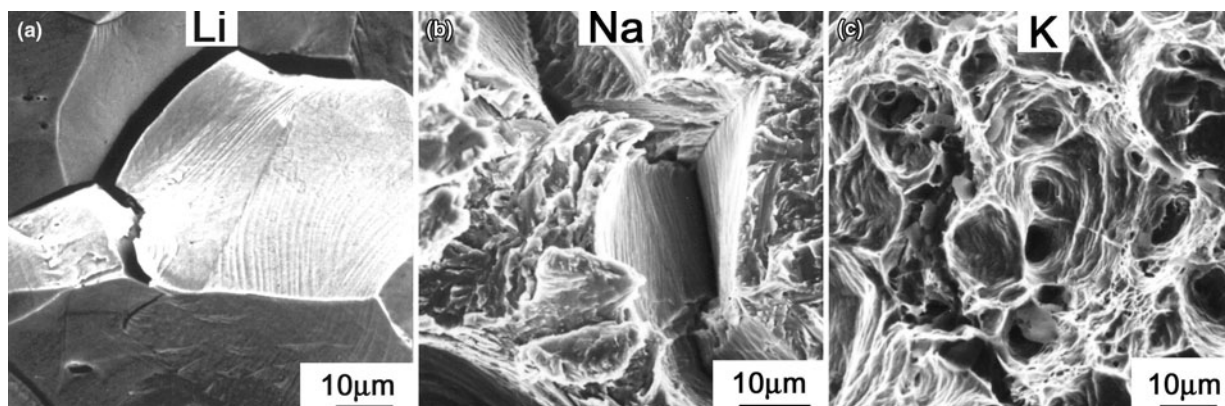


Fig. 7—SEM of fracture surface of pure nickel after tensile tests in (a) liquid lithium at ~483 K (~210 °C) showing brittle intergranular cracking, (b) liquid sodium at ~393 K (~120 °C) showing cleavage-like areas and intergranular splitting, and (c) liquid potassium at ~348 K (~75 °C) showing ductile dimpled fracture.^[22]

magnitude depending on (1) the alloy and ageing condition, (2) the embrittling liquid metal (and its oxygen concentration), (3) crack-plane orientation with respect to the rolling direction of plate, and (4) testing procedures, *e.g.*, increasing- K or decreasing- K tests (Figure 8). Capillary flow would not be expected to be that sensitive to these variables. However, capillary flow could be rate-controlling for the highest velocities observed for stage-II cracking.

Other processes such as dislocation emission and decohesion at crack tips would be expected to be strongly dependent on K and, hence, are unlikely to be rate-controlling in the stage-II regime (but could well be rate-controlling in the stage-I regime). Thus—by default—adsorption kinetics may sometimes control the rate of stage-II cracking. The decreasing crack-growth rates with increasing temperature in some systems, *e.g.*, a steel in liquid Pb-Bi^[47] and an aluminium alloy in liquid mercury,^[44] are also best explained in terms of adsorption kinetics, which are known to be generally slower at higher temperatures.^[47] Neither the crack-growth rates nor the effect of temperature are consistent with capillary flow being rate-controlling.*The somewhat higher stage-II

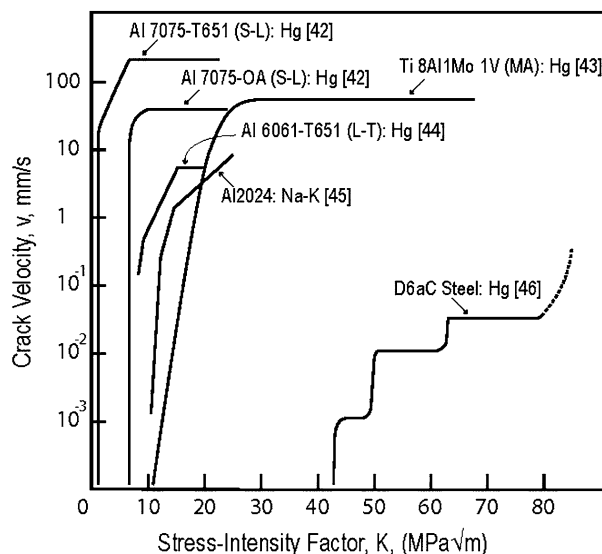


Fig. 8—Plots of crack velocity (v) versus stress-intensity factor (K) (for decreasing K tests) for various LME systems at 293 K to 298 K (20 °C to 25 °C), showing that crack velocities in the (intermediate-to-high- K) stage-II regime can vary by orders of magnitude depending on the material and environment. Data replotted from references indicated.

substrate-metal strength/microstructure, on crack-growth rates in a variety of systems. Surface-science studies of the effects of metal adsorbates on substrate bonding, especially on stressed surfaces, would also be valuable. Another aspect that requires further investigation is the presence of regularly spaced crack-arrest (or crack-blunting) markings on cleavage-like fracture surfaces observed for a few systems, *e.g.*, Cd-Ga, β -brass-Hg.^[49,50] The reason for these markings is not clear, but one possibility is that intermittent ‘de-wetting’ (loss of intimate contact between liquid and solid metals) occurs at crack tips for some reason.^[50]

III. HYDROGEN EMBRITTLEMENT

A. Overview of Mechanistic Aspects

HE (for materials tested in hydrogen or hydrogen-sulphide gas) is more complex than adsorption-induced

*These effects of temperature are also opposite to what one would expect if dissolution was involved in crack growth. Increasing temperature decreases the severity of LME (measured from elongations or reductions of area after tensile tests) in other materials,^[8–10] but the data are difficult to interpret since both crack initiation and growth are involved. For LME involving grain-boundary diffusion, increasing temperature increases the kinetics of embrittlement as would be expected.

crack velocities, and substantially lower threshold values, for an aluminium alloy cracked in mercury treated to remove oxygen (compared with untreated mercury) can also be explained in terms of adsorption kinetics. Thus, the surface coverage of adsorbed mercury at crack tips should be higher in the absence of oxygen, which could adsorb preferentially and inhibit embrittlement.^[48]

Further understanding of crack-growth kinetics in embrittling metal environments would be obtained from more extensive studies of the effects of variables such as temperature, embrittling-metal composition, and

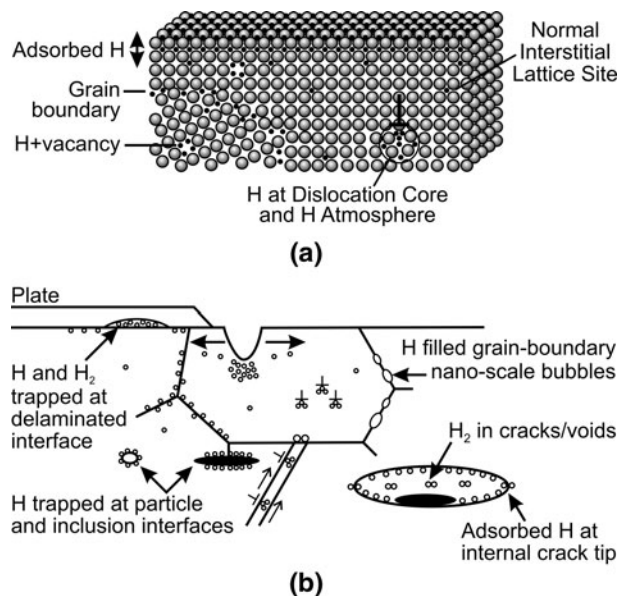


Fig. 9—Schematic illustrations of sites and traps for hydrogen in materials (a) on the atomic scale (adapted from^[51]), and (b) on a microscopic scale.^[1,6] Note the high concentration of hydrogen on and between the first and second layers at the surface ('adsorbed' hydrogen). 'Adsorbed' hydrogen at external and internal crack tips or hydrogen trapped at grain boundaries is mainly responsible for HE.^[1,6,24]

LME because hydrogen can not only adsorb at crack tips but can usually diffuse ahead of cracks. Moreover, the adsorption process is more complex since hydrogen molecules physically adsorb and then dissociate (on most clean metal surfaces) resulting in atomic hydrogen at surface sites and just-subsurface sites (between the first few atomic layers), which are stronger trap sites than normal interstitial lattice sites^[1,6,51,52] (Figure 9). Unless otherwise specified, the term adsorbed hydrogen is used to denote hydrogen at both surface and just-subsurface sites in this paper.

Hydrogen that is present ahead of cracks (having diffused from crack tips or which was already present for hydrogen-charged material) can adsorb at internal crack/void tips. Hydrogen ahead of cracks can also concentrate at various locations, *e.g.*, lattice sites where high hydrostatic stress results in lattice dilations, and various trapping sites such as particle-matrix interfaces, grain boundaries, and vacancy clusters. Hydrogen can also be present at dislocation cores and as atmospheres around dislocations (and can be transported by them) in the plastic zone ahead of cracks (Figure 9).^[1,6,51] Thus, there have been long-standing arguments regarding whether HE (in non-hydride forming materials) is due to adsorbed hydrogen or solute hydrogen in the plastic zone ahead of cracks (or both), and also whether crack growth occurs by decohesion or by localised slip (or both).^[1,5,6]

Several mechanisms of HE could, of course, occur conjointly or different mechanisms could predominate depending on the material, testing conditions, and other variables.^[1,6,53–56] For example, it has been proposed^[1,6,54] that (1) an AIDE/void-coalescence

mechanism predominates for dimpled intergranular and dimpled transgranular cracking (including cleavage-like cracking when nano-scale dimples are present), (2) a hydrogen-enhanced decohesion (HEDE) mechanism (due to hydrogen segregated along grain boundaries or adsorbed at crack tips) predominates for brittle intergranular cracking associated with limited plasticity, and (3) a hydrogen-enhanced localised-plasticity (HELP) mechanism (due to solute hydrogen ahead of cracks facilitating dislocation activity and promoting planar slip) contributes to slip-band cracking. HELP may also occur in conjunction with AIDE, *e.g.*, by facilitating the movement of emitted dislocations away from crack tips, for other fracture modes.

