PROGRESS TOWARDS UNDERSTANDING MECHANISMS OF HYDROGEN EMBRITTLEMENT AND STRESS CORROSION CRACKING

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ABSTRACT

This review describes the present state of knowledge and current controversies concerning mechanisms of hydrogen embrittlement (HE), especially in steels, nickel, and titanium alloys. Mechanisms of stress-corrosion cracking (SCC) in aluminium alloys, magnesium, and other materials where hydrogen effects are involved are also discussed. HE involving the formation of brittle hydrides ahead of crack tips is only briefly described, and the main focus of the review is on mechanisms of HE and SCC when hydrides do not form. In these circumstances, there are three principal mechanisms that have significant experimental and theoretical support, viz. mechanisms based on: (i) hydrogen-enhanced localised plasticity (HELP), (ii) hydrogen-enhanced decohesion (HEDE), and (iii) adsorption-induced dislocation emission (AIDE). It is concluded that combinations of these mechanisms are likely in many cases, with the dominant process depending on the fracture mode. For example, AIDE probably predominates for cleavage-like fractures and dimpled intergranular fractures, HEDE possibly occurs for some brittle intergranular fractures, and HELP contributes particularly to slip-band fractures.

Keywords: hydrogen-embrittlement, stress-corrosion cracking, liquid-metal embrittlement, surface relaxations and reconstructions, adsorption-induced dislocation emission, hydrogen-enhanced localised plasticity, hydrogen-enhanced decohesion, fracture modes, cleavage-like fracture, intergranular fracture, slip-band fracture, environmentally assisted fatigue, fractography.

INTRODUCTION

The first notable attempt at explaining hydrogen embrittlement (HE) was made in 1874 by W.H. Johnson [(1)] in a classic paper entitled “On some remarkable changes produced in iron and steel by the action of hydrogen and acids”. Johnson suggested that “*… for as amalgamated zinc is made brittle in consequence of the pores or interstices between the molecules of the metal being filled up by mercury, motion of one molecule over another being then impeded, so in like manner iron becomes brittle when its pores are filled up with condensed hydrogen gas; and naturally, when the hydrogen or mercury is driven out of the molecular interspaces, movement of*

the molecules on one another is less impeded, and hence the former toughness or elasticity is restored." Put in modern terms, Johnson appears to have been suggesting that HE results from interstitial hydrogen impeding the movement of dislocations. Modern techniques do indeed show that solute hydrogen can inhibit dislocation activity (as well as promote it), and such effects could contribute to embrittlement in some circumstances. Johnson's suggestion that mechanisms of embrittlement by hydrogen and mercury were the same was also far-sighted, since there is now compelling evidence that mechanisms of HE and LME (liquid-metal embrittlement) are the same in steels (and some other) materials, as discussed in more detail later in this review.

Another notable, early paper concerning mechanisms of HE appeared in 1926, in which Pfeil [(2)] proposed that hydrogen decreased the cohesion across cubic cleavage planes (and grain boundaries). 'Decohesion' theories of HE were further developed in 1960 by Troiano [(3)], and later by Oriani [(4,5)], Gerberich [(6-8)], Gangloff [(9)] and others, with Troiano possibly being the first to attempt to explain weakening of interatomic bonds by hydrogen in terms of electron-charge transfer (donation of the hydrogen 's' electron to the unfilled 3d shell of the iron atoms). Decohesion theories of HE became widely accepted in the 1960's and early 1970's, but now compete with theories based on localised plasticity.

Beachem [(10)] (in 1972) was the first to suggest, on the basis of fractographic and other observations, that solute hydrogen facilitated the movement of dislocations in local regions near the crack tip, leading to a more localised microvoid-coalescence fracture process. This idea, which was highly controversial at the time, was subsequently supported by Birnbaum, Robertson, Sofronis, and co-workers [(11-16)], based initially on *in-situ* transmission-electron microscopy (TEM) of thin foils exposed to hydrogen gas in the early 1980's, and later supported by theoretical modelling. Observations of softening and strain-localisation in hydrogen-charged bulk specimens under certain conditions have provided additional support.

From the mid-1970's to late 1980's, Lynch [(17-25)] carried out high-resolution fractographic studies of HE and SCC (and also LME) in a wide variety of materials, and proposed that it was adsorbed hydrogen rather than solute hydrogen that promoted localised-plasticity/microvoid-coalescence processes at crack tips. In essence, Lynch suggested that adsorbed hydrogen (and some adsorbed metal atoms) weakened interatomic bonds at crack tips, thereby facilitating the emission of dislocations and promoting the coalescence of cracks with voids. Theories of HE based on adsorbed hydrogen had been suggested earlier by others, such as Petch in 1950 [(26)], but were couched in thermodynamic terms rather than mechanistic terms. Early theories of SCC in the late 1950's and 1960's were also based on adsorption-induced decreases in surface energies [(27-29)], with Uhlig being one of the main proponents.

A mechanism based on the formation and fracture of hydrides at crack tips was first proposed by Westlake [(30)] in 1969, and it is now widely accepted for certain materials such as Zr, Nb, V, and Ta which readily form hydrides under appropriate conditions [(11,12)]. Hydrides have been directly observed at crack tips in hydrogen-charged thin foils by high-voltage TEM [(31)] and have also been observed on both halves of cleavage-like fracture surfaces in bulk specimens. Crack-arrest markings are sometimes observed on fracture surfaces indicating a discontinuous cracking process. [(24)] Thus, crack growth is thought to occur by repeated sequences of (i) hydrogen diffusion to regions of high triaxial stress ahead of cracks, (ii) nucleation and growth of a hydride phase, (iii) cleavage of the hydride when it reaches a critical size, and (iv) crack-arrest at the hydride-matrix interface (Fig. 1).

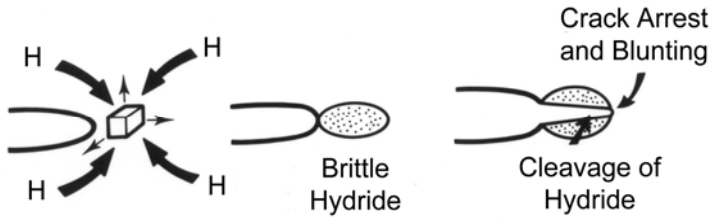

FIGURE 1 - Schematic diagram illustrating sub-critical crack growth involving hydrogen diffusion to hydrostatically stressed regions, then formation and fracture of brittle of hydrides at crack tips.

Variations to the hydride mechanism illustrated in figure 1 may occur in some circumstances, e.g. pre-existing hydrides may dissolve and re-orient so that hydride plates are perpendicular to the tensile stress axis, hydrides may dissolve after fracture owing to relaxations of hydrostatic stresses, and ductile tearing may occur between discrete, closely spaced hydrides. A hydride mechanism only occurs in the temperature and strain-rate regimes where hydrogen has time to diffuse to regions ahead of crack tips, and only at temperatures where the hydride phase is stable [11,12]. When hydrogen is present as solute, embrittlement is not observed, and specimens sometimes undergo considerable plastic strain before hydrides are nucleated and brittle fracture occurs.

While a hydride mechanism is generally accepted for certain materials and conditions, there is on-going disagreement regarding both the site of embrittlement and the atomic mechanism of cracking for HE and hydrogen-induced SCC in non-hydride forming materials (and hydride-forming materials under conditions where hydrides do not form). Establishing the mechanisms of HE when hydrides do not form has proved difficult because there are no direct techniques for observing atomic-scale events at crack tips in bulk specimens. Mechanisms therefore have to be deduced from (i) metallographic, fractographic, and surface-science observations, (ii) comparisons with less complex cases of environmentally assisted cracking, (iii) kinetics of cracking compared with other processes, (iv) dislocation theory, and (v) atomistic and continuum modelling. Moreover, combinations of mechanisms are likely to occur in many cases, with the dominant mechanism depending on the fracture mode – which is dependent on variables such as strength, microstructure, slip-mode, stress-intensity factor, and temperature.

Essentially, when hydrides do not form, there are three principal mechanisms of HE and hydrogen-induced SCC that have significant experimental and theoretical support. [9] These are (i) Hydrogen Enhanced DEcohesion (HEDE), (ii) Hydrogen Enhanced Localised Plasticity (HELP), and (iii) Adsorption-Induced Dislocation Emission (AIDE). These mechanisms have been proposed for both hydrogen-environment embrittlement (HEE) (in hydrogen or hydrogen-sulphide gas), internal-hydrogen embrittlement (IHE) (owing to hydrogen introduced into materials prior to loading in air), and hydrogen-induced SCC (where hydrogen is generated at crack tips by chemical dissociation of water or by electrochemical reactions). The mechanisms of embrittlement are usually presumed to be the same regardless of the source of hydrogen (although there may be exceptions), and other processes such as film formation and dissolution are probably often involved in hydrogen-assisted SCC. The rate-controlling processes for HEE, IHE, and hydrogen-assisted SCC are often different, e.g. hydrogen diffusion may control the kinetics of IHE and a hydrogen-adsorption process may determine the rate of HEE. The embrittlement site may also differ for these different processes.

