

CONCERNING THE RELATIVE IMPORTANCE OF DECOHESION VERSUS SLIP AND ADSORBED VERSUS SOLUTE HYDROGEN ON FRACTURE BEHAVIOUR

S. P. LYNCH¹

¹Defence Science and Technology Organisation, Melbourne, Australia

ABSTRACT

Internal hydrogen embrittlement, hydrogen-environment embrittlement, and stress-corrosion cracking in non-hydride-forming materials could be associated with localised hydrogen concentrations at (i) surface and just-sub-surface sites ('adsorbed' hydrogen) at external or internal crack tips, (ii) grain boundaries and particle-matrix interfaces, (iii) normal interstitial sites subjected to high triaxial stresses, and (iv) dislocations. There seems to be emerging consensus that the relative importance of these sites of localised hydrogen concentrations in producing embrittlement depends on the fracture mode – which, of course, depends on the material, microstructure, strength, environment, and other variables. It also seems likely that embrittlement occurs due to localised plasticity, decohesion, or combinations of these processes – again depending on the fracture mode. For example, cleavage-like fractures appear to be promoted mainly by an adsorption-induced dislocation-emission (AIDE) process, brittle intergranular fractures probably occur mainly by hydrogen enhanced decohesion (HEDE), and slip-band fractures probably involve hydrogen-enhanced localised-plasticity (HELP). There are, however, many outstanding issues that need to be addressed before there is more general agreement regarding mechanisms of hydrogen embrittlement.

In the present paper, some of the outstanding issues are critically discussed with the aim of provoking further debate and providing suggestions for future experimental and modelling studies. Important questions addressed include: (i) Can one distinguish between decohesion and localised plasticity mechanisms using fractographic or other methods?, (ii) Are there critical experiments which enable the relative importance of 'adsorbed' and 'solute' hydrogen to be assessed?, (iii) What effects do 'adsorbed' hydrogen have on bonding at crack tips that could facilitate an AIDE process, and what other parameters control dislocation emission from crack tips? It is concluded from discussion of these and other questions that the process of dislocation emission from crack tips is arguably the most important and least understood of all the possible processes involved in embrittlement.

1 INTRODUCTION

There are three mechanisms proposed for hydrogen-embrittlement (HE) that have significant experimental and theoretical support, viz. (i) Hydrogen-Enhanced Decohesion (HEDE) involving weakening of interatomic bonds in regions of high hydrogen concentrations (crack-tips, high triaxial-stress regions ahead of crack tips, and interfaces) leading to atomically brittle fracture, (ii) Hydrogen-Enhanced Localised-Plasticity (HELP) involving easier dislocation motion when dislocations, and obstacles to them are surrounded by hydrogen atmospheres, and (iii) Adsorption-Induced Dislocation-Emission (AIDE) involving weakening of interatomic bonds at crack tips due to 'adsorbed' hydrogen. Combinations of mechanisms, with the dominant mechanism depending on the fracture mode (and, hence, the material, microstructure, strength, environment, stress-intensity factor, and other variables), have been proposed (Lynch [1]). There appears to be some consensus emerging that cleavage-like fractures are mainly promoted by AIDE, brittle intergranular fractures probably occur mainly by HEDE, and slip-band fractures probably involve HELP (Lynch [1], Hänninen [2]). However, there are still significant disagreements regarding mechanisms of embrittlement, and some of the critical issues are discussed in this paper.

2 SOME CRITICAL ISSUES

2.1 *Can one distinguish between decohesion and localised-slip processes using fractographic or other methods?*

Decoherence theories of HE were dominant in the 1960's and 70's but declined in popularity as high-resolution fractographic studies and in-situ TEM observations of hydrogen-assisted cracking suggested that crack growth often occurred by localised-plasticity/microvoid-coalescence processes (Lynch [1,3]). Many papers in the literature unjustifiably supported decohesion theories on the basis that essentially featureless fracture surfaces are observed using scanning-electron microscopy (SEM) with a resolution not capable of detecting small, *shallow* features such as dimples on fracture surfaces. State-of-the-art SEM, using field-emission guns, is now capable of resolving much finer details than previously, but it is debatable whether modern SEM is capable of resolving sufficiently shallow dimples to conclude that atomically brittle decohesion has occurred when fracture surfaces are featureless.