The AIDE/void-coalescence model seems not to have received the same level of acceptance as HELP and HEDE models in the literature despite the evidence for it, so it is worth briefly reviewing this evidence in the next section, especially as some advocates of the HELP mechanism have recently dismissed the AIDE mechanism without giving due consideration to the overall evidence^[57,58] or have ignored it completely.^[59] Conversely, the HELP mechanism of HE continues to be proposed by many workers without considering arguments that suggest that this mechanism does not play a major role for some fracture modes. Thus, it is worth re-iterating some of these arguments in a subsequent section, and also commenting on recent work where HELP has been unjustifiably invoked.

B. Summary of Evidence for the AIDE/Void-Coalescence Mechanism

The AIDE model for HE is supported by or consistent with:

1. The high hydrogen concentrations that are known to occur on surfaces and within a few atomic distances of surfaces.^[1,6,51,52]
2. Surface-science observations that adsorbed hydrogen can produce substantial changes in bonding at surfaces (change in surface relaxations/reconstructions/surface stresses)^[60–67] such that an effect on dislocation emission would be expected.
3. Quantum-mechanical-based modelling indicating that adsorbed hydrogen can facilitate dislocation emission from crack tips (when slip planes intersect crack fronts along their length as is often the case).^[68–70]
4. Predictions that dislocations would be emitted from crack tips more easily when hydrogen is present due to lowering of the unstable-stacking-fault energy.^[71,72]
5. The thermodynamic 'defactant' concept^[73] involving hydrogen lowering the formation energy of defects such as dislocations, thereby enhancing defect production (analogous to surfactants reducing surface energies in liquids).
6. Field-ion microscopy observations suggesting that hydrogen (used as an imaging gas) might facilitate dislocation emission,^[74] along with *in situ* TEM observations that dislocation emission occurs from

- crack tips (in addition to HELP within foils) when stressed thin foils are exposed to hydrogen gas.^[75]
7. TEM observations of dislocation arrangements around crack tips in bulk specimens after cracking in hydrogen environments.^[30]
 8. Remarkably similar characteristics for HE and adsorption-induced LME in some materials, *e.g.*, steels, Fe-Si, Ni, along with metallographic and fractographic evidence that cracking generally occurs by localised plasticity/void-coalescence.^[1,6,21–24]
 9. Its ability to account for (1) nano-dimpled cleavage-like cracking on {100} planes in <110> directions, with localised slip on planes intersecting crack tips, as observed in some fcc and bcc materials, (2) ‘non-crystallographic’, transgranular fractures that exhibit shallower dimples than those for ‘normal’ ductile fractures, and (3) dimpled intergranular fractures.^[1,6,21–24]
 10. Observations that hydrogen-assisted cracking (involving substantial localised plasticity) can occur at sufficiently high crack velocities, v , relative to hydrogen diffusivities, D , in some materials that hydrogen would not have time to diffuse more than one to two atomic distances ahead of cracks.^[1,6,21–24]
 11. Similarities between fracture surfaces produced under conditions where hydrogen can diffuse ahead of cracks, *e.g.*, during slow crack growth, and those formed at high crack velocities when only adsorbed hydrogen is present—with fracture surfaces indicating that crack growth occurs by localised plasticity.^[1,6,21–24]
 12. Abrupt transitions in crack-growth kinetics/fracture-surface appearance on changing environmental conditions, *e.g.*, adding oxygen to hydrogen environments, changing cycle frequency during fatigue, along with analyses of the effects of hydrogen-gas pressure and temperature on crack-growth kinetics, all of which indicate that embrittlement occurs very close to crack tips (within 5 nm) rather than in the general plastic zone—consistent with an adsorption mechanism (AIDE or HEDE).^[1,6,21–24,76]

The above observations and analyses provide compelling evidence for an AIDE mechanism in some circumstances. There is also no doubt that void nucleation often occurs in the plastic zone ahead of cracks in many cases, so that the AIDE process can facilitate the coalescence of cracks with voids. Voids are most easily nucleated by separation of particle-matrix interfaces (or fracture of large particles) but, if particles are few and far between, voids can also be nucleated at dislocation-cell walls, slip-band intersections, and vacancy clusters (promoted and stabilised by the presence of solute hydrogen).^[77–79] Solute hydrogen at all these sites could also facilitate nucleation (perhaps by HEDE) but, based on fractographic observations for adsorption-induced LME, and HE in circumstances where only adsorbed hydrogen is present, solute hydrogen is not essential.

The AIDE/void-coalescence process can occur on an extremely fine scale, such that the dimples on fracture surfaces may not be resolved by conventional SEM. Recent high-resolution SEM studies of cleavage-like fractures of a steel tested in hydrogen gas have revealed dimples that are as small as 50 nm diameter and 5 nm depth.^{[80]**} Previous studies, especially using

**In the original paper,^[58] the dimples were described as ‘mounds’, but it is now accepted that the features were dimples^[80] after it was pointed out that this was probably the case.^[81] Fine dislocation cells were observed beneath the fracture surfaces in the study,^[58] and voids could well have been nucleated at dislocation-cell boundaries, as has been observed by *in situ* TEM studies in the absence of hydrogen.^[79] It was originally suggested that decohesion was involved^[58] but, given that it is now accepted that fracture surfaces were dimpled, it seems more likely that AIDE predominates.^[81]

TEM of well-shadowed replicas, have also shown that nano-scale dimples are present on some intergranular and cleavage-like fractures that appeared to be featureless when observed by SEM.^[1,6,19–24,26] Some topographical features are so fine that it is not clear how they were formed, but a nano-void-coalescence process (producing dimples ~20 nm diameter and ~2 nm depth on fracture surfaces) is a possibility.[†]

[†]Recent ultra-high resolution SEM of mating areas of opposite fracture surfaces of a steel confirms that cleavage-like facets are dimpled on a nanoscale (15–20 nm diameter and 1–5 nm depth). See Ref. [82].

C. Suggestions for Further Work in regard to the AIDE Mechanism

The similarities between HE and LME are especially remarkable for pure nickel single crystals tested in Hg and H₂ (101 kPa) environments at 293 K (20 °C), in that the detailed fracture-surface appearance and crystallography (near {100}<110>), and the slip distribution around cracks, are exactly the same (Figure 10), as is the degree of embrittlement.^[1,22,24,81] Moreover, the fracture-surface characteristics depend somewhat on the crystal orientation, but are the same in Hg and H₂ environments for each orientation. In other words, the experimental observations clearly suggest that the mechanisms of cracking in H and Hg are the same (and involve adsorption). Thus, it would be interesting to use the quantum-mechanical-based modelling techniques (mentioned in section II-B) to compare the atomistic behaviour for {100}<110> cracks in nickel in Hg and (dissociated) H₂ (versus the behaviour in vacuum) to shed light on the electronic interactions/bond-weakening involved in the adsorption process, and the consequences of bond weakening. These comparisons would be an interesting test of the capabilities of the modelling techniques to see if they produced the same behaviour in H and Hg, as experimental observations suggest they should. If they do not, then seeing what modifications to the models would appear to be necessary to obtain the same behaviour may be instructive, *e.g.*, surface-coverages and sites of ‘adsorbed’