In the present review, which draws heavily on previous reviews [23-25] by the present author, these three basic mechanisms of HE are first outlined, and then background supporting

evidence for each mechanism is reviewed. The background support for the occurrence of AIDE, HELP, and HEDE does not necessarily indicate that a particular process plays a dominant role in facilitating crack growth. The relative importance, if any, of each mechanism for various fracture modes are discussed in the light of metallographic and fractographic observations, and also kinetic data, in a subsequent section. It is concluded that AIDE predominates for cleavage-like fractures and dimpled intergranular fractures, HEDE possibly occurs for some brittle intergranular fractures, and HELP contributes particularly to slip-band fractures.

OUTLINE OF PROPOSED HELP, HEDE, AND AIDE MECHANISMS

Hydrogen-Enhanced Localised Plasticity (HELP)

HELP is based on localised softening owing to solute hydrogen in the form of hydrogen atmospheres around both mobile dislocations and obstacles to dislocations (e.g. other dislocations, solute atoms) in a volume of material ahead of cracks. [11-16] It has been proposed that, since hydrogen diffusion rates are rapid in the temperature and strain-rate regimes where HE generally occurs, these atmospheres can re-configure themselves readily in response to changing elastic stress fields, such that the total elastic energy is minimised when dislocations approach obstacles (Fig. 2(a)). The resistance to dislocation motion due to obstacles is therefore decreased, and dislocation velocities are increased, when hydrogen is present.

Since hydrogen concentrations are localised near crack tips due to hydrostatic stresses or entry of hydrogen at crack tips, it is proposed that deformation is facilitated locally near crack tips so that crack growth occurs by a more-localised microvoid-coalescence process than that which occurs in inert environments. Thus, HELP should result in smaller dimples on fracture surfaces than those produced in inert environments, and crack paths could be either transgranular or intergranular (depending on whether hydrogen concentrations adjacent to grain boundaries are higher than within grains). Details regarding how the HELP process accounts for some fractographic features, such as cleavage-like characteristics, however, have not been clarified.

Hydrogen-Enhanced Decohesion (HEDE)

HEDE is based on weakening of metal-metal bonds at or near crack tips by high, localised concentrations of hydrogen, so that tensile separation of atoms (decohesion) occurs in preference to slip [2-9] (Fig. 2(b)). Sufficiently high hydrogen concentrations might occur in the lattice ahead of cracks if very high elastic stresses are present owing to strain-gradient hardening. The weakening of bonds is thought to result from decreases in electron-charge density between metal-metal atoms owing to the presence of hydrogen. Some dislocation activity may accompany decohesion, and may locally increase stresses at decohesion sites, but should not be so extensive as to continually blunt crack tips.

High concentrations of hydrogen and the decohesion event could occur at a variety of locations, namely (i) exactly at atomically sharp crack tips (or within a few atomic distances of them), (ii) several tens of nanometers ahead of cracks where dislocation-shielding effects result in a tensile-stress maximum, (iii) positions of maximum hydrostatic stress at a distance of the order of twice the crack-tip-opening displacement (several micrometers in high-strength steels), (iv) particle-matrix interfaces ahead of cracks, and (v) specific polyhedral structural

units along grain boundaries. It is, however, debatable whether hydrogen concentrations in the lattice ahead of transgranular cracks (locations (ii) and (iii) above) are sufficiently high to produce decohesion. Intergranular and transgranular fracture surfaces produced by decohesion should be essentially atomically smooth, although plasticity and tearing could occur between decohered regions.

Decohesion is usually envisaged as a simple, sequential tensile separation of atoms when a critical crack-opening displacement (COD) (~half the interatomic spacing) is reached. However, separation of atoms at crack tips is constrained by surrounding atoms and, hence, the separation process could be more complex and involve incipient shear movement of atoms ('atomic shuffles') to enable a critical COD to be achieved. [32] Such a process might explain why there are preferred crystallographic directions for atomically brittle crack-growth. [33]

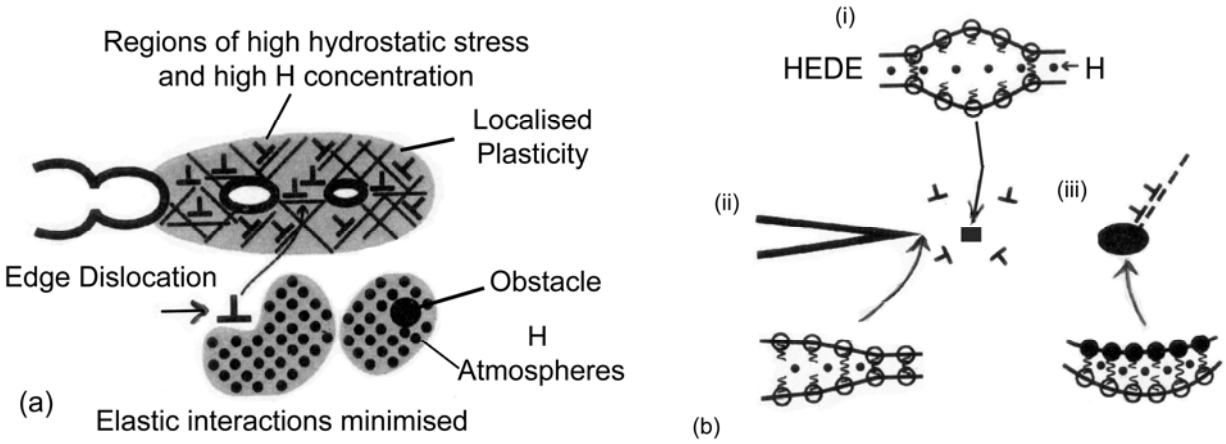

FIGURE 2 - Schematic diagrams illustrating (a) the HELP mechanism, involving a microvoid-coalescence process, with plasticity localised in regions of high hydrogen concentrations, and (b) the HEDE mechanism, involving tensile separation of atoms owing to weakening interatomic bonds by (i) hydrogen in the lattice, (ii) adsorbed hydrogen, (iii) hydrogen at particle-matrix interfaces.

Adsorption-Induced Dislocation Emission (AIDE)

The AIDE mechanism is based on hydrogen-induced weakening of interatomic bonds (as for HEDE) but with crack growth occurring by localised slip (as for HELP), and was first proposed by the present author twenty years ago [17-25]. Both the location of bond weakening and the details of the crack-growth process are specified for the AIDE mechanism. Thus, it has been proposed that "adsorbed" hydrogen (i.e. hydrogen on the surface and between the first few atomic layers of atoms at crack tips) weakens substrate interatomic bonds and thereby facilitates the emission of dislocations from crack tips.

The stresses required for dislocation emission are sufficiently high that it is accompanied by general dislocation activity in the plastic zone ahead of cracks, resulting in the formation of small voids at particles or at slip-band intersections. Thus, crack growth occurs primarily by dislocation emission, but dislocation egress at crack tips and void formation ahead of cracks also contribute. Void formation ahead of cracks also serves to maintain small crack-tip radii and small crack-tip-opening angles. If sufficient hydrogen diffuses or is transported by dislocations to voids ahead of cracks, then AIDE could also occur from tips of voids, but this is not an essential requirement of the process.

To understand why facilitating dislocation emission from crack tips results in 'embrittlement', it is necessary to consider how crack growth occurs in inert environments for ductile materials. Ductile crack growth appears to occur predominantly by dislocations nucleated from sources in the plastic zone ahead of crack tips *egressing at* the crack-tip surface, with little or no emission of dislocations occurring from crack tips. Only a small proportion of dislocations emanating from near-crack-tip sources would *exactly* intersect crack tips to produce crack advance – most would produce only blunting or contribute to the strain ahead of cracks. Large strains ahead of cracks are therefore needed to produce crack growth by microvoid-coalescence (MVC) and deep dimples, with smaller dimples within them, are produced on fracture surfaces. The small dimples within large dimples arise because coalescence of large voids (nucleated from large particles) involves nucleation and growth of smaller voids (nucleated from smaller particles or other sites at higher strains) between large voids.

When hydrogen adsorption promotes dislocation emission from crack-tips, a greater proportion of the dislocation activity results in crack growth since dislocation emission on suitably inclined slip planes produces crack advance as well as crack opening. Thus, coalescence of cracks with voids occurs at lower strains and shallower dimples are produced on fracture surfaces when AIDE occurs (Fig.3). The dimples resulting from an AIDE/MVC process also appear to be smaller (as well as shallower) than those produced by ductile fracture since, for the latter, small dimples within large dimples are often stretched and difficult to resolve.