Transmission-electron microscopy (TEM) of replicas of fracture surfaces (which pre-dates SEM and is now rarely used) still appears to be better at resolving small, shallow features than SEM, providing that replicas are shadowed at low angles ($\sim 10^\circ$) and viewed under optimum conditions (Lynch [3]). TEM of replicas of fracture surfaces, or techniques with higher resolution of shallow profiles such as Atomic Force Microscopy (AFM) or Scanning Tunnelling Microscopy, need to be used to show that fracture surfaces are atomically smooth before one can conclude that crack-growth has occurred primarily by decohesion. The fact that dimples could be as small as 50nm diameter, with cusps possibly only 10-20nm high, needs to be borne in mind – as does the fact that dimples (or flutes) can be very elongated (particularly in hcp metals).

Small, shallow dimples have been observed on cleavage-like, intergranular, and slip-band fractures after environmentally assisted cracking in a number of materials, including Fe, Ni, Al, Mg, Ti, and Cu alloys. Interestingly, it appears that a nano-void coalescence process can occur even in the most brittle of materials, viz. during SCC of glasses where AFM observations of cracks on the sides of specimens show voids ~ 20 nm several nanometres ahead of cracks (Célarié et al. [4]). Molecular dynamics and other modelling techniques also show nano-sized voids forming ahead of cracks under some conditions [5].

The presence of dimples on fracture surfaces indicates that growth and coalescence of voids ahead of cracks occurs predominantly by localised plasticity. However, decohesion could be involved in nucleation of voids at particle-matrix interfaces, slip-band intersections, slip-band/grain-boundary intersections, and vacancy clusters – and could be aided by hydrogen concentrations at these locations. Determining whether this is the case from fractographic observations is probably not possible.

Observations that cleavage-like cracks produced by HE and SCC in fcc and bcc materials occur preferentially in $\langle 110 \rangle$ directions on $\{100\}$ planes, i.e. such that crack fronts lie along the line of intersection of slip planes and crack planes, suggest that crack growth occurs, at least in part, by a slip process – particularly when there is evidence that slip planes intersecting crack fronts are active (Lynch [3]). However, $\{100\} \langle 110 \rangle$ cleavage cracks have also been observed in circumstances where little slip appears to be associated with cracking, e.g. tungsten single crystals in inert environments at low temperatures (Riedle et al. [6]). Decoherence is presumed to occur in this case, with the unexpected preference for $\langle 110 \rangle$ directions of cracking explained in terms of a lattice-trapping effect. For example, separation of atoms at crack tips may involve *incipient* shear movement of atoms, in combination with tensile separation of atoms, which is easier for crack fronts intersecting potential slip planes. Thus, one can not assume that crack growth involves

actual emission of dislocations from crack tips just based on the preference for $\{100\} \langle 110 \rangle$ cracking – evidence of slip on planes intersecting crack tips is also required.

Examples of HAC and SCC where $\{100\} \langle 110 \rangle$ cracking occurs with extensive slip on planes intersecting crack tips – evident from slip bands on specimen sides and diffuse electron-back-scattered-diffraction patterns – include Fe-Si and Ni single crystals in hydrogen gas, and Al alloys and stainless steels in aqueous environments (Lynch [3]). However, even in such cases, it could be argued that crack growth occurs by a combination of alternate-slip and decohesion. Further high-resolution fractographic observations in combination with other techniques such as TEM of thin foils just beneath fracture surfaces and TEM of sections through cracks are needed to resolve some of these issues.

The evidence to date suggests that a localised-slip/microvoid coalescence process is more common than a process involving predominantly decohesion. The most likely instances where HEDE predominates are those where brittle intergranular fracture in high-strength alloys (especially steels) occurs along grain boundaries that are already weakened by segregation of metalloid impurities.