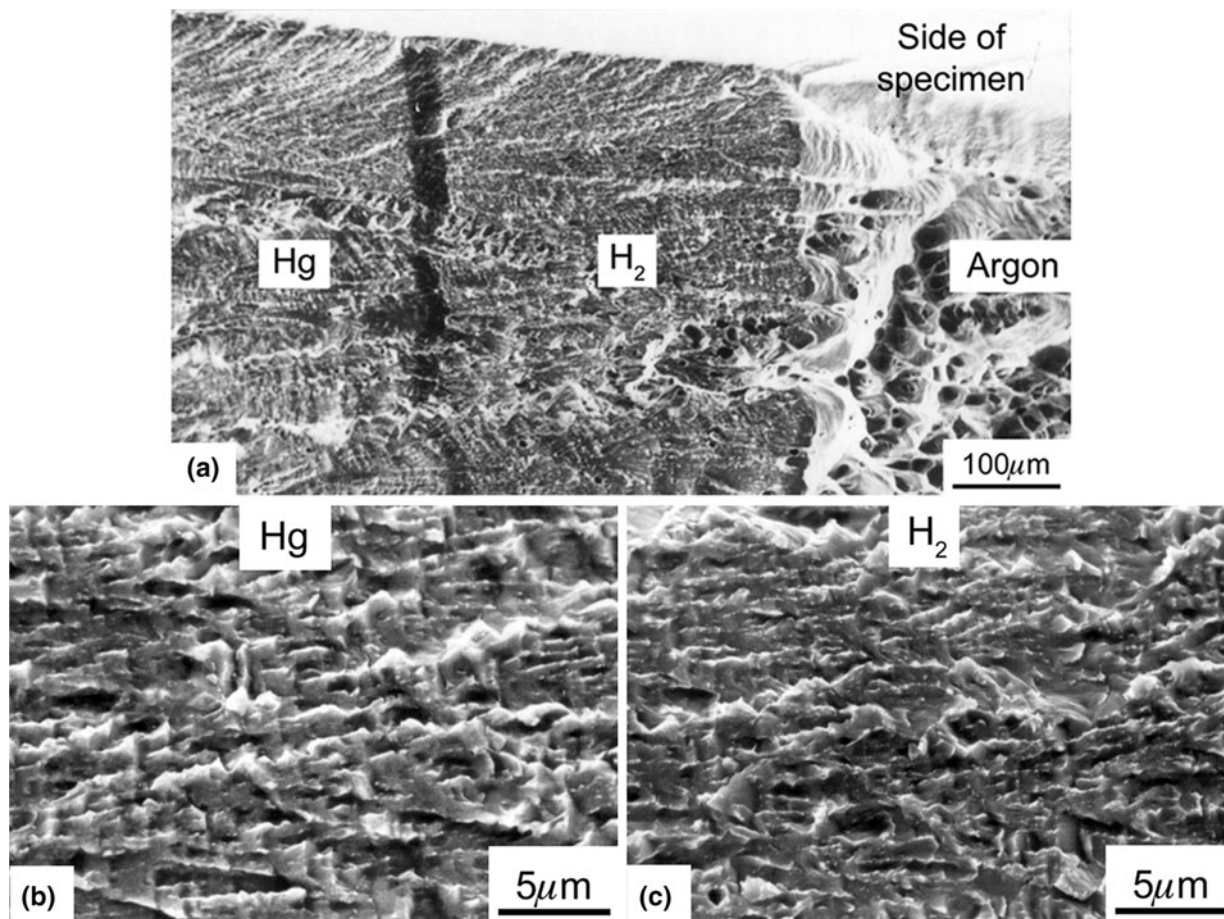


Fig. 10—(a) SEM of fracture surface of notched fatigue-precracked nickel single crystal cracked under monotonically increasing displacements ($v \sim 0.1$ mm/s) at 293 K (20 °C) in liquid Hg and then in gaseous H_2 (101 kPa) after completely evaporating mercury from cracks (and unloading slightly to produce a crack-front marking), and finally in dry argon, showing essentially identical cleavage-like appearance with numerous serrated steps after cracking in Hg and H_2 , and ductile dimpled fracture after cracking in argon: Higher magnification SEMs of the cleavage-like regions produced in Hg and H_2 are shown in (b) and (c), respectively. Note that testing separate specimens of the same crystal orientation in Hg and H_2 also produced fracture surfaces with the same appearance.^[1,22,24]

hydrogen and mercury atoms could be varied, and interatomic potentials ‘tweaked’, or solutions to quantum-mechanical calculations refined. This, of course, would not necessarily validate the models, but might provide insights into how the modelling could be improved.

It would also be worthwhile comparing (experimentally and theoretically) the characteristics of HE (for internal and external hydrogen environments) with LME for a variety of nickel-alloy single crystals, *e.g.*, solid-solution Ni-Cu alloys with Cu contents systematically varied. The degree of embrittlement, which could be measured from crack-tip-opening angles or spacings of fatigue striations, for example, would probably change with alloy content, and would probably be different in hydrogen and mercury environments. If this were the case, modelling studies and surface-science observations may shed further light on the electronic interactions involved in embrittlement. Other variables such as test temperature and hydrogen pressures could also be studied to gain further insights into the mechanisms involved. Such studies should be carried out on bi-crystals or polycrystals as well as single crystals.

Indeed, some comparisons of HE and LME have been carried out for Monel (Ni33 wt pct Cu) polycrystals, which showed close similarities in intergranular fracture behaviour for slow-strain-rate specimens tested in air after hydrogen-charging and those tested in liquid mercury, although there were sometimes differences in the degree of embrittlement.^[83]

Further work needs to be carried out to check the lowest D/v ratio at which hydrogen-environment embrittlement can occur. Previous work^[1,22,24] has shown that, for fatigue pre-cracked nickel single crystals tested in bending at high deflection rates in hydrogen (101 kPa) at 293 K (20 °C) ($D \sim 2$ to 5×10^{-10} cm²/s), cleavage-like cracking (associated with substantial plasticity) occurred at velocities of up to ~ 2 to 5×10^{-2} cm/s. This gives a D/v ratio of $\sim 10^{-8}$ cm—which is the value below which hydrogen should not diffuse more than one to two atomic distances ahead of cracks.^[84] In another study,^[85] tensile tests for notched nickel single crystals in H_2 resulted in cleavage-like cracking (and a similar degree of embrittlement) at temperatures from 293 K to 143 K (20 °C to -130 °C). Crack velocities were not measured but, based on the strain rates used ($\sim 10^{-5}$ s⁻¹), the crack velocities were probably

such that D/v ratios at 143 K ($-130\text{ }^{\circ}\text{C}$) were several orders of magnitude below that at which hydrogen could diffuse ahead of cracks. (The value of D at 143 K ($-130\text{ }^{\circ}\text{C}$) is $\sim 10^{-17}\text{ cm}^2/\text{s}$ based on a linear extrapolation of higher-temperature data [223 K to $>1273\text{ K}$ ($-50\text{ }^{\circ}\text{C}$ to $>1000\text{ }^{\circ}\text{C}$)]^[86]). Further studies along these lines need to be complemented by detailed metallographic and fractographic studies to determine whether ‘adsorbed’ hydrogen promotes crack growth by localised plasticity (as the initial observations suggest) or whether decohesion is also involved.

The contention that embrittlement can occur solely due to ‘adsorbed’ hydrogen is further supported by fatigue tests of nickel polycrystals in hydrogen gas (100 kPa), where transgranular crack-growth rates were substantially higher (up to 50 times), and ΔK thresholds were lower, in gaseous H_2 than in inert (N_2) environments, even at temperatures as low as 77 K ($-196\text{ }^{\circ}\text{C}$) (Figure 11).^[87] Linear extrapolation of ‘higher-temperature’ D versus $1/T$ (K^{-1}) data to 77 K ($-196\text{ }^{\circ}\text{C}$) gives a D value of $\sim 10^{-29}\text{ cm}^2/\text{s}$ —such an extremely low value that hydrogen would be unable to diffuse ahead of cracks even during slow fatigue crack growth.[‡] Given the significance of the data,

[‡]Linear extrapolation of diffusion data for Ni appears to be reasonable down to at least 123 K ($-150\text{ }^{\circ}\text{C}$), based on magnetic-relaxation measurements of jump frequencies at 173 K to 123 K ($-100\text{ }^{\circ}\text{C}$ to $-150\text{ }^{\circ}\text{C}$), and comparisons with jump frequencies calculated from diffusion measurements at high temperatures.^[88] Linear extrapolation to even lower temperatures is also probably valid since quantum-tunnelling effects, leading to diffusion faster than predicted from linear extrapolation of high-temperature diffusion data, appear not to be significant for fcc metals (unlike bcc metals). The difference between fcc and bcc metals probably occurs due to the greater distance (by a factor of about two) between the octahedral interstitial sites of hydrogen in fcc metals and the tetrahedral interstitial sites of hydrogen in bcc metals.^[88]

showing that solute hydrogen is not necessary for HE (contrary to widespread opinion), it would be worthwhile repeating the tests and carrying out more detailed fractographic observations, including characterising the dislocation structures beneath fracture surfaces, than carried out in this previous study in order to compare the observations with those where solute hydrogen is present ahead of cracks.

While the indirect evidence that hydrogen adsorption facilitates dislocation emission from surfaces/crack tips is reasonably convincing, direct experimental evidence is sparse, and there are no obvious experiments that could be carried out to demonstrate that AIDE occurs. Stress-strain behaviour in specimens with large surface-to-volume ratios might be sensitive to adsorption-induced dislocation emission from surfaces, but comparisons would have to be made between specimens with clean (film-free) surfaces and those covered by adsorbed hydrogen (without hydrogen in the bulk) in order to establish if adsorption facilitated dislocation emission. However, adsorbed hydrogen would diffuse into the bulk (and could affect stress-strain behaviour), and surface (oxide) films would re-form on clean surfaces quite rapidly except in ultra-high

vacuum. Such films could affect near-surface plasticity in a number of ways, *e.g.*, due to elastic interactions between film and substrate, mismatch of lattice parameters resulting in interfacial dislocations, and film-induced stresses.^[89] In fact, the observed effects of the environment on near-surface plasticity in metals^[89] are probably associated with environmentally induced changes in oxide-film properties rather than with a direct effect of adsorption on the metal surface. Notwithstanding these complexities, further thought should be given to experiments aimed at determining the effects of adsorption on dislocation emission from surfaces/crack tips.

D. Evidence for the HELP Mechanism for HE and Outstanding Issues

The HELP mechanism was first proposed by Beauchem in 1972^[90] for HE involving various fracture modes (including cleavage-like and intergranular fractures), and he was more concerned with the evidence that hydrogen-assisted cracking occurred by localised plasticity (not decohesion) rather than whether solute or adsorbed hydrogen was responsible^[91] (although he assumed it was the former). Since then, overwhelming evidence has been obtained that solute hydrogen can facilitate dislocation activity.^[1,6,55,57,71,72,80,92–94] Thus, HELP is supported by (1) *in situ* TEM observations of stressed thin foils exposed to hydrogen gas, (2) observations of slip lines on surfaces and dislocation arrangements in the interior for hydrogen-charged and hydrogen-free specimens, (3) some stress-strain data, (4) nano-indentation tests, (5) elasticity theory, (6) atomistic simulations, and (7) the ‘defactant’ concept mentioned earlier. The extent to which HELP is caused by hydrogen atmospheres around dislocations (which shield dislocations from repulsive interactions with other dislocations and other obstacles)^[93,94] and by hydrogen at dislocation cores^[71,72] does, however, require further investigation.

TEM observations, and observations of slip on the surfaces of bulk specimens, also show that solute hydrogen inhibits cross-slip and increases slip planarity, and these effects are probably instrumental in initiating slip-band fractures in some materials such as Ni-based superalloys and stainless steels.^[95–98] As the name implies, slip-band cracking occurs parallel to $\{111\}$ slip planes in fcc materials, and macroscopically flat facets exhibiting slip steps (from slip on intersecting systems) and, at high magnifications, shallow dimples, are observed. (Such fractures are distinctly different from cleavage-like fractures on $\{100\}$ or $\{110\}$ planes, which exhibit evidence of localised plasticity, with river lines and tear ridges parallel to specific crystallographic directions of crack growth.) Since strains within slip bands are more localised when solute hydrogen is present, voids are initiated within them more readily, either at slip-band intersections or at second-phase particles.