Crack paths produced as a result of the AIDE mechanism could be intergranular or transgranular depending on where dislocation emission and void formation occurred most easily. For transgranular cracking, *alternate slip* on planes on either side of cracks would tend to occur in order to minimise the back-stress from previously emitted dislocations. Macroscopic planes for transgranular cracking would therefore bisect the angle between the slip planes, and crack fronts would lie along the line of intersection of crack planes and slip planes, e.g. along {100} planes in <110> directions when {111} or {112} slip planes are active in fcc and bcc materials. However, deviations from low-index planes and directions would occur if unequal amounts of slip occurred on either side of cracks owing to large differences in shear stresses on the different slip planes. Deviations of fracture planes away from low-index planes could also occur depending on the locations of void nuclei ahead of cracks.

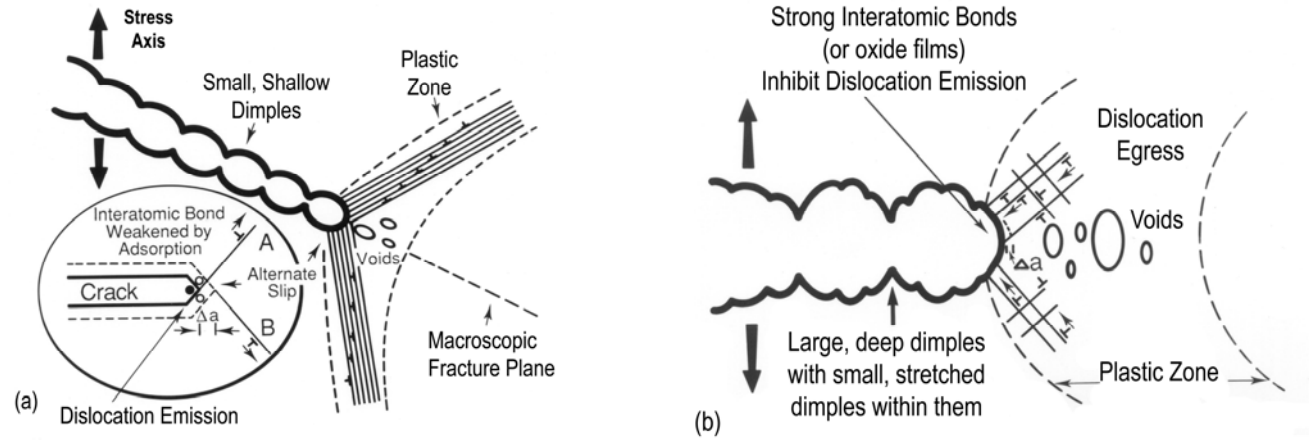

FIGURE 3 - Schematic diagrams illustrating (a) the adsorption-induced dislocation emission (AIDE) mechanism for transgranular crack growth, which involves alternate-slip from crack tips facilitating coalescence of cracks with voids formed in the plastic zone ahead of cracks, and (b) ductile crack growth involving coalescence of cracks with voids by egress of dislocations nucleated from near-crack-tip sources. (Lynch [24])

BACKGROUND SUPPORT FOR AN AIDE MECHANISM

An AIDE mechanism for HE and SCC is supported by (i) the likelihood of high concentrations of hydrogen on surfaces (and within a few atomic distances of surfaces), (ii) surface-science observations that adsorbed hydrogen (and other species) can have marked effects on structure and bonding at surfaces, and (iii) miscellaneous experimental observations and theoretical calculations.

Hydrogen Adsorption at Surfaces

For clean metal surfaces of many metals, e.g. Fe, Ni, Ti, exposed to hydrogen gas, it is well established that hydrogen molecules dissociate, and that hydrogen atoms chemisorb at specific surface sites with a deep potential-energy trough relative to normal interstitial lattice sites. The interstitial sites between the first and second atomic layers (and perhaps second and third layers) are also a stronger trap site for hydrogen than normal interstitial sites in some materials (Fig. 4). Thus, much higher hydrogen concentrations would be expected at (crack-tip) surface sites and just sub-surface sites than at normal interstitial lattice sites. The adsorption process can be complex, involving physical adsorption of hydrogen molecules and other precursor steps, and is known to be strongly influenced by the substrate metal, strain, temperature, surface crystallography, surface-coverage, and roughness. [34-44] Hydrogen diffusion to internal voids/cracks would produce similarly high concentrations of 'adsorbed' hydrogen at these internal surfaces. (As mentioned in the introduction, surface and just sub-surface sites are referred to as 'adsorbed hydrogen' in regard to the AIDE mechanism).

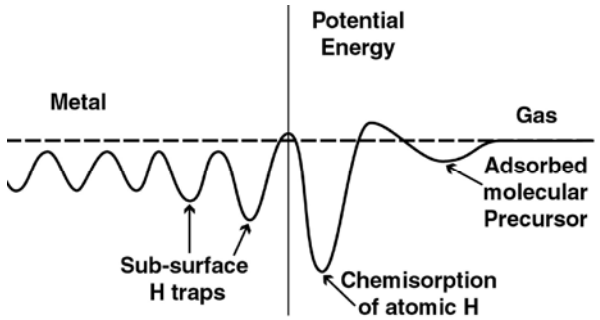

FIGURE 4 - Schematic illustration showing deeper potential-energy 'wells' for hydrogen 'adsorption' on (and for one or two lattice spacings beneath) clean surfaces compared with normal interstitial lattice sites, which would result in high hydrogen concentrations at surface and just-sub-surface sites.

For stressed materials containing solute hydrogen, second-phase particles or particle-matrix interfaces may be cracked, so that internal surfaces are present at which hydrogen can adsorb after hydrogen diffusion or dislocation transport to these sites. The presence of hydrogen trapped at particle-matrix interfaces can, of course, facilitate their separation, and recombination of hydrogen atoms on internal surfaces can result in high pressures of hydrogen gas within voids. However, for equivalent hydrogen pressures and stress-states, the situation at internal surfaces should be the same as for external surfaces exposed to hydrogen gas, although 're-surfacing' hydrogen may be transitorily more energetic than hydrogen adsorbed from a gas phase. [45] Hydrogen diffusing to external surfaces (usually exposed to air) would be prevented from adsorbing on surface sites by preferential adsorption of oxygen or oxide films, although hydrogen could be present in greater concentrations near external crack tips than in normal interstitial sites, depending on how adsorbed oxygen and oxide films affected surface stresses.

For materials exposed to aqueous environments, hydrogen adsorption is much more complex than adsorption from the gas phase. Thus, water molecules can adsorb and then dissociate chemically or electrochemically (and dissolved hydrogen can also dissociate and adsorb). [38] Physically adsorbed water molecules would probably not be as effective in decreasing substrate bond strengths as chemisorbed hydrogen and, hence, dissociation is probably required for AIDE to occur. The reaction products of water dissociation are atomic hydrogen, OH species and, if OH dissociates, also atomic oxygen. Adsorbed hydrogen interacts not only with the substrate but also with surrounding water molecules, and can also re-combine so that hydrogen gas is evolved. The adsorption sites and relative surface-coverages of the dissociation products depend on many variables such as potential and pH, but high concentrations of 'adsorbed' hydrogen at external crack-tip surfaces would be expected in many circumstances. If hydrogen can diffuse to internal crack-tip surfaces, then 'adsorbed' hydrogen concentrations may be greater than at external surfaces since there would be no other competing adsorbed species or films inhibiting hydrogen adsorption.

Effects of Adsorption on Surface Relaxations and Reconstructions

The atomic structure and bonding at unstressed, low-index crystallographic surfaces have been extensively studied for a wide range of materials using low-energy electron diffraction (LEED), scanning tunnelling microscopy (STM), and other techniques. [46-52] For 'clean' metal surfaces (without adsorbates or films), the lattice spacings up to 4-5 atomic layers beneath the surfaces can be different from those in the bulk (with the lattice structure unchanged). Contractions of the normal 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 normal lattice spacings can also occur parallel to the surfaces in the first (and perhaps second) layer. For a few metals, clean surfaces can be 'reconstructed' rather than just 'relaxed', e.g. the {100} surfaces of fcc gold, platinum, and iridium have a hexagonal crystal structure.

The clean-surface lattice-perturbations occur essentially because atoms at the surface have fewer neighbours than those in the bulk and, hence, electron charge has to be redistributed. Thus, it is not surprising that adsorption of environmental atoms (including hydrogen), which involves electron-charge transfer, often affects the extent and nature of the perturbations (Fig.5). [46-52] In some cases, adsorption reduces the perturbations, while in other cases, adsorption produces an expansion of previously contracted surface lattices, or results in a reconstruction of previously unreconstructed clean surfaces. For reconstructed clean surfaces, adsorption can eliminate or change the nature of the reconstruction. These changes can sometimes produce buckling or rumpling of the surface, involving lateral and vertical shear movements of atoms.

The exact effect of adsorption depends on variables such as the adsorbed species, surface-crystallography, surface-coverage of adsorbed species, temperature, and electrochemical potential. Whether adsorbates donate or accept electrons, and whether strong or weak chemisorption occurs are particularly important factors. [46-52] Weakly adsorbed atoms tend to reduce the extent of the perturbations while strongly adsorbed species, such as oxygen on many metals, tend to produce reconstructions, with adsorbed atoms sometimes incorporated

into the topmost layer of substrate atoms. Some metal-atom adsorbates can also be incorporated into the topmost layers of substrate atoms, i.e. 'surface alloying' occurs, even in systems where there is no bulk miscibility. [49] Generalizations are difficult to make because such a diversity of effects has been observed, and an understanding of all these effects is far from complete.