2.2 *Are there definitive experiments which enable the relative importance of ‘adsorbed’ hydrogen and ‘solute’ hydrogen to be assessed?*

For most testing conditions, both ‘adsorbed’ and ‘solute’ hydrogen at various sites ahead of crack tips are present since (i) hydrogen can adsorb at and then diffuse ahead of crack tips during crack growth in hydrogen-bearing environments, and (ii) hydrogen can diffuse from lattice sites and ‘adsorb’ at internal crack tips during crack growth in pre-charged specimens tested in air. There are, however, specific conditions where only ‘adsorbed’ hydrogen or only ‘solute’ hydrogen are present. While these conditions are unusual, it is instructive to examine and compare the characteristics of fracture under such conditions with those under ‘normal’ conditions.

2.2.1 *Crack growth at high velocities*

For crack growth in hydrogen-bearing environments, environmentally assisted cracking (with brittle characteristics) can occur at such high velocities under certain conditions that, although there is time for adsorption to occur, there is no time for hydrogen diffusion ahead of cracks. Specific conditions favouring such behaviour include (i) material-environment combinations where rapid dissociation of hydrogen or water molecules occur at crack tips, (ii) testing notched, pre-cracked specimens in bending at high deflection rates ($\sim 50^\circ/\text{s}$) so that plasticity is constrained around crack tips, and (iii) using single crystals or bi-crystals with potential cleavage planes or grain boundaries normal to the axis of bending.

Under such conditions, environmentally assisted cracking has been observed at velocities up to 0.5mm/s for Ni alloys in hydrogen gas and for Ti alloys in aqueous environments, up to 10mm/s for age-hardened Al-Zn-Mg single crystals and bi-crystals in aqueous environments, and up to 50mm/s for pure Mg ‘single crystals’ and ‘bi-crystals’ in aqueous environments (Lynch [1,3]). Hydrogen-diffusivity/maximum-crack-velocity (D/v) ratios are $\leq 10^{-8}\text{cm}$ these cases and, according to an analysis by Johnson [7], hydrogen should not diffuse more than a few atomic distances ahead of cracks. (For Al alloys, there is some doubt regarding hydrogen diffusivities, and, hence, some doubt regarding D/v ratios.) The orientation of slip planes and crack planes, and crack-tip strain rates, are such that rapid hydrogen transport by dislocations *directly* ahead of cracks can probably be discounted.

The characteristics of environmentally assisted cracking at high velocities are similar to those at low velocities, where hydrogen can diffuse over large distances (Lynch [3]). The implications of these results are that ‘adsorbed’ hydrogen *can* produce embrittlement and *can* account for

commonly observed fracture modes such as cleavage-like and intergranular fractures, and that, just because hydrogen can diffuse significant distances ahead of crack tips, does not *necessarily* mean that ‘solute’ hydrogen is always involved in embrittlement.

2.2.2 Fracture of hydrogen-charged specimens

For hydrogen-charged specimens tested in air, solute hydrogen *without* adsorbed hydrogen (at internal voids) may be present in some circumstances. For example, only solute hydrogen may be present during fatigue crack growth in hydrogen-charged pure Ni single crystals testing in bending in air at low-to-intermediate ΔK , where plasticity is localised around crack tips such that no significant voids (internal surfaces) form ahead of cracks. Providing crack-tip strain rates and temperatures are not too high, hydrogen atmospheres around dislocations should be sufficiently mobile to keep up with dislocations and result in HELP. Observations of fracture surfaces of Ni single crystals (tested in air at 20°C at 1Hz), however, show that the striation spacing and appearance are the same for hydrogen-charged and uncharged specimens – in contrast to striation spacings and appearance for (uncharged) specimens tested in hydrogen gas (at 20°C and 1Hz), where larger, ‘brittle’ striations are observed (Lynch [1,3]). These observations suggest that ‘adsorbed’ hydrogen is much more important than ‘solute’ hydrogen in the above circumstances. Further comparisons for Ni and other materials in charged and uncharged conditions, under circumstances where ‘adsorbed’ hydrogen at internal crack/void tips is absent, would be valuable in determining the relative importance of ‘adsorbed’ and ‘solute’ hydrogen.