Increased slip planarity due to solute hydrogen could also influence intergranular and interfacial fractures to some extent since stress concentrations at dislocation

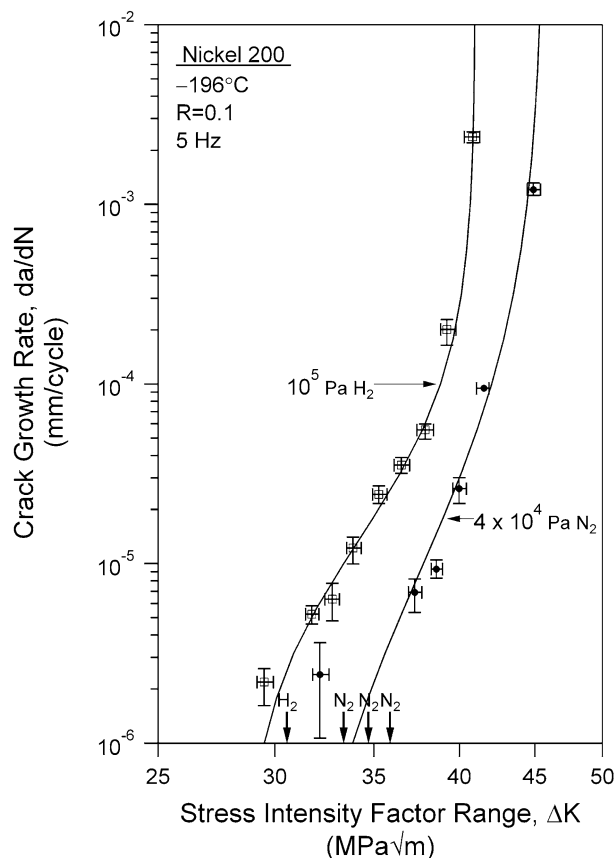


Fig. 11—Fatigue crack-growth rate (da/dN) versus ΔK for nickel 200 polycrystalline specimens tested in gaseous H_2 and N_2 at 77 K (-196°C), showing substantially faster crack-growth rates, and somewhat lower ΔK threshold, in H_2 due to the effects of adsorbed hydrogen. (Hydrogen diffusivity in nickel at 77 K (-196°C) is so low ($\sim 10^{-29} \text{ cm}^2/\text{s}$) that diffusion ahead of cracks can be discounted.) Data re-plotted from W. Wei, Ph.D thesis.^[87]

pile-ups at boundaries could be increased, thereby facilitating nucleation of cracks/voids at boundaries. On the other hand, hydrogen at grain boundaries can facilitate movement of grain-boundary dislocations, and slip transmission across boundaries could be promoted so that pile-up stresses could be reduced. Thus, the overall effect of solute hydrogen on intergranular fracture is uncertain,^[99] but could well be small since stresses at grain boundaries, especially around triple junctions, are often high, regardless of slip mode, due to local strain incompatibilities in adjacent grains.

It has been suggested, based on finite-element analysis (FEA) of crack growth in a steel, that local softening of material ahead of cracks due to HELP can promote void-growth and coalescence in general.^[57,100,101] These studies showed that several voids grew and coalesced simultaneously when there was a hydrogen-induced softened zone ahead of crack tips (whereas only the void closest to the crack tip coalesced with the crack in the absence of hydrogen), such that the fracture resistance was substantially reduced. However, a number of assumptions were made regarding the (pre-existing) void size and spacing, hydrogen concentrations, and softening parameters, so that whether or not the model is

realistic is debatable. For example, loss of hydrogen to voids (by dislocation transport) was not considered, and the extent of softening that was assumed (based on *in situ* TEM observations of dislocation activity in thin foils exposed to hydrogen gas^[102]) may be higher than that which occurs around crack tips in bulk specimens.

The *in situ* TEM observations—showing large increases in dislocation activity when hydrogen is introduced around stressed specimens for a wide variety of materials^[75,80]—at first sight do suggest that the degree of softening around crack tips due to HELP could be large, but there are other factors to consider. Firstly, hydrogen fugacities are probably much greater in the thin foils than at crack tips in bulk specimens (exposed to hydrogen gas) because electron irradiation promotes dissociation of hydrogen molecules.^[80,103] Secondly, introducing hydrogen around thin foils could result in surface effects on plasticity^[89] (due to reduction of oxide films and adsorption) as well as HELP. Thirdly, uneven hydrogen concentrations may occur within foils, owing to electron irradiation locally facilitating hydrogen entry, resulting in additional (dilatation-induced) stresses.^[53] Thus, it is difficult to estimate the degree of softening around crack tips due to HELP based on TEM studies. The degree of local softening around crack tips in bulk specimens due to HELP is also difficult to estimate from macroscopic behaviour (such as stress-strain curves) since local softening can have a variety of effects, including apparent hardening in some circumstances.^[104]

Another issue with the FEA model is that it does not capture the details of the dislocation activity involved in the growth and coalescence of cracks/voids, such as the relative extents of dislocation emission from crack/void tips and dislocation egress from nearby sources around crack/void tips. Thus, the model does not appear to predict that less blunting occurs during crack/void coalescence, leading to shallower dimples on fracture surfaces, as often observed after hydrogen-assisted cracking compared with cracking in inert environments—an observation that can be explained by the AIDE mechanism.^[1,6,24]

Whether HELP has a substantial effect on void growth and coalescence is also questionable because ductile behaviour is sometimes observed in materials with high concentrations of solute hydrogen. For hydrogen-charged nickel single crystals, cracking is initially ductile, producing deep dimples on fracture surfaces, but then transitions to cleavage-like fracture (Figure 12). This transition probably occurs when sufficient hydrogen has precipitated in voids to produce a critical surface concentration of adsorbed hydrogen to enable cleavage-like cracking (*via* AIDE) to occur from the voids.^[1,22,24] During the initial growth/blunting of the voids, solute hydrogen would have been present around them, but does not apparently produce any significant embrittlement. For hydride-forming materials, with high concentrations of solute hydrogen, large strains can sometimes be accommodated without embrittlement (from incipient cracks/voids), and it is only when brittle hydride phases are formed that embrittlement occurs.^[93]

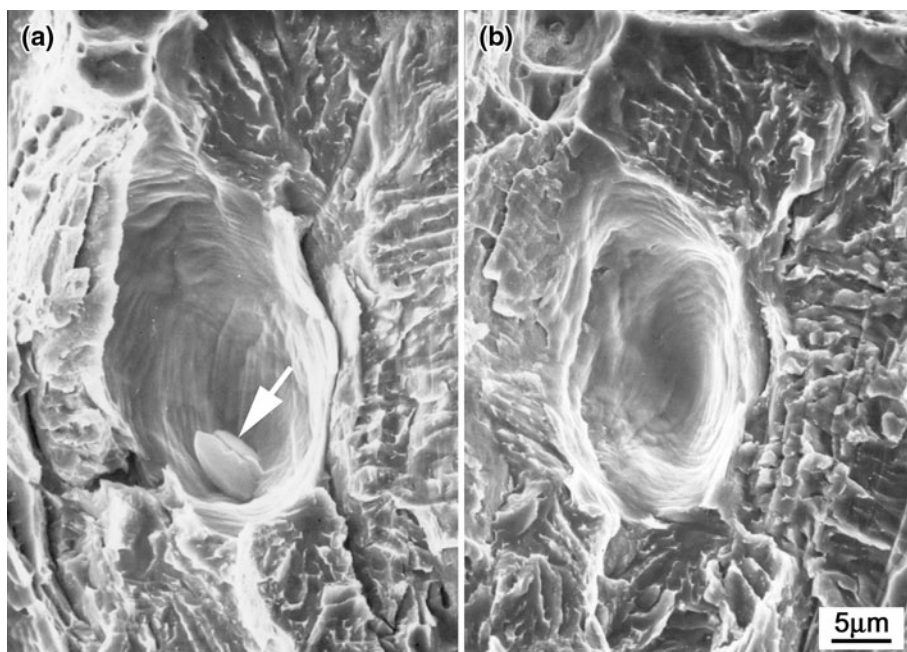


Fig. 12—SEMs of mating areas of opposite fracture surfaces of hydrogen-charged nickel single crystal tested at slow strain rate at 293 K (20 °C), showing large, deep dimple and associated second-phase particle (arrowed) surrounded by cleavage-like area, suggesting that hydrogen did not produce embrittlement until sufficient hydrogen had diffused to the void around the second-phase particle such that there was a critical surface coverage of ‘adsorbed’ hydrogen.^[1]

For a hydrogen-charged β -titanium alloy,^[105] specimens containing high concentrations of solute hydrogen exhibited transgranular, ductile (dimpled) fracture surfaces, with no change in ductility from 0 to ~0.2 H/M at 298 K (25 °C). However, increasing the hydrogen concentration to slightly higher levels resulted in an abrupt, temperature-dependent transition to cleavage-like cracking (Figure 13). These observations would not be expected if HELP had a major influence on void growth and coalescence (since HELP would be expected to operate in the ductile regime near the transition hydrogen-concentration). The observations could, however, be explained by the AIDE or HEDE mechanisms. For example, ‘adsorbed’ hydrogen at crack tips may cause a crack-tip-surface phase-transition (resulting in weakening of interatomic bonds) during crack growth when the hydrogen concentration was above a critical, temperature-dependent value.^[1,6]

In the above-mentioned study of β -titanium,^[105] detailed characterisation of fracture surfaces was not carried out, and it would be worth repeating the experiments (perhaps over a wider range of temperatures) to determine whether crack growth occurred by a localised nano-void-coalescence process or a decohesion process. High-resolution SEM and TEM of replicas of mating halves of fracture surfaces, and TEM studies of dislocation arrangements beneath fracture surfaces, should be performed to answer this question. Further studies of hydrogen-charged nickel single crystals, using different test temperatures, strain rates, and hydrogen concentrations, could also be instructive in regard to determining if HELP plays any role, in conjunction with AIDE or HEDE, in promoting cleavage-like cracking.