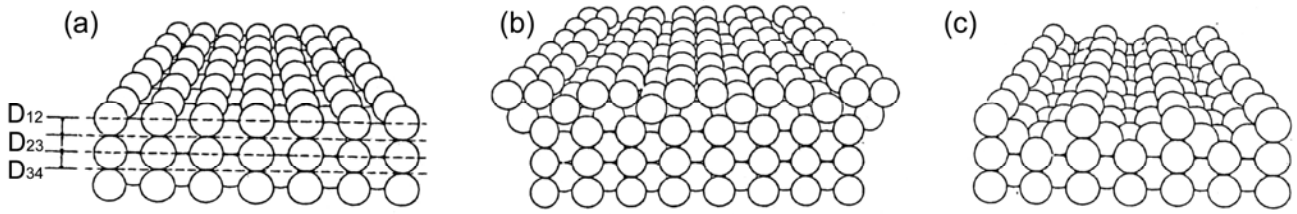

FIGURE 5 - Perspective views of {110} nickel surfaces: (a) clean surface with oscillatory contractions and expansions in the first few layers, and (b), (c) possible reconstructions resulting from adsorbed hydrogen (not shown). (Adapted from Moritz et al. [50])

In many cases, crack tips are not atomically sharp but have a finite radius, not only for ductile fracture but also for 'quasi-brittle' fracture typical of HE and SCC in normally ductile materials, so that surface-lattice relaxations and reconstructions should occur at crack tips. Surface-lattice perturbations occur in pico-second time-frames so that there should generally be time for the phenomenon to occur during crack growth. Indeed, the phenomenon of adsorption-induced LME, involving sub-critical cracking at velocities of up to 100's mm/s, shows that adsorption-induced changes to bonding at crack tips must have time to occur even at high crack velocities. However, the crack-tip surface-lattice perturbations could be significantly different from those at plane surfaces owing to:

(i) the curvature and varying crystallography around crack tips with finite radii,
(ii) the higher elastic (and plastic) strains and the higher density of steps resulting from dislocation activity, and
(iii) insufficient time to achieve an equilibrium state during crack growth.

Notwithstanding the last factor, these differences could well lead to larger perturbations at crack-tip surfaces than those observed at plane surfaces. There might also be greater adsorption-induced reductions in the extent of the perturbations at crack tips than at plane surfaces if, for example, stresses promoted adsorption. If crack growth was intergranular (and crack tips were not atomically sharp), and if grain-boundary segregants were present, then there would be variations in composition around the crack-tip surface, which would probably influence crack-tip surface relaxations and reconstructions.

Changes in the crack-tip surface-lattice perturbations and interatomic bond strengths would be expected to influence dislocation emission from crack tips because the dislocation-emission process, i.e. the simultaneous formation of a surface step and a dislocation core, involves the co-operative shear movement of atoms over several atomic distances at crack tips. In general, small crack-tip surface perturbations (and weak adsorbate-substrate bonding) should favour emission of dislocations, while large crack-tip-surface lattice perturbations (or strong adsorbate-substrate bonding), would be expected to inhibit dislocation emission. [53,54] However, large relaxations and reconstructions occurring at the crack-tip surface during crack growth might also facilitate dislocation emission if they involved shear movement of atoms in the same directions as those required for the formation of a dislocation core and surface step.

The egress of dislocations at surfaces is probably less affected by surface-lattice perturbations than dislocation emission since the former does not require the formation of a dislocation core in a perturbed lattice, and would be promoted by an attractive image force and their kinetic energy.

Effects of Adsorption on Surface Stresses

Surface stresses are linked to the extent that surface relaxations and reconstructions (induced by electron-charge-redistributions) are restrained by the sub-surface lattice, and can be tensile or compressive. [55-57] Adsorption would be expected to produce significant changes to surface stresses owing to its effect on surface-lattice perturbations, and theoretical calculations suggest that dislocation emission from crack tips would be affected. [56] (Surface energies are also affected by adsorption, but there is not always a straightforward relationship between surface stresses and surface energies.) Surface stresses are difficult to measure so that predictions of their effects are not well established. However, in one study, 'cluster calculations' for adsorbed hydrogen on beryllium, suggested that high surface tensile stresses could be induced by adsorption, thereby facilitating dislocation emission. [58]

Miscellaneous Observations

Field-ion microscope observations of iron surfaces exposed to hydrogen gas (used for imaging) showed what appeared to be slip traces under some conditions, and it was proposed [59] that adsorbed hydrogen facilitated dislocation emission from surfaces. Atomistic calculations of crack growth in nickel using an embedded-atom method also suggest that adsorbed hydrogen [60,61], or just-sub-surface hydrogen interstitials escaping to the crack tip surface [62], facilitate dislocation emission from crack tips, providing that slip planes are favourably oriented with respect to the crack plane.

AIDE is supported to some extent by *in situ* TEM observations of stressed thin foils of numerous materials, where dislocation emission from crack tips (as well as dislocation activity in general) was facilitated when hydrogen gas was introduced around specimens. [11-16] However, HELP owing to solute hydrogen and other effects rather than AIDE from crack tips could be involved, as discussed in the next section. TEM observations of stressed Ti thin foils, before and after exposure to mercury vapour (*ex situ*), showed that dislocation emission from cracks was facilitated by exposure to mercury, and it was proposed [63] that AIDE was responsible. However, a thin oxide film was presumably present at crack tips, and this oxide could rupture or thicken (possibly aided by exposure to mercury), so that the observations are not unequivocal evidence of AIDE. Similar observations have been made for foils of other materials exposed to various liquids, and enhanced dislocation emission explained in terms of film growth and increasing film-induced stresses. [64]

There is a large volume of literature on environmentally induced surface effects on crystal plasticity (stress-strain curves) [65], and AIDE has been invoked to account for some observations. (Both environmentally induced increases and decreases in yield strength and work-hardening rates have been observed depending on the material, environment, crystal orientation, and other variables.) The mechanisms responsible for such effects are controversial, however, because so many different processes could be involved. For example, film formation or removal, dissolution, vacancy generation, and adsorbate diffusion into specimens, could influence both surface and near-surface dislocation sources, in addition to

adsorbate-induced changes to surface relaxations and reconstructions affecting surface dislocation sources.

Although there is no unequivocal evidence from stress-strain behaviour to determine whether or not adsorption can facilitate dislocation emission from surfaces (owing to experimental difficulties in carrying out definitive experiments), there is some evidence that dislocation emission from clean surfaces is a difficult process. Thus, compression loading of dislocation-free, single-crystal, microscopic-sized pillars of gold (where oxide films are not formed) resulted in yield strengths approaching significant fractions of theoretical strengths (probably owing to sub-surface homogeneous dislocation nucleation), even when previous loadings had produced surface slip-steps/stress-concentrations. [66] Such behaviour would not be expected if dislocation sources were easily activated from clean surfaces, but is consistent with the idea that large surface-lattice perturbations inhibit dislocation emission.

BACKGROUND SUPPORT FOR A HELP MECHANISM

The idea that solute hydrogen facilitates dislocation activity is supported by (i) elasticity theory, (ii) *in situ* transmission-electron microscopy (TEM) observations of thin foils exposed to hydrogen gas, (iii) softening and strain-localisation in bulk specimens under some conditions, and (iv) nano-indentation tests.

Elastic-Shielding Theory

Linear-elasticity and finite-element calculations of the interaction between elastic-stress centres around dislocations, solute atoms, and hydrogen atmospheres show that the short-range elastic interactions can be decreased when hydrogen atmospheres can rapidly reconfigure themselves in response to changing elastic stress fields. In effect, the hydrogen atmospheres “shield” the dislocations from the full force of the repulsive interactions between dislocations and obstacles. [11-16] Edge dislocations should be more effectively shielded than screw dislocations since the dilatational stress-field around edge dislocations promotes hydrogen atmospheres. The shielding effect would only be expected in the temperature and strain-rate regimes where hydrogen atmospheres are present and have time to re-arrange their configurations as dislocations approach close to obstacles. For example, for nickel at strain rates greater than about $10^{-5}s^{-1}$, HELP should not occur below about -80^{o}C where hydrogen diffusion rates are too slow, or above about 200^{o}C where hydrogen atmospheres are dispersed. For steels, the effective temperature range for HELP is expected to be between minus180^{o}C and 200^{o}C. [12-14]

In situ TEM Observations

Direct observations of hydrogen-induced increases in dislocation activity have been made using high-voltage TEM in which hydrogen gas can be introduced into an environmental cell around thin foils subjected to stress. [11-16] On introducing hydrogen, which rapidly dissociates under the influence of the electron beam and then diffuses into specimens, dislocations that were stationary start to move, those that were moving increase their velocity (by typically 10-100 times), and the rate of dislocation generation from sources is increased. These effects have been observed for edge, screw, and mixed dislocations, which may be entirely within foils or intersect the surface, in a wide range of materials. Decreases in the spacings of dislocations in pile-ups and decreases in the extent of cross-slip have also been observed on

the introduction of hydrogen (Fig.6). [67]

When stable cracks were present in foils held under constant displacement, introduction of hydrogen gas resulted in crack growth, with cracks arresting when hydrogen was removed Crack growth occurred by a mode-III sliding-off process involving dislocation emission from crack tips and local thinning near the crack tip due to increased dislocation activity. [67,68] In thicker regions of foils, nucleation and growth of voids were observed (Fig.7). Crack growth under increasing displacement in vacuum was similar to that in hydrogen, but deformation was not as localised and occurred at higher strains.