2.2.3 Comparisons between hydrogen-embrittlement and liquid-metal embrittlement

At first sight, it might appear that comparisons of HE and LME are not relevant to the question of whether ‘adsorbed’ or ‘solute’ hydrogen is more important in producing embrittlement. However, since it is accepted that only adsorption (of metal atoms) occurs during most instances of LME, examining the characteristics of LME fractures at least indicates what effects adsorption can have on fracture behaviour. Moreover, the charge transfer for metal-atom adsorption might be similar to that for hydrogen adsorption in some case, e.g. for alkali-metal adsorption where only ‘s’ electrons are involved. The fact that LME can produce richly detailed cleavage-like fractures, dimpled intergranular and transgranular fractures, and ‘brittle’ intergranular fractures with very similar characteristics to those produced by HE therefore supports the view that ‘adsorbed’ hydrogen is important (Lynch [1,3]).

2.2.4 Effect of oxygen on hydrogen-environment embrittlement

Observations that cleavage-like cracking in Fe-Si single crystals in gaseous hydrogen can be arrested almost immediately (within 1s) on adding oxygen to the environment also suggests that cracking is due to a surface or very-near surface effect (Vehoff [8]). It was estimated that solute hydrogen (as atmospheres around dislocations) would be present for about 1 μ m ahead of cracks, whereas cracks were arrested by oxygen *within* about 100nm of crack growth. If HELP were a predominant mechanism of cracking, then cracking would have been expected to continue for greater distances. Cracking predominantly by AIDE (or HEDE at crack tips) would, however, be expected to arrest almost immediately due to preferential adsorption of oxygen at crack tips.

2.3 What effects do adsorbed species have on bonding at crack tips that could facilitate dislocation emission, and what other parameters control dislocation emission?

Dislocation emission from crack tips involves the simultaneous formation of a dislocation core and step at the crack-tip surface – processes which involve the shear movement of atoms and breaking/reforming of interatomic bonds between surface and near-surface atoms. These

processes should be strongly affected by the atomic arrangements and bonding within the first few atomic layers at crack-tip surfaces since the core radius of nucleating dislocations probably extends over several atomic distances. Adsorbed species, including hydrogen on the surface and in interstitial sites within the first few atomic layers, would be expected to influence surface atomic arrangements and bonding due to a redistribution of electron charge. However, details of atomic structure and bonding at (non-atomically sharp) crack-tip surfaces, and the effects of adsorption, are not accessible experimentally and, hence, these details have to be deduced from observations on plane surfaces and from atomistic modelling.

For 'clean' metal surfaces, the lattice spacings up to 4-5 atomic layers beneath the surface can be different from those in the bulk, although the crystal structure is unchanged. Contractions of the bulk lattice spacings between the first and second layers of 5% or less for low-index crystallographic surfaces but up to 30% for high-index surfaces have been observed. Small expansions between the second and third layers, and small contractions between the third and fourth layers may also occur for a number of metal surfaces, although other sequences of contraction and expansion are sometimes present. Expansions or contractions of the lattice spacings can also occur parallel to the surface in the first (and perhaps second) layer. The extent of these surface-lattice '*relaxations*' depend on the material, crystal structure, temperature, and surface crystallographic plane, with the extent of the relaxations often increasing for more open, higher order crystallographic planes. For a few metals, clean surfaces can be *reconstructed*, i.e. have a different crystal structure than the bulk, rather than just relaxed (e.g. Van Hove [9]).

In some cases, adsorption reduces the contractions between the first and second layers while in other cases, adsorption produces an expansion between the first and second layers, or results in a reconstruction of previously unreconstructed clean surfaces. For reconstructed clean surfaces, adsorption can change the nature of the reconstruction. The exact behaviour depends on variables such as the surface crystallography, surface coverage of adsorbed species, temperature, and whether strong or weak chemisorption occurs. Weakly adsorbed atoms such as hydrogen tend to reduce the extent of surface-lattice perturbations while strongly adsorbed species, such as oxygen, tend to produce reconstructions, with adsorbed atoms sometimes incorporated into the top most layer of substrate atoms. However, generalisations are difficult to make because such a diversity of effects has been observed, and an understanding of all these effects is far from complete (e.g. Van Hove [9]).