For cleavage-like fractures in normally ductile materials, it is difficult to see how just localising and facilitating dislocation activity ahead of cracks (due to HELP) would result in a change from a ‘non-crystallographic’, ductile dimpled fracture to a cleavage-like fracture with specific crystallographic planes and directions often inclined to the applied-stress direction. One would expect the HELP mechanism would just result in a more localised microvoid-coalescence process, with small, shallow dimples on fracture surfaces, without a change in the overall fracture plane—which would be expected to be macroscopically normal to the applied-stress direction in plane-strain regions (although cracking could occur along alternate-shear bands on a more microscopic scale as sometimes occurs for steels during fast fracture in air^[106]).

For intergranular hydrogen-assisted cracking, the experimental observations also suggest that HELP probably plays only a minor role, and that AIDE or HEDE are more likely to predominate. For example, when fracture surfaces show no obvious signs of dimples, and Auger-electron spectroscopy (AES) on both fracture surfaces provides evidence of equilibrium grain-boundary-impurity segregation having been present prior to intergranular cracking, fracture probably occurs along the grain boundaries by HEDE.^[92,107,108] If fracture occurred by HELP in a narrow zone adjacent to grain boundaries (due to high concentrations of hydrogen within ~100 nm of grain boundaries as advocates of HELP have suggested^[92]), then intergranular fracture surfaces should be clearly dimpled—as observed when fracture in aluminium alloys occurs within soft precipitate-free-zones (≥ 100 nm width) adjacent to grain boundaries.^[109] Moreover, fracture surfaces should not

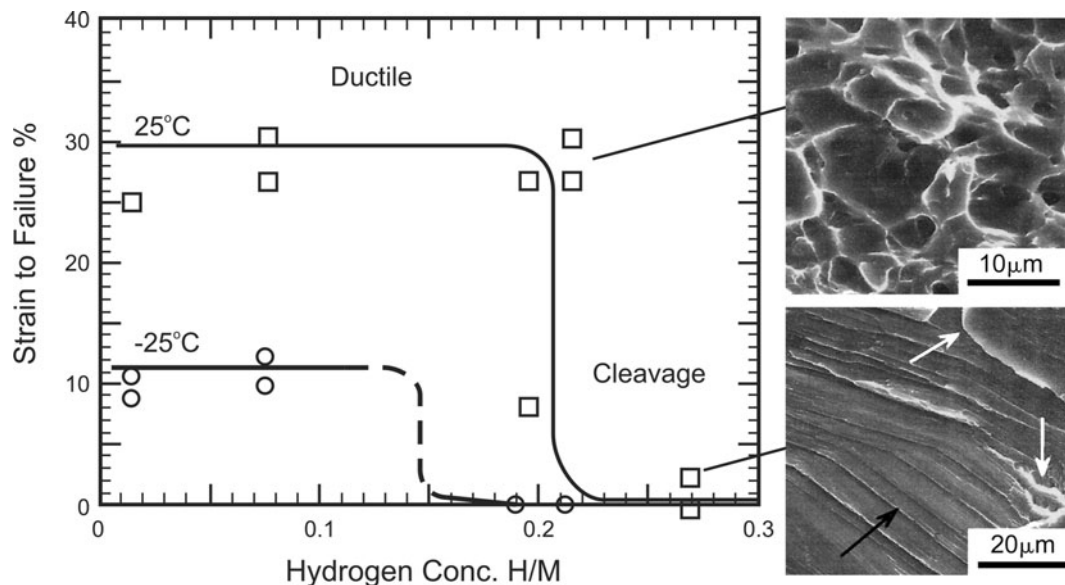


Fig. 13—Plot of strain-to-failure versus hydrogen concentration for β -titanium alloy tensile specimens tested in air at a slow strain rate, showing sharp, temperature and hydrogen-concentration dependent transitions, associated with changes from ductile dimpled fracture to cleavage-like fracture, as shown in the accompanying SEMs.^[105]

exhibit high concentrations of impurities if fracture occurred adjacent to grain boundaries and impurities were segregated exactly at the grain boundaries.

Where dimples are evident on intergranular facets after hydrogen-assisted cracking,^[1,6,24] the HELP mechanism could play some role as discussed previously, but the AIDE mechanism probably predominates. For the AIDE mechanism, intergranular cracking in hydrogen-gas environments (rather than transgranular cracking) could occur due to preferential dissociation and adsorption of hydrogen at grain boundaries intersecting crack tips. For internal hydrogen embrittlement, the highest concentration of hydrogen would be exactly at grain boundaries owing to pre-existing segregation at grain-boundary sites and transport of hydrogen by dislocations to boundaries (and voids at boundaries) during testing, *i.e.*, ‘adsorbed’ hydrogen would always be present to facilitate dislocation emission (or decohesion).

Recent claims^[59] that HELP promotes the formation of fine (200 to 400 nm) dislocation cell structures, observed just beneath intergranular fracture surfaces in a hydrogen-charged nickel tensile specimen, thereby establishing the conditions necessary for decohesion, are not justified. Firstly, no high-resolution fractographic observations were made to determine if fractures were dimpled on a fine scale, as observed on some facets in previous work for Ni,^[22] so that there was no basis for concluding that decohesion had occurred. Secondly, there were also no grounds for concluding that “dislocation processes and interactions are accelerated and enhanced by the presence of hydrogen” based on the dislocation-cell size beneath the fracture surface and comparisons with those reported for hydrogen-free nickel tensile specimens. Thus, it was assumed^[59] that the strain beneath the fracture surface would be the same as the macroscopic strain to failure, but the strain

beneath the fracture surface is not known, as it is made up of the (unknown) strain for crack-initiation plus the (unknown) (probably larger) *localised* strain associated with crack growth—with the latter not making much contribution to the macroscopic strain to failure.

The other claim in this study,^[59] that slip steps observed on intergranular facets produced by HE also provided “support for the importance of the dislocation processes accelerated by hydrogen”, is also without foundation. Such steps are observed on intergranular fracture surfaces to a similar extent when hydrogen effects are not involved, such as for LME of nickel.^[22] Moreover, previous work (*e.g.*, [110,111]) has shown that solute hydrogen does not have large effects on dislocation structures in strained nickel specimens. Solute hydrogen can also produce serrated yielding in nickel at low temperatures, where hydrogen atmospheres cannot keep up with dislocations and, hence, inhibit their movement. Brittle intergranular cracking is still observed in these circumstances,^[112] again suggesting that HELP is not that important for this fracture mode.

Notwithstanding all the unresolved issues and arguments to the contrary outlined above, the HELP mechanism does seem to have become accepted for HE in general (regardless of fracture mode) by some workers. However, they appear to have unjustifiably concluded that solute hydrogen must be responsible for HE simply because (1) hydrogen is generally present in the plastic zone ahead of cracks, (2) solute hydrogen can facilitate dislocation activity, and (3) fractographic observations suggest that cracking is accomplished by localised plasticity. Whether solute hydrogen (by itself) can have significant effects on intergranular and cleavage-like crack growth is, in fact, difficult to establish because adsorbed hydrogen at external or internal crack/void tips (or both) is generally present in conjunction with solute hydrogen, so that cracking could

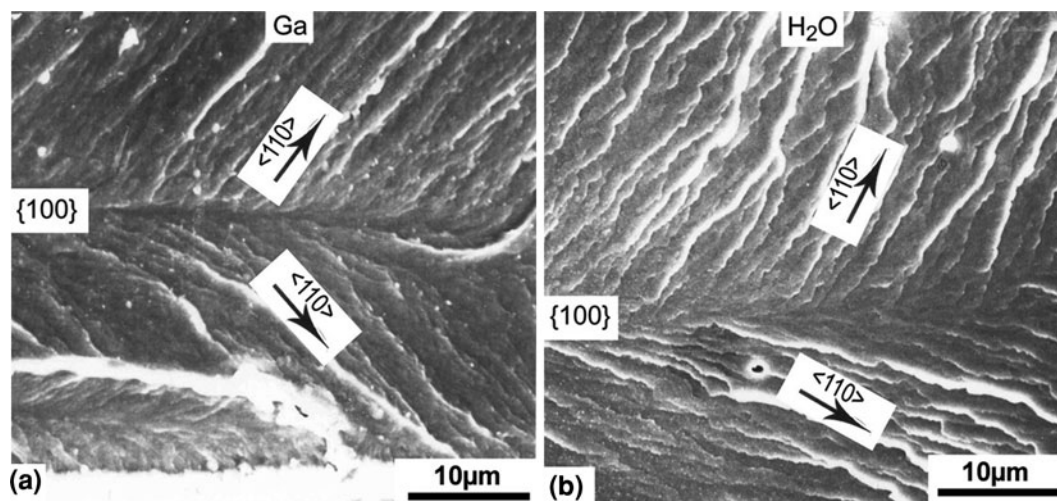


Fig. 14—SEMs of cleavage-like fracture surfaces of β -brass single crystals cracked in (a) liquid gallium at 303 K (30 °C) ($v \sim 5$ mm/s) and (b) distilled water at 293 K (20 °C) ($v \sim 10^{-3}$ mm/s), showing herringbone patterns of steps.^[1]

occur predominantly (or solely) by the AIDE mechanism (or adsorption-induced decohesion) rather than by the solute-hydrogen based HELP mechanism.