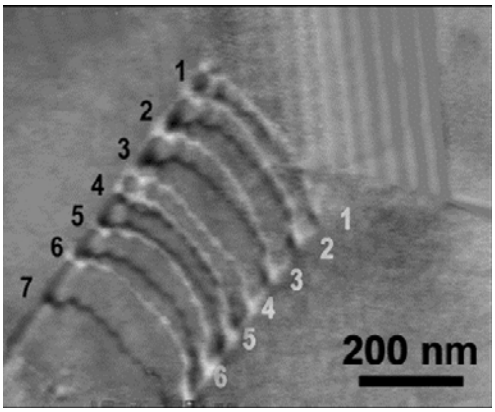

FIGURE 6 - TEM showing effect of solute hydrogen on a dislocation pile-up at a grain boundary in a fcc stainless steel. Images before (black dislocations) and after (white dislocations) gaseous hydrogen was introduced around specimens have been superimposed, showing that piled-up dislocations move closer to each other and to the grain boundary when hydrogen is introduced. (Ferreira et al. [67])

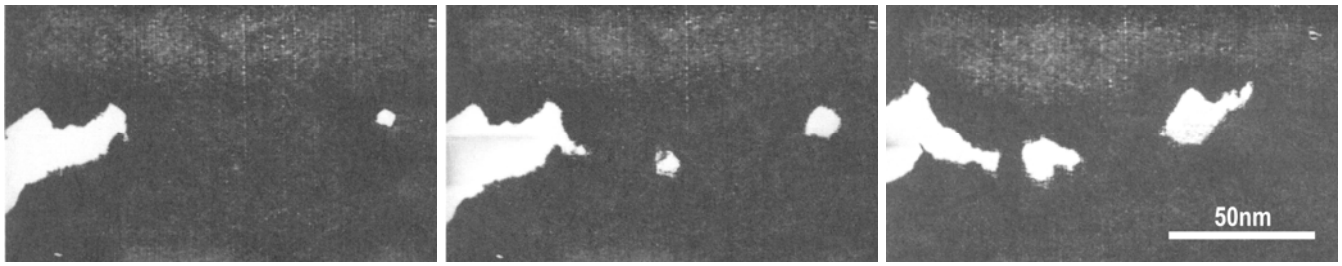

FIGURE 7 - TEM of a 'thick' region of a thin foil of a steel under constant deflection in a hydrogen atmosphere showing successive stages of hydrogen-assisted crack growth (from left to right) involving nucleation, growth, and coalescence of voids ahead of cracks. (Adapted from Hanninen et al. [68])

The effects of introducing hydrogen into thin foils, on both deformation and cracking, have generally been attributed entirely to HELP, i.e. reductions in elastic interactions between dislocations owing to solute hydrogen. [11-16] However, other effects of introducing hydrogen such as (i) generation of stresses owing to non-uniform hydrogen concentrations, (ii) hydrogen-induced reduction of thin oxide films, and (iii) AIDE from foil surfaces and crack tips, could possibly also make a contribution to increasing dislocation activity. [5,7,25] The likelihood that a much higher hydrogen concentration is present in electron-irradiated foils exposed to hydrogen gas than ahead of crack tips in bulk material also needs to be borne in mind when considering the contribution of HELP to HE in bulk material.

Softening in Bulk Specimens

Lower flow stresses have sometimes been observed during tensile tests for hydrogen-charged specimens (or specimens tested at very slow strain rates in hydrogen gas) compared with uncharged specimens tested in air, and this softening could be associated with the HELP effect. The influence of hydrogen on stress-strain curves depends on the material, its purity, strain rate, temperature, and other variables, and softening is favoured at low strain-rates and intermediate temperatures (whereas hardening is often observed in other circumstances). The degree of softening is usually quite small, e.g. in hydrogen-charged Al (Fig.8(a)) [14] and nickel [69], but is sometimes large, e.g. in hydrogen charged pure iron single crystals at low temperatures and low strain rates [70,71] (Fig.8(b)). Cyclic stress-strain curves for nickel single crystals (oriented for single slip) also exhibit a lower saturation stress (by about 10%) for hydrogen-charged specimens compared with uncharged specimens. [72] Measurements of stress-relaxation and the temperature dependence of the flow stress in nickel and nickel-carbon alloys are consistent with HELP, in that the activation volume and activation enthalpy for thermally activated motion of dislocations are decreased when hydrogen is present. [12-14] These observations provide support for HELP, but the possibility that other effects could sometimes be involved must be considered.

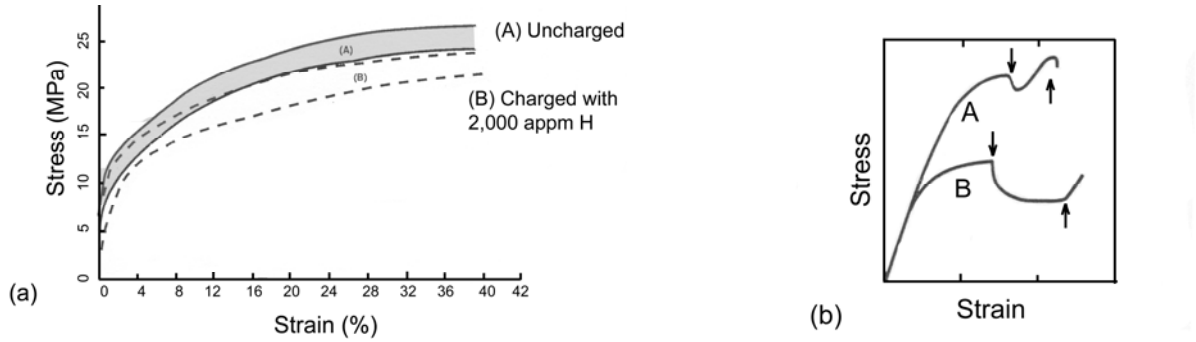

FIGURE 8 - Stress-strain curves for (a) high-purity aluminium in hydrogen-charged and uncharged conditions (or charged and vacuum-annealed condition) at 22°C, showing small decreases in flow stresses when hydrogen is present (Adapted from Sirois et al. [14]), and (b) high-purity iron, with hydrogen charging switched on and off during testing, at less than about minus 80°C (curve A) and greater than about minus 80°C (curve B), showing substantially lower flow stresses during charging, especially at low temperatures. (Adapted from Hirth [70] summarising data from Matsui et al.[71])

Effects of hydrogen-charging prior to or during testing which could change stress-strain behaviour besides HELP in bulk specimens are: (i) intrinsic hardening owing to hydrogen atmospheres around dislocations pinning or inhibiting dislocations (in the temperature and strain-rate regimes where hydrogen cannot keep up with dislocations), (ii) generation of dislocations due to non-uniform hydrogen concentrations that result in locally high stresses near the surface, (iii) changes in the properties of oxide films, (iv) generation of vacancies and formation of vacancy-hydrogen complexes, (v) formation of hydrogen-filled bubbles, and (vi) formation of hydride films or phases or, in unstable austenitic stainless steels, formation of stress-induced martensite. Some of the effects could result in softening, e.g., if there were few pre-existing dislocation sources present, introducing some dislocations by hydrogen-damage could produce softening. Many of the extrinsic effects, however, would result in hardening, which could mask intrinsic softening due to HELP. Furthermore, when HELP produces strain localisation, increases in the macroscopic flow stress could occur even though intrinsic softening occurs within slip bands. [73]

Observations of Slip Lines and Dislocation Arrangements

Increases and decreases in the spacing and height of slip steps, and in the number of active slip systems (produced by tensile or indentation tests) have been reported for hydrogen-charged specimens compared with uncharged specimens (Figs 9-11). The exact behaviour depends on the material, hydrogen content, microstructure, degree of strain, and other variables, and HELP has been invoked to explain all these effects. [74-79] An ability to accommodate higher shear strains in slip bands (owing to HELP) could result in fewer active slip systems and coarser slip steps in some circumstances, while decreased elastic interactions between adjacent slip bands (owing to HELP) could lead to more closely spaced slip bands and smaller slip steps in other circumstances. Preferential activity of edge-dislocation components over screw components (owing to HELP) could lead to inhibited cross-slip and strain-localisation, resulting in coarser slip bands, but could also lead to enhanced hardening in slip bands leading to other slip systems being activated. Some of the extrinsic effects of hydrogen-charging mentioned previously could also influence slip characteristics and, hence, the above observations cannot always be interpreted as unequivocal evidence for HELP.