The surface at crack tips (assuming there is a significant crack-tip radius) during fracture is, of course, much different from plane surfaces. For transgranular crack growth, the crack-tip surface will be elastically strained and will be stepped due to high plastic strains (prior to dislocation activity) around cracks. When crack growth is intergranular, as it often is, crack tips will also be intersected by grain boundaries. During rapid crack growth, equilibrium conditions may not be attained, although relaxations should have time to occur. There may well be greater relaxations at crack-tip surfaces than at low-index planes due to the high density of steps and other defects at crack-tip surfaces. The effects of adsorption at crack tips may also be greater than those at plane surfaces due to preferential adsorption at steps or at strained bonds. Thus, there may be greater reductions in the extent of surface-lattice perturbations due to weak chemisorption at crack tips than at plane surfaces.

Perturbations of the lattice *in the bulk*, inhibit dislocation motion, and it therefore seems likely that lattice perturbations at the crack-tip surface would inhibit dislocation nucleation. Thus, reductions in surface-lattice perturbations at crack tips due to weak chemisorption could facilitate the nucleation of dislocations. It is also possible that relaxations or reconstructions at the crack-tip surface *induced* by adsorption could facilitate dislocation nucleation in some circumstances, e.g. when the relaxations or reconstructions result in incipient shear movements of atoms in the same sense as those required for the formation of a dislocation core.

Dislocation emission from crack tips is likely to be affected not only by crack-tip surface-lattice perturbations (and associated surface stresses) but also by a number of other parameters (e.g. Schoeck [10]) such as:

- (i) crack-tip nucleation sites, e.g. on inclined planes or on oblique planes at ledges along the crack front, and the angle of these planes with respect to the crack plane,
- (ii) the crack-tip radius and core-width of nucleating dislocations,
- (iii) the shape of the emitted dislocation loop, and whether full or partial dislocations are involved,
- (iv) the extent of shielding/back-stresses from previously emitted dislocations – which will depend on the mobility of emitted dislocations, and their ability to cross-slip, etc.
- (v) stress mode, and the extent of ‘shear-softening’ due to tensile stresses (as well as shear stresses) across slip planes.

Obviously, modelling dislocation emission from crack tips (and effects of adsorption) is a formidable task, and none of the analyses carried out to date consider the crack-tip surface-lattice perturbation issue or incorporate all the other important features. Increasing degrees of sophistication of computer modelling of crack growth in the future will, hopefully, be able to shed more light on the AIDE process.

3 REFERENCES

- [1] Lynch, S.P. ‘Mechanisms of Hydrogen-Assisted Cracking – A Review’, *Hydrogen Effects on Material Behavior and Corrosion Deformation Interactions*, N. R. Moody et al. (Eds.), pp. 449-466, 2003, and references therein.
- [2] Hänninen, H.E. ‘Stress Corrosion Cracking’, *Comprehensive Structural Integrity*, vol.6, Milne, I. et al. (Eds.), pp. 1-29, 2003.
- [3] Lynch, S.P. ‘Environmentally Assisted Cracking: Overview of Evidence for an Adsorption-Induced Localised-Slip Process’, *Acta Metall.*, vol.36, pp. 2639-2661, 1988, and references therein.
- [4] Célarié, F. et al. ‘Glass Breaks like Metal, but at the Nanometer Scale’, *Phys. Rev. L.*, vol.90, pp. 75504-1-4, 2003.
- [5] *Atomistic Theory and Simulation of Fracture*, Selinger L.B. and Farkas D. (Guest Eds.), MRS Bulletin, May 2000.
- [6] Riedle, J. et al. ‘Cleavage Anisotropy in Tungsten Single Crystals’, *Phys. Rev. L.*, vol.76, pp. 3594-3597, 1996.
- [7] Johnson, H. H. ‘Hydrogen Gas Embrittlement’, *Hydrogen in Metals*, Bernstein, I.M. and Thompson, A.W. (Eds.), TMS, pp. 35-49, 1974.
- [8] Vehoff, H. ‘Hydrogen Related Material Properties’, *Topics in Appl. Phys.*, vol.73, pp. 215-278, 1997.
- [9] Van Hove, M.A. ‘Crystal Surfaces’ *Materials Science and Technology: A Comprehensive Treatment*, Cahn, R.W. et al. (Eds.), vol.1, pp. 485-531, 1991, and references therein.
- [10] Schoeck, G. ‘The Emission of Dislocations from Crack Tips: A Critical Assessment’, *Mater. Sci. Engng*, vol.A356, pp. 93-101, 2003, and references therein.