IV. STRESS-CORROSION CRACKING

A. HE Mechanisms

There is broad agreement that the mechanisms of SCC in many systems, *e.g.*, steels, Al, Mg, Ti, Ni alloys in aqueous environments, involve an effect of hydrogen generated by electrochemical reactions or by chemical dissociation of water at crack tips.^[1–6] However, there are the same controversies as discussed for HE, *viz.* whether AIDE, HELP, or HEDE are involved. Thus, the further work suggested for resolving some of the issues for HE would also have relevance to hydrogen-assisted SCC. Combinations of AIDE, HELP, and HEDE processes are likely to occur, with the dominant process depending on the fracture mode (which is material/environment/ K dependent) as discussed for HE. Thus, AIDE probably predominates for cleavage-like and dimpled intergranular fractures, HEDE probably predominates for brittle intergranular fractures, and HELP may make a minor contribution in some cases.^[1]

Evidence for an adsorbed-hydrogen mechanism for SCC includes: (1) the similarities between SCC, HE, and adsorption-induced LME (*e.g.*, same fracture plane and direction, and similar slip distributions around cracks in some cases) (Figure 14),^[1,24] and (2) observations that cleavage-like and intergranular fractures in Al, Ti, and Mg alloys can occur at such high velocities (under special testing conditions) that hydrogen would probably not have time to diffuse more than a few atomic distances ahead of cracks.^[1,24] For example, environmentally assisted cracking in notched, fatigue-pre-cracked Mg and Al-Zn-Mg single crystals and bicrystals tested in bending at high deflection rates in

aqueous environments, can occur at crack velocities ~ 10 mm/s, and characteristics of rapid and slow SCC are similar (Figure 15). Scepticism has sometimes been expressed about the high-velocity data (obtained by the present author), but the data are really not that surprising given that (1) Al and Mg are highly reactive metals where hydrogen dissociation and adsorption kinetics would be fast, and (2) it is well established that adsorption-induced LME can occur at even higher crack velocities (~ 100 mm/s).

An issue that needs to be resolved in regard to whether hydrogen can diffuse ahead of cracks (based on D/v ratios) are the hydrogen-diffusivity values in materials such as Al and Mg alloys. For Al alloys, data for hydrogen diffusivities at 293 K (20 °C) range from $\sim 10^{-6}$ to $\sim 10^{-10}$ cm²/s,^[113,114] while only estimates of D values at 293 K (20 °C) for Mg ($\sim 10^{-8}$ cm²/s) are available—based on extrapolation of limited high-temperature data (guided by activation energies for hydrogen diffusion in other hcp metals such as Ti and Zr).^[114] For many systems, it is also not clear whether hydrogen can diffuse more rapidly along grain boundaries than within grains.^[114] Clearly, further experimental data on hydrogen diffusivities (and trapping) need to be obtained to clarify the relative importance of adsorbed hydrogen at external crack tips vis-a-vis hydrogen at various sites ahead of cracks.

B. Adsorption Mechanisms Involving Species other than Hydrogen

1. Supporting evidence

Adsorption mechanisms based on dislocation emission or decohesion at crack tips may account for SCC in some systems where hydrogen is not involved. For example, cleavage-like SCC of zirconium alloys in iodine vapor is probably due to adsorption of iodine since other reactions can be discounted.^[115] There is also a strong case to be made that adsorption of ionic species

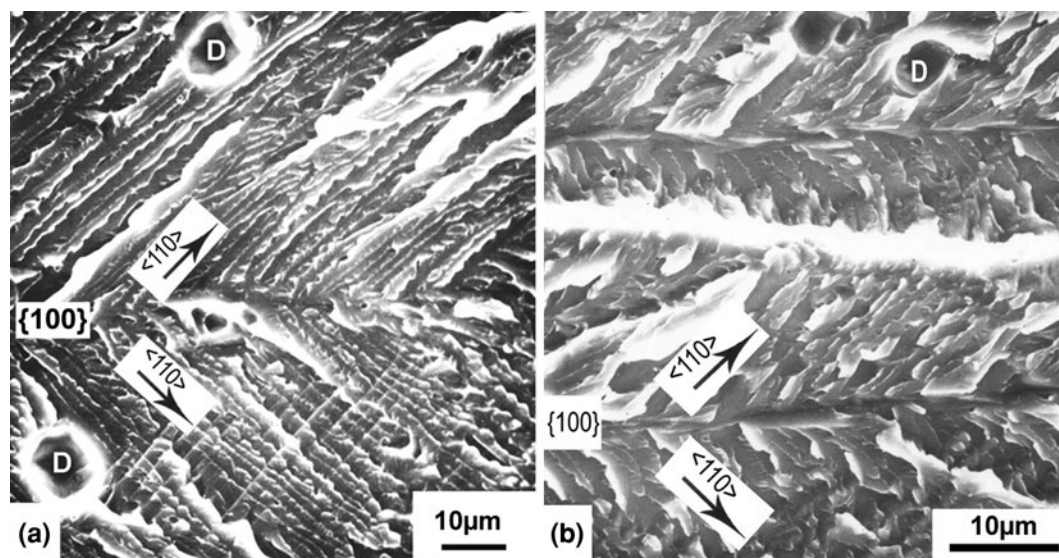


Fig. 15—SEMs of fracture surfaces of a peak-aged Al-Zn-Mg single crystal ($VH \sim 160$) (a) after SCC in water at 293 K (20 °C) using rapid dynamic straining ($v \sim 10$ mm/s), and (b) moist air at 293 K (20 °C) under sustained loading ($v \sim 10^{-7}$ mm/s), showing $\{100\}\langle 110 \rangle$ cleavage-like fractures with essentially identical appearance - a herringbone pattern of steps and isolated large dimples (D) - despite the eight orders of magnitude difference in crack growth rates. Nano-scale dimples are just resolvable using TEM of replicas.^[1,24] Also note close similarities with the characteristics for LME and SCC in β -brass in the preceding figure.

resulting from de-alloying at crack tips results in embrittlement.^[1,116,117] Thus, for some copper and silver alloys, *e.g.*, Cu-Zn, Cu-Au, Ag-Au, rapid cleavage-like or brittle intergranular fracture ($v \sim 10$ mm/s) has been observed in thin specimens tested immediately after superficial de-alloying (Figure 16).^[118–120] It has been proposed^[1] that adsorption of metal ions (perhaps co-adsorbed with anions) from highly concentrated solutions produced by de-alloying, and retained for short times in the nano-porous de-alloyed layer, is responsible for embrittlement since there would be no time for other reactions to occur during rapid cracking. If specimens are not tested immediately (within seconds to minutes) after de-alloying, brittle fracture does not occur—probably because the concentrated ionic solution in the nano-porous layer adjacent to the substrate mixes with, and becomes diluted by, less concentrated solution further from the interface, such that adsorbates are no longer embrittling.^[1]

The mechanism of slow, sustained-load SCC in alloys that undergo de-alloying is probably the same as that which occurs during rapid fracture in thin films since (1) fracture-surface characteristics are the same, and (2) there is convincing evidence that ‘slow’ SCC occurs by rapid crack jumps followed by periods of crack arrest.^[1,2] Thus, slow SCC could occur by the following repeated sequence of events: (1) formation of a nano-porous de-alloyed film at the crack tip, along with the production of an embrittling solution in the pores, (2) fracture of the film, followed by adsorption-induced cleavage-like or intergranular cracking of the substrate, and (3) crack-arrest and blunting, leading to the observed crack-arrest markings (CAMs) on fracture surfaces, when the supply of embrittling solution was exhausted. The above sequence (except for crack-arrest) would similarly account for transitions from brittle to

ductile behaviour sometimes observed during dynamic fracture tests in superficially de-alloyed thin specimens. Film-induced cleavage has been proposed as an alternative explanation for the above observations,^[2,118–120] but can probably be discounted for various reasons as discussed in a subsequent section and elsewhere.^[1]

Adsorption mechanisms have not been widely accepted in the past for a number of reasons that now do not stand up to scrutiny.^[1] For example, early adsorption mechanisms for SCC were based on surface-energy reductions, and it was argued that the overall fracture energy (dominated by a plastic-work term) would not be significantly reduced by decreasing the surface energy. This objection is not applicable to the AIDE mechanism, where the plastic strain required for crack growth is smaller (more localised) than that for cracking in inert environments. An adsorption mechanism for SCC based on decohesion, as proposed in early work, was considered questionable on the grounds that significant dislocation activity was observed and, hence, cracks were unlikely to be atomically sharp during SCC in ductile materials. The observations are, however, consistent with the AIDE mechanism. Further discussion regarding previous objections to adsorption mechanisms, and their rebuttal, can be found in a recent review of SCC.^[1]

2. Unresolved issues and suggestions for further work

An unresolved issue concerning rapid cleavage-like and brittle intergranular fracture in superficially de-alloyed specimens is that such fractures occur after testing not only at 293 K (20 °C) but also at near 77 K (−196 °C). Hence, it has been argued^[2,118] that the solution in de-alloyed layers would be frozen at low temperatures, so that it would be unable to be drawn into propagating cracks, as required for an adsorption

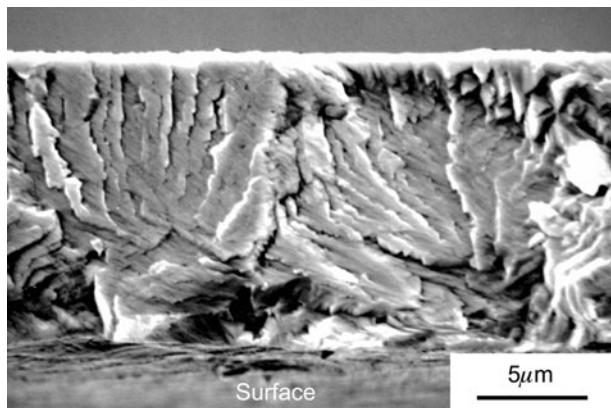


Fig. 16—SEM of fracture surfaces of α -brass foil rapidly fractured near 77 K (-196°C) after superficially de-alloying, showing cleavage-like appearance. Ductile fracture occurred if specimens were not de-alloyed.^[1,118]

mechanism. However, a counter-argument is that fracture of nano-porous ligaments in the de-alloyed film occurs by localised shear, thereby resulting in local heating.^[1] Frozen solution in the nano-porous layer could therefore melt and flow into growing cracks such that adsorption-induced embrittlement could occur even for tests carried out at nominally low temperatures.