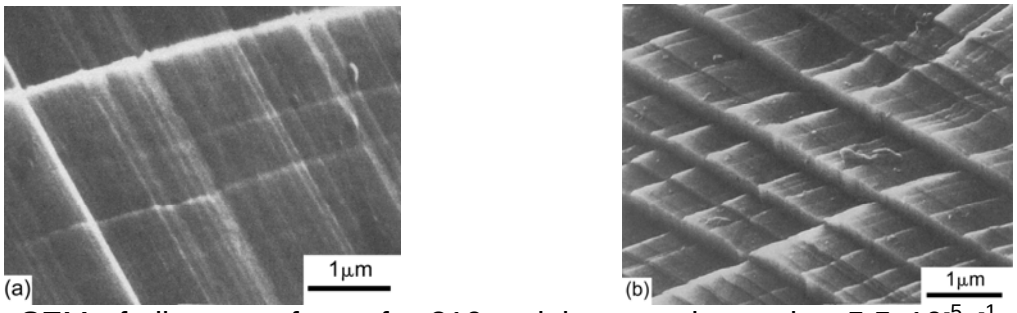

FIGURE 9 - SEM of slip on surface of a 310 stainless steel tested at $5.5x10^{-5}s^{-1}$ and $22^{o}C$ in (a) uncharged, and (b) charged (2.7at.%H) conditions. (Adapted from Abraham & Altstetter [74])

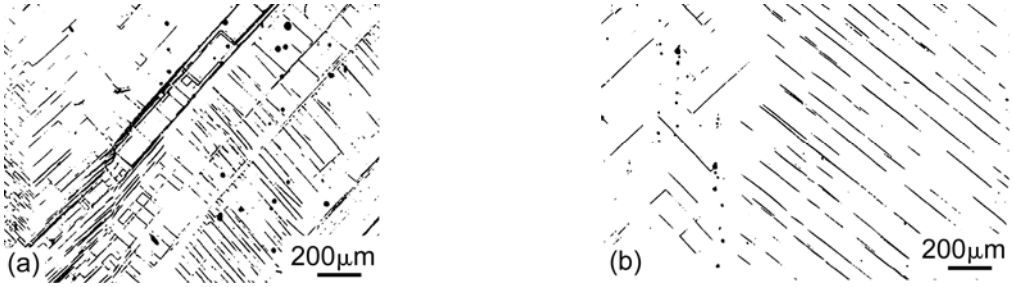

FIGURE 10 - Optical micrographs of slip on (100) face of nickel-base superalloy single crystals strained 5% at $10^{-4}s^{-1}$ and $20^{o}C$ in (a) uncharged, and (b) charged conditions (Adapted from Brass & Chene [75])

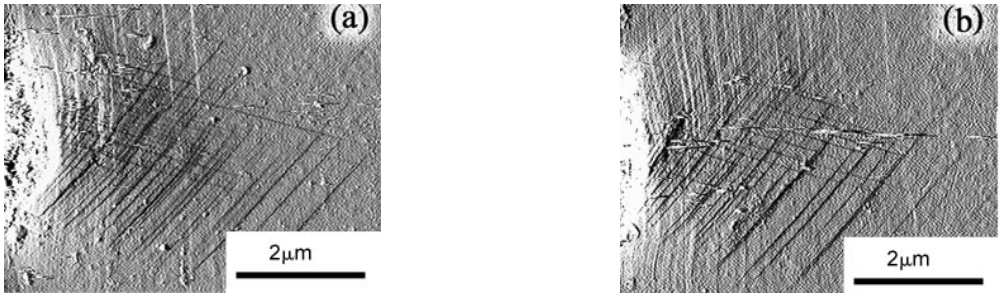

FIGURE 11 - AFM images of slip around nano-indentations in a stainless steel for (a) uncharged, and (b) charged conditions in the same grain. (Adapted from Nibur et al.[76])

Observations of dislocation arrangements beneath surfaces by TEM of thin foils of hydrogen-charged and uncharged specimens strained to various extents also indicate that solute hydrogen can produce strain localisation in some materials such as iron and stainless steel [79,80] For some materials, such as nickel, however, dislocation arrangements were similar for strained hydrogen-charged and uncharged specimens. [81]

Nano-indentation Experiments

Besides observations on the effects of hydrogen on slip characteristics around indentations (discussed above), load-depth and load-time data obtained from nano-indentation tests on hydrogen-free and hydrogen-charged material can also provide information on hydrogen effects during deformation. For example, for nickel single crystals (with a {111} surface) introducing hydrogen into specimens decreased the pop-in load (under increasing loads) and decreased the pop-in time (under constant load). [82] Hydrogen could be introduced and removed electrochemically, and the effects on pop-in were reversible, suggesting that they were intrinsic ones associated with solute hydrogen. Oxide-film effects could be discounted, and the results were explained on the basis that solute hydrogen reduced the shear modulus and facilitated the homogeneous nucleation of dislocations in a volume of material underneath the indenter.

BACKGROUND SUPPORT FOR A HEDE MECHANISM

Unequivocal, direct experimental evidence for HEDE (like AIDE) is difficult to obtain, and the background support for HEDE is mostly theoretical. For example, the embedded-atom method applied to the nickel-hydrogen system, previously mentioned as supporting AIDE, also supports HEDE, with HEDE occurring when slip planes at crack tips are not favourably oriented for slip and AIDE occurring when they are favourably oriented. [60-62] Other quantum-mechanical calculations also suggest that hydrogen reduces interatomic bond strength between metal atoms by reducing the electron-charge density between them, particularly at grain boundaries where hydrogen concentrations can be high. [83,84]

Atomistic calculations also show that bonds across grain boundaries in a variety of materials are weakened by segregated metalloid impurity atoms, e.g. S in Ni, P in Fe, Bi in Cu, [85] and there is experimental evidence (from TEM observations of fracture of thin foils) that atomically brittle fracture (with little or no dislocation activity) can occur in some of these systems. [86] Thus, it would not be surprising if hydrogen segregated at grain boundaries had the same effect, with decohesion particularly likely to occur if both hydrogen and metalloid impurities were present. [87] Perhaps the most direct experimental evidence that hydrogen can weaken interatomic bonds is the easier field-evaporation of surface atoms observed during from field-ion microscopy. [88]

RELATIVE CONTRIBUTIONS OF AIDE, HELP, AND HEDE FOR DIFFERENT MODES OF HYDROGEN-ASSISTED FRACTURE

Cleavage-like Fractures in FCC and BCC Materials

A variety of observations suggest that AIDE predominates for many cleavage-like fractures produced in fcc and bcc materials by HE and hydrogen-induced SCC. Thus, AIDE best accounts for (i) the detailed metallographic and fractographic characteristics of fracture, (ii) the remarkable similarities between HE, SCC, and adsorption-induced LME, (iii) observations that

cleavage-like cracking can occur at very high velocities, (iv) the effects of hydrogen-pressure, temperature, and oxygen additions on kinetics of cracking, and (v) the absence of embrittlement in some hydrogen-charged materials under certain conditions, as discussed in the following.

Characteristics of Cleavage-like Cracking produced by HE, SCC, and LME: The characteristics of cleavage-like cracking produced by HE, SCC, and LME are remarkably similar for a number of different fcc and bcc single-crystal and polycrystalline materials in a variety of environments, e.g. Fe-Si cracked in hydrogen gas and in liquid lithium, nickel cracked in hydrogen gas, aqueous environments, and in liquid mercury, Al alloys cracked in moist air or water and in some liquid metals, and β-brass cracked in water and in liquid gallium. [18,21,23,24] In all these cases, fracture surfaces were macroscopically parallel to {100} planes with crack fronts along <110> directions, i.e. parallel to the line of intersection of {111} or {112} slip planes with the crack plane. Crack growth often occurred in two different <110> directions in adjacent areas so that serrated steps and tear ridges parallel to the directions of cracking formed herringbone patterns (Figs. 12-14). These crystallographic crack planes and directions were observed regardless of whether or not crystal orientations with respect to the stress-axis favoured this plane and direction, although deviations of up to 15° sometimes occurred when {100} planes were unfavourably oriented with respect to the tensile-stress axis.