The suggestion that localised heating occurs during fracture of de-alloyed films is based on (1) observations that micro-pillars do fracture by localised shear,^[121] and (2) observations in other materials, such as metallic glasses, that localised shear can produce substantial temperature rises [up to 800 K (800°C)].^[122,123] However, there is no direct experimental evidence that sufficient local heating occurs during fracture of nano-porous films to melt frozen solution within pores, and it is difficult to envisage what experiments could be done to show whether or not this occurs. For example, thermographic techniques would probably not be sufficiently sensitive. Nevertheless, further consideration should be given to this issue.

Further characterisation of cleavage-like and brittle intergranular fractures produced by fast fracture of superficially de-alloyed thin specimens should also be undertaken, *e.g.*, (1) SEM at higher magnifications than has been reported to date (plus examination of mating areas of opposite fracture surfaces), (2) electron-back-scattered diffraction to estimate strains and determine crystallographic orientations of fracture planes, and (3) TEM examination of thin foils adjacent to fracture surfaces to determine dislocation distributions. In regard to the last point, fracture surfaces of alloys should be electroplated, and then electron-transparent thin foils normal to the fracture surface prepared by electropolishing techniques, to avoid introducing damage (additional dislocations) that can be produced by ion-beam thinning techniques.

Further SEM and TEM fractographic studies also need to be carried out for slow SCC, as suggested for fast fracture of thin specimens, so that a more detailed comparison can be made between the two phenomena. In general, high-resolution fractography for slow SCC is

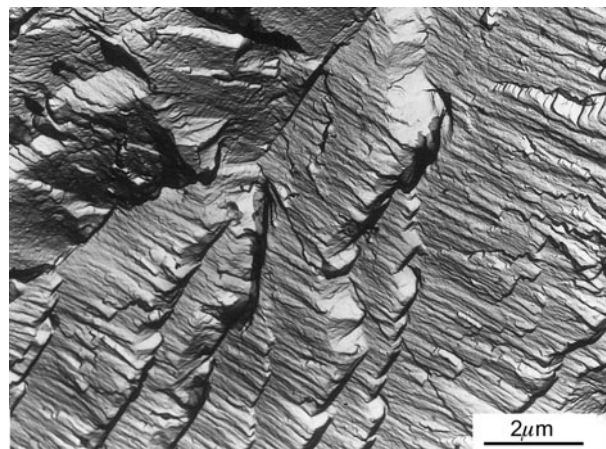


Fig. 17—TEMs of secondary-carbon replicas of cleavage-like fracture surfaces produced by SCC of α -brass in an ammoniacal environment containing a high concentration of copper ions (so that insignificant corrosion occurred) showing fine serrated steps, slip lines, undulations, and nanoscale dimples. Replicas were shadowed with Ge at low angles and examined at 30° tilt to maximise contrast.^[1]

not worthwhile owing to corrosion/de-alloying of fracture surfaces after crack growth, but testing in a highly concentrated ionic solution appears to prevent such corrosion.^[124] The fracture-surface characteristics after SCC in such solutions suggested that cleavage-like crack growth occurred by a localised-plasticity/nano-void coalescence process (probably AIDE) rather than by a decohesion process (Figure 17).^[1,116] Interestingly, no CAMs were detected after SCC in the concentrated ionic solution, suggesting that crack growth may have been continuous—perhaps because intermittent de-alloying to produce concentrated ionic solutions was unnecessary. Further work is required to investigate these aspects more thoroughly.

The effects of adsorption on substrate bonding also need to be better characterised and understood, and substantial advances are being made using electrochemical scanning-probe-microscopy techniques.^[125–128] For example, potential-induced reconstructions (reflecting changes in surface bonding) have been observed for Au and Cu surfaces in aqueous environments, and transition potentials depend on the ionic species present. Surface-relaxations (as well as reconstructions) are also likely to be affected by potential-dependent adsorption of ionic species, but few experimental studies have been carried out. Most electrochemical surface-science studies are directed towards understanding catalysis, but there is much to be learnt that is relevant to EAC from using these techniques (and complementary atomistic modelling studies), even though plane surfaces have to be examined experimentally. Studying stressed specimens with highly defective surfaces would, of course, go some way towards reproducing the conditions at crack tips.

C. Dissolution Mechanisms

It needs to be emphasised that adsorption mechanisms are not ‘universal’, and that other mechanisms such as those based on dissolution are applicable in

some circumstances. There is evidence that intergranular SCC occurs by dissolution along grain boundaries in systems where grain-boundary phases or segregation of elements results in regions that are anodic to their surroundings.^[129] Dissolution mechanisms could, of course, occur in conjunction with other processes, *e.g.*, anodic dissolution behind crack tips along with cathodic production of hydrogen at crack tips leading to HE, or dissolution of anodic grain-boundary precipitates at crack tips with HE of regions between precipitates.

Particularly convincing evidence for a slip-dissolution mechanism has been obtained for Fe-Si bicrystals in ammonium-carbonate solutions, based on testing specimens with well-defined grain-boundary misorientations (with respect to slip systems intersecting crack fronts) and known levels of segregation at grain boundaries. These tests used a range of crack-tip strain rates and applied potentials, and were supplemented by electrochemical measurements on plane surfaces and by comparisons with single-crystal behaviour.^[129] A similarly rigorous approach needs to be taken for other cases of intergranular SCC where it is suspected that dissolution results in crack growth.

D. Other SCC Mechanisms

The proposed film-induced cleavage (FIC) mechanism for SCC (and rapid fracture in superficially de-alloyed thin films)^[130] involves rapid fracture in a corrosion-induced film (especially nano-porous de-alloyed films), which continues to propagate into the substrate by cleavage or brittle intergranular fracture for distances of up to $\sim 100\ \mu\text{m}$ (but more typically $\sim 1\ \mu\text{m}$ during sustained-load SCC). It was envisaged that (1) dislocation activity is suppressed during crack growth at high velocities so that brittle fracture occurs even in normally ductile fcc materials, and (2) crack-arrest and blunting occurs, producing crack-arrest markings (CAMs) on fracture surfaces, when sufficient dislocation sources are activated.

A number of observations cast doubt on the FIC mechanism, such as (1) the fact that fracture of ligaments in de-alloyed films would be individual events that would not be coupled to fracture in the substrate, (2) fractographic observations showing that significant localised plasticity is associated with ‘cleavage’ fractures, contrary to expectations, (3) estimates of crack velocities during ‘cleavage’ that are orders of magnitude less than would be theoretically required for cleavage in fcc materials, (4) the difficulty in explaining the large variations in crack-jump distances (from $\sim 1\ \mu\text{m}$ to $100\ \mu\text{m}$) (which depend on material, potential, *etc.*), and (5) observations on model systems, where cracks in a brittle phase or a brittle surface coating do not continue in a brittle manner into a ductile material.^[1,131] The explanation, in terms of the FIC mechanism, for the effects of delay times in preventing brittle fracture in superficially de-alloyed thin specimens, *viz.* that coarsening of ligaments in de-alloyed layers during delay times somehow prevents them triggering brittle fracture in the substrate, is also vague and unconvincing.^[1] It would, of course, be interesting to obtain the views and

possible counter-arguments from proponents of the FIC model regarding all the above issues.

Other proposed mechanisms include those based on vacancies ahead of crack tips, corrosion-enhanced localised plasticity, and surface-mobility. These mechanisms have been discussed in detail elsewhere,^[1–4] and will not be discussed further here, except to comment that numerous workers consider that the surface-mobility mechanism (SMM),^[132] based on surface-diffusion of atoms from the crack-tip to sites on crack walls just behind the crack tips, is not viable (see references in [1]). It is, however, worth noting that the concept of environmentally enhanced surface-mobility is, in some respects, also the basis of the AIDE mechanism. Thus, dislocation nucleation at crack tips (*i.e.*, the formation of a dislocation core and surface step by shear movement of atoms) involves mobility of surface and near-surface atoms, which is facilitated by adsorption-induced weakening of substrate interatomic bonds. Some of the apparently successful predictions of the SMM, such as correlations between rates of SCC and measures of surface mobility, *e.g.*, exchange-current density, might therefore be due to a link between surface mobility and dislocation nucleation at crack tips, and further consideration of this idea is warranted.

V. RATE-CONTROLLING PROCESSES FOR HE AND SCC

The dependence of crack velocity (v) on stress-intensity factor (K) for HE and SCC is similar to that observed for LME, *viz.* a marked dependence at low K , and little or no dependence at intermediate to high K .^[1–5] Likewise, several plateau velocities are sometimes observed for SCC, and the plateau velocity for a given material and environment can depend on testing procedures, such as whether K increases or decreases with increasing crack length. However, general similarities in the shape of v - K plots do not necessarily indicate that similar rate-controlling processes are involved. Indeed, while basic mechanisms may be the same in some cases, the rate-controlling processes undoubtedly depend on the material and environment.

For HE, the temperature dependence of crack-growth rates indicates that the rate-controlling process is different for internal hydrogen embrittlement (IHE) and hydrogen-environment embrittlement (HEE), with the former (below a certain temperature) probably controlled by hydrogen diffusion to hydrostatically stressed crack-tip regions, and the latter probably controlled by adsorption kinetics in most circumstances^[5,133–135] (but perhaps not all^[136]). Precipitous decreases in crack velocities above a critical temperature (which depends on the steel composition, *etc.*) for both IHE and HEE are probably best explained in terms of abrupt reductions in the concentrations of adsorbed hydrogen (at surface and just-sub-surface sites).^[5,137–139] However, it would be worthwhile revisiting this topic to see if the latest surface-science and modelling techniques can provide additional understanding.