Considerable slip on {111} or {112} planes intersecting crack tips is observed on side surfaces of specimens (Fig.15) (and in the interior when special etching techniques are used), and the active slip planes intersect crack fronts for {100} <110> fracture planes and directions (Fig.16). More general plasticity (with larger plastic zones) and larger crack-tip-opening angles are observed around ductile cracks than cleavage-like cracks. Other evidence that cleavage-like fracture surfaces are associated with locally high strains includes diffuse electron-channelling patterns (and electron back-scattered diffraction patterns) and high dislocation densities observed just beneath fracture surfaces by TEM. [89,90] Isolated large dimples sometimes observed on cleavage-like fracture surfaces owing to formation of voids at isolated second-phase particles are also indicative of large strains ahead of crack tips. The tear ridges are also the result of cracks intersecting (somewhat smaller) voids, although the 'leading edge' of dimples is often not obvious, so that the tear ridges have a Y-shaped appearance.

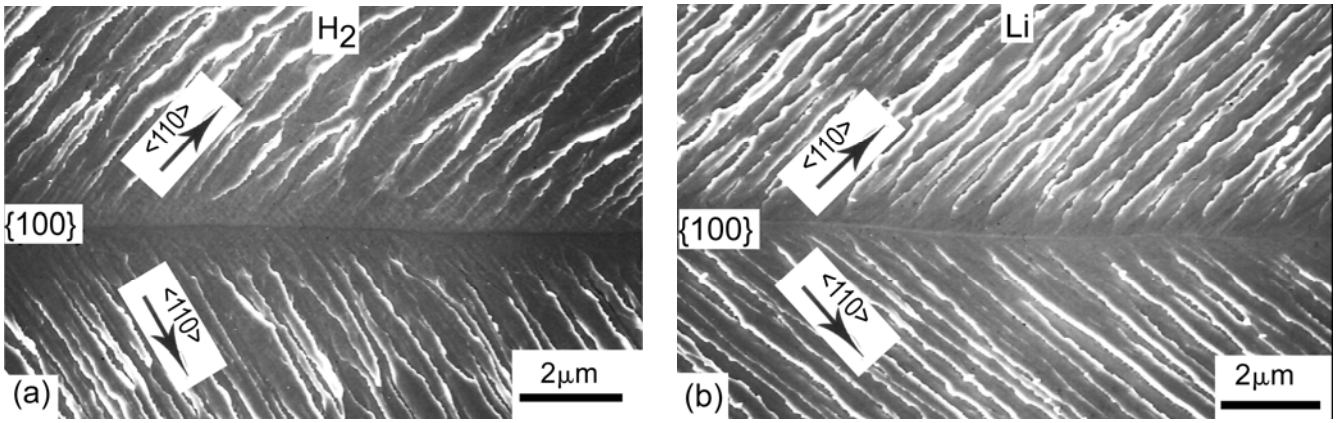

FIGURE 12 - SEM of cleavage-like {100} fracture surfaces produced in Fe2.6%Si single crystals by (a) slow crack growth (~10^{-3}mm/s) in gaseous hydrogen (101kPa) at 25°C, and (b) rapid crack growth (>1mm/s) in liquid lithium at 210°C, showing herringbone pattern of steps owing to crack growth in two <110> directions in adjacent regions. (Lynch [23])

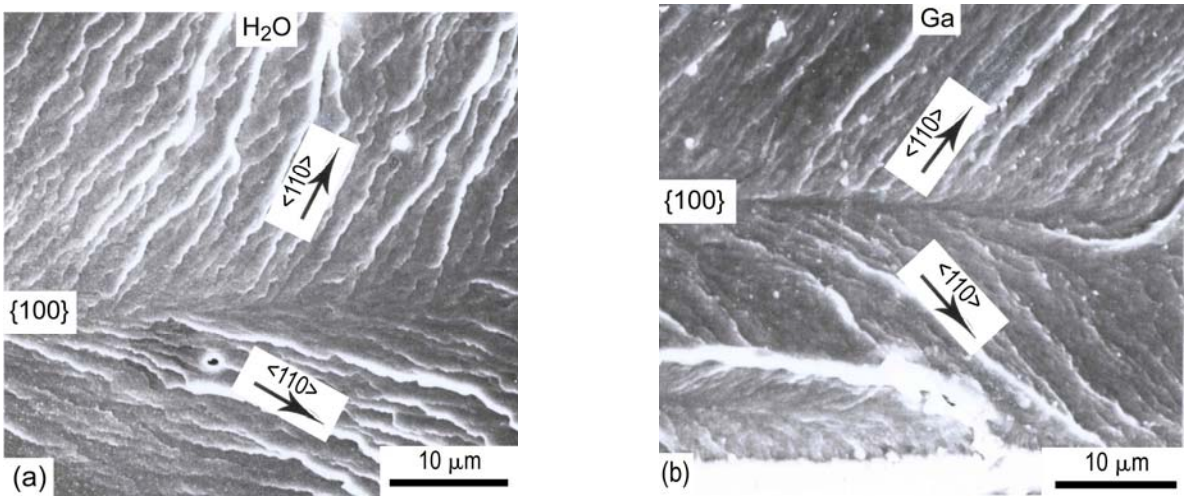

FIGURE 13 - SEM of cleavage-like fracture surfaces for β-brass single crystals produced by (a) slow crack growth (~10^{-3}mm/s) in distilled water at 20°C, and (b) rapid crack growth (~10mm/s) in liquid gallium at 30°C, showing herringbone patterns of steps. (Lynch [23])

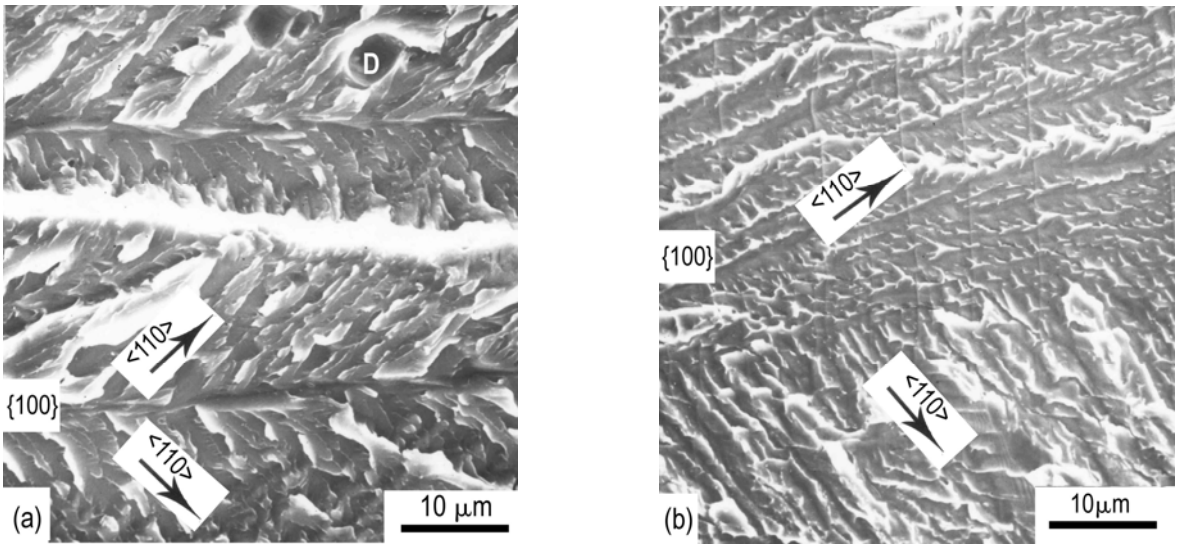

FIGURE 14 - SEM of cleavage-like fracture surfaces in (a) a peak-aged Al-Zn-Mg single crystal cracked in moist air (20% humidity) at 20°C (v ~10^{-7}mm/s), and (b) a nickel single crystal cracked in H_2 (101kPa) at 20°C (v ~10^{-3}mm/s), showing herringbone patterns. (Lynch [18,21,23])

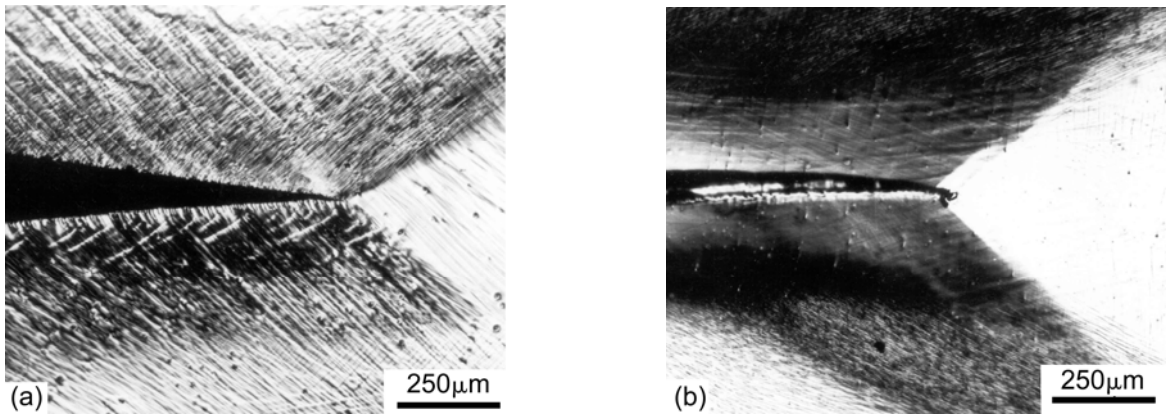

FIGURE 15 - Optical micrographs of slip on the side surfaces of specimens around crack tips for (a) an Al-Zn-Mg single crystal cracked rapidly (~10mm/s) in distilled water at 20°C, and (b) an Fe-Si single crystal cracked rapidly (~10mm/s) in liquid indium at 160°C. (Lynch [23])