For SCC, the rate-controlling processes are generally not well established since there are more sequential steps to consider compared with LME and HE. As well as adsorption and hydrogen-diffusion kinetics, other possible rate-controlling steps for SCC include (1) transport of environmental species to and from crack tips (and crack-tip chemistry changes), (2) electrochemical reactions (anodically or cathodically controlled) (3) repassivation kinetics, and (4) the crack-advance processes themselves. For Cu-Zn and Cu-Al alloys, there are good correlations between rates of de-alloying (on plane surfaces) and rates of SCC, suggesting that de-alloying kinetics are critical.^[1,2] For Al-Zn-Mg-Cu alloys in NaCl solutions, data suggest that there are correlations between stage-II crack velocities and electrochemical-reaction rates.^[140] Thus, the plateau velocity was higher when there was a greater potential difference between anodic $\text{MgZn}_2(\text{Cu})$ grain-boundary precipitates and adjacent cathodic areas (due to less Cu in precipitates), such that there was a greater driving force for the generation of hydrogen.

There have been numerous attempts to establish the rate-controlling steps from the temperature dependence of crack-growth rates, and comparison of the activation energies for crack growth with activation energies for the various processes obtained from independent data, *e.g.*, hydrogen-permeation rates in unstressed specimens. However, the legitimacy of such comparisons is debatable, especially for SCC where there are so many possible processes involved, since the activation energy of the rate-determining step will generally be affected by all the preceding steps.^[141] For example, if hydrogen diffusion were rate-controlling for SCC, then the kinetics of hydrogen generation and hydrogen adsorption would affect the hydrogen flux, with hydrogen-generation rates depending on corrosion potential, solution chemistry, ionic diffusion rates, and film-formation rates—all of which are temperature dependent. In addition, activation energies for some processes are sometimes quite similar, while the activation energies for some processes such as adsorption at stressed crack tips are usually not available. Another issue is that a line of best fit is sometimes drawn through crack-growth rate versus $1/T$ (K^{-1}) data to determine the activation energy, when two (or more) lines with somewhat different slopes would better fit the data. Different activation energies in different temperature regimes are known to occur in some systems, and could be more common (and less obvious) in other systems.

Observations of environmentally assisted cracking of Al-Zn-Mg single crystals (under cyclic loads) provide an interesting example of the subtleties and complexities involved in establishing rate-controlling steps from the temperature dependence of crack-growth rates. Thus, crack-growth rates per cycle at high ΔK (measured from fatigue-striation spacings) decreased with increasing temperature for a distilled water environment, but increased with increasing temperature for an NaCl solution (Figure 18).^[142] There were abrupt changes in the spacing of striations on changing temperature, but no change in the general characteristics of crack growth, which occurred on $\{100\}$ planes in $\langle 110 \rangle$

directions—consistent with the AIDE model involving adsorbed hydrogen. Another example of subtle behaviour is that changing the electrochemical potential had no effect on crack-growth rates in ternary Al-Zn-Mg alloys, but had marked effects for Al-Zn-Mg-Cu alloys containing 1 to 2 wt pct Cu [at 293 K (20 °C)].^[142,143] Surface-reaction kinetics for the dissociation of water molecules are probably critical for these effects, especially since hydrogen-diffusion rates would increase with increasing temperature regardless of the environment. However, further work using various electrochemical and surface-science probes is required to obtain a more detailed understanding, not only for the above systems but more generally.

VI. CONCLUSIONS

1. Liquid-metal embrittlement (LME) in systems where crack-growth rates are 10 to 100 mm/s is almost certainly due to adsorption-induced weakening of substrate interatomic bonds at crack tips. An adsorption-induced dislocation-emission (AIDE)/void-coalescence mechanism best accounts for the observations when slip is localised on planes intersecting cracks and fracture surfaces are dimpled—noting that the void-coalescence process may occur on such a localised scale that dimples on fracture surfaces may not be resolved by SEM fractography. However, an adsorption-induced decohesion process cannot be discounted when fracture surfaces are featureless.
2. Solid-metal induced embrittlement (SMIE), metal-vapor induced embrittlement (MVIE), and LME probably occur by the same mechanisms in many systems given that the characteristics of embrittlement are similar. The rate-controlling steps for the different types of metal-induced embrittlement, however, are different: Surface self-diffusion of embrittling metal atoms to crack tips controls the rate of SMIE, while vapor transport probably controls the rate of MVIE. For LME, capillary flow may limit crack-growth rates (to ~ 100 mm/s) in some systems, but adsorption kinetics are probably the limiting step in other cases.
3. Mechanisms of hydrogen-assisted cracking (when hydrides do not form) are probably different for different fracture modes, which depend on the material/heat-treatment/strength, testing conditions, and other variables. An AIDE/void-coalescence process probably predominates for microscopically dimpled fractures along transgranular and intergranular paths in steels, and for nano-dimpled cleavage-like fractures. A hydrogen-enhanced decohesion (HEDE) mechanism probably predominates for brittle intergranular fractures especially if other embrittling segregants are present at grain boundaries. A (solute) hydrogen-enhanced localised-plasticity (HELP) mechanism probably makes a significant contribution to slip-band fractures, but probably makes only a minor contribution to facilitating crack growth for other fracture modes.

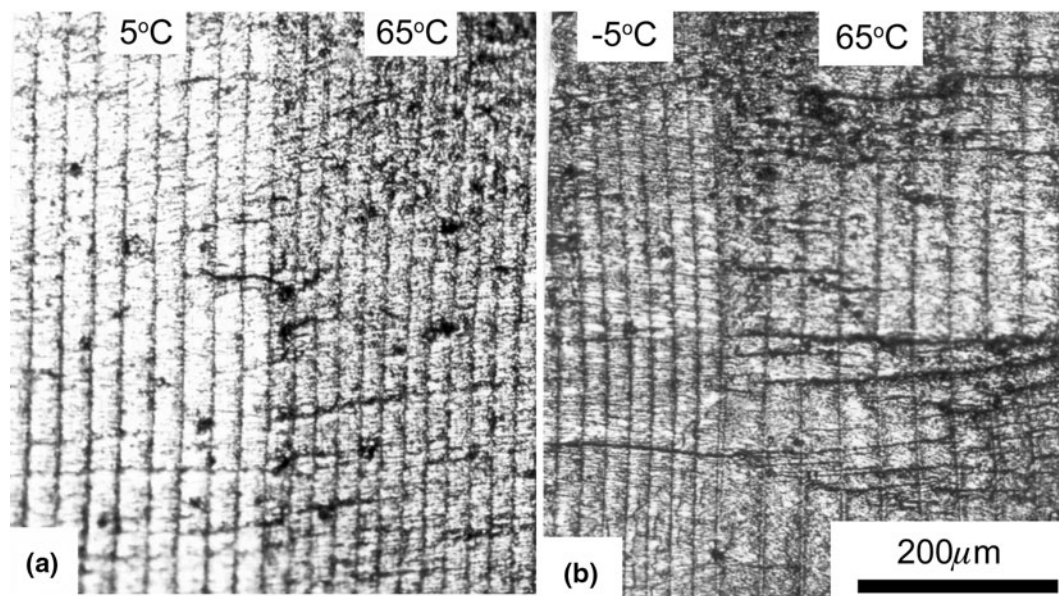


Fig. 18—Optical micrographs of fracture surfaces of Al-Zn-Mg single crystals (at same magnification) showing (a) decrease in striation spacing with increased temperature in distilled-water, and (b) increase in striation spacing with increased temperature in 3.5 pct NaCl solution.^[142]

4. Stress-corrosion cracking (SCC) in many systems (e.g., steels, Al, Ti, Mg, Ni alloys in aqueous environments) involves hydrogen generated by electrochemical reactions or chemical dissociation of water, and AIDE or HEDE mechanisms are probably responsible. For SCC in systems where de-alloying occurs (and hydrogen effects can be discounted), adsorption of ions from highly concentrated solutions produced by de-alloying and retained in nano-porous de-alloyed films, is probably responsible for cleavage-like and brittle intergranular cracking by way of facilitating dislocation emission or decohesion.
5. Objections to previously proposed adsorption mechanisms (based on surface-energy reductions or decohesion) are not valid for the AIDE mechanism, which involves reductions in the plastic work of fracture. SCC mechanisms based on adsorption are also no longer considered to be universally applicable, and it is generally acknowledged that slip-dissolution and other mechanisms occur in some materials and environments.
6. The film-induced cleavage mechanism, proposed to account for SCC in de-alloying systems in particular, can be discounted for various reasons—not the least being that brittle fracture in de-alloyed films involves fracture (localised shear) of discrete nano-scale ligaments that are not directly contiguous with the substrate (at the location of fracture) so that there is no reason why cracks in the de-alloyed film should continue by cleavage into the normally ductile substrate. The detailed fracture-surface characteristics are also inconsistent with the postulated atomically brittle cleavage process.
7. The surface-mobility mechanism (SMM), based on environmentally enhanced surface diffusion, also proposed for SCC involving de-alloying (and more generally) is also considered to be unviable for a

variety of reasons, but the concept of environmentally enhanced surface mobility has interesting parallels with the AIDE mechanism (where adsorption weakens interatomic bonding at crack tips thereby facilitating shear movement of atoms within the first few atomic layers). Thus, some of the claimed predictive capabilities of the SMM may arise because the AIDE mechanism is applicable.

8. There have been a number of ‘critical’ experiments (or at least ones that are particularly informative) regarding the processes that are the most likely to be responsible for cracking in particular systems, and these experiments should not be ignored when considering mechanisms of EAC. There are further critical experiments (and atomistic modelling), that could be carried out to advance the understanding of environmentally assisted cracking, and it would be worthwhile repeating some previous experiments using more advanced characterisation and measurement techniques, as outlined in the present paper. Further studies of LME are merited in particular, not only for understanding LME *per se*, but to provide a better basis for understanding the more complex embrittlement phenomena of HE and SCC.

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