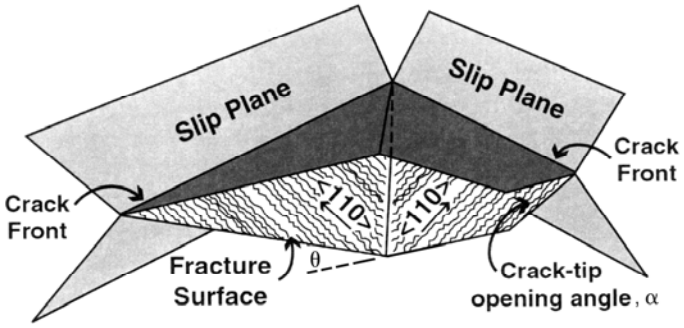

FIGURE 16 - Schematic diagram showing geometry of crack front and slip planes for {100}<110> fracture surfaces exhibiting herringbone patterns in fcc and bcc materials. Note that the fracture surfaces are tilted across the central spine of the herringbone pattern, with the extent of the tilt, θ, related to the crack-tip-opening angle, α, by the equation: $\text{Tan}\theta/2=\text{Tan}\alpha/2.\text{Cos}45^{o}$ (Lynch [23]).

At high magnifications, considerable fine detail is evident on cleavage-like fracture surfaces between the steps and tear ridges. The small, shallow depressions observed are probably dimples resulting from the nucleation, growth, and coalescence of 'nano'-voids ahead of crack tips, and the fine lines are almost certainly the result of slip at or just behind crack tips. These features can sometimes be resolved by SEM, but TEM of replicas of fracture surfaces show them more clearly (Fig. 17). In this respect, it is important to note that the procedure for preparation and examination of replicas for resolving very shallow features on fracture surfaces is critical. [23] Carbon replicas should be thin, shadowed sufficiently with a heavy element (such as germanium) at low angles (10-15˚), usually in two orthogonal directions, and then examined at high tilt angles (30-40˚) at 60 kV using a small objective aperture – procedures that are have not often been used in the past and are now very rarely used. Little or no corrosion after fracture is, of course, another requirement for observing fine-scale features produced by the fracture process.

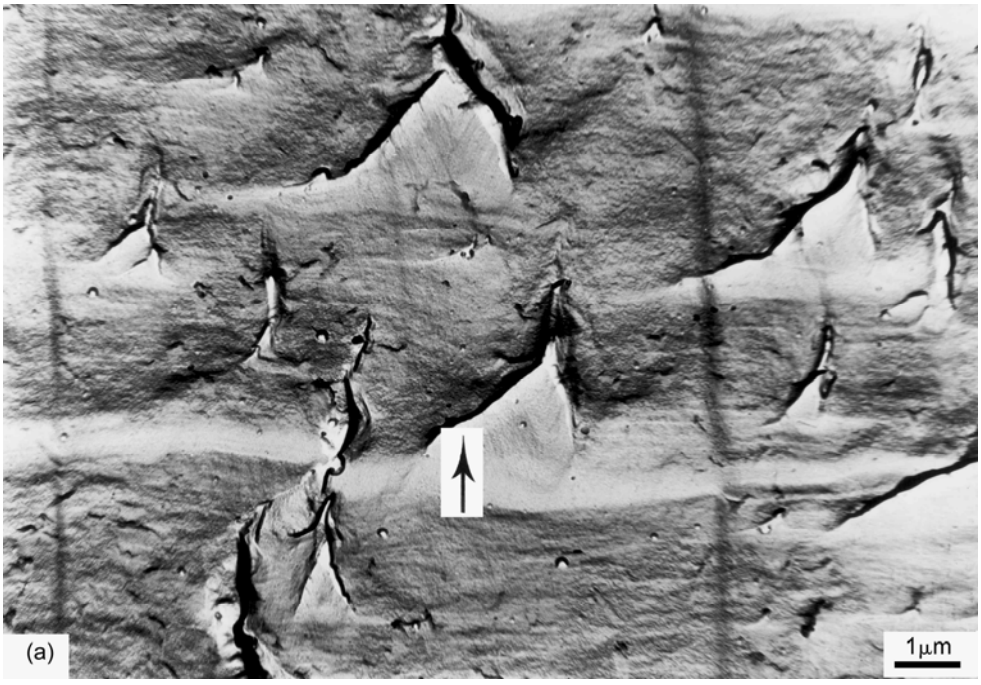

FIGURE 17(a). Caption on next page.

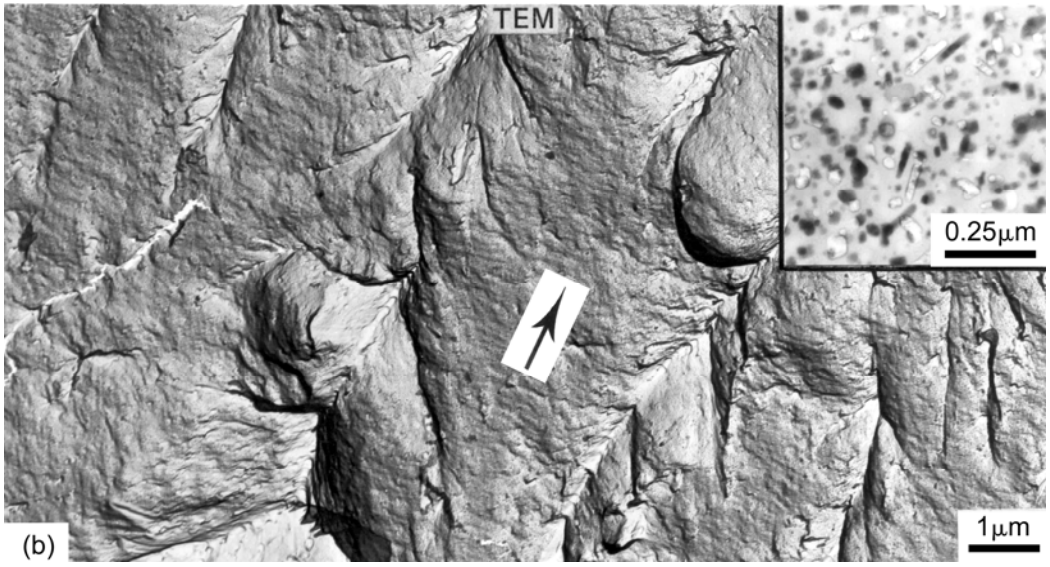

FIGURE 17 – TEM of secondary-carbon replicas of cleavage-like fracture surfaces for (a) a nickel single crystal cracked slowly (~10^{-3}mm/s) in hydrogen gas, and (b) an overaged Al-Zn-Mg single crystal cracked rapidly (~10mm/s) in distilled water, showing fine details, which are probably small dimples (initiated from age-hardening precipitates shown in the inset for the Al alloy), between the steps and tear ridges. (Lynch [18,21,23])

Whether the small depressions observed on cleavage-like fracture surfaces by TEM of replicas are, in fact, small dimples is debatable when they are extremely small. The depressions are unlikely to be an artefact of the replicating technique since similarly sized steps and slip traces are faithfully replicated, and no significant corrosion (besides formation of very thin oxide films) should occur on fracture surfaces for the materials and testing conditions used. Moreover, for cleavage-like SCC fracture surfaces of Al-Zn-Mg alloy single crystals aged to different extents, the depressions were larger for more overaged conditions, consistent with dimples resulting from voids nucleated at age-hardening precipitates. Isolated large dimples resulting from void nucleation around inclusions were clearly identifiable (by SEM) for all ageing conditions, indicating that strains associated with cleavage-like fractures were substantial, and likely to be sufficiently high to nucleate voids at small age-hardening precipitates.

For ‘pure’ materials, there may be sufficient impurities present to result in numerous particles of sufficient size (>50nm) to nucleate voids. [91] For materials without large numbers of precipitates and particles, such as ‘pure’ nickel, voids could be nucleated at slip-band intersections, dislocation-cell boundaries, or vacancy clusters. [92-94] Thus, there is no shortage of void-nucleation sites even when few particles are present, providing that strains are locally high – as they evidently are, given that isolated large dimples associated with widely dispersed particles are often observed on cleavage-like fracture surfaces and that extensive slip is observed around crack tips. Thus, the supposition that the small depressions are dimples resulting from a nano/micro-void coalescence process is supported by both direct and indirect observations.

The {100} <110> crystallography of fracture surfaces, with extensive slip on {111} or {112} planes intersecting crack tips, and the presence of small dimples on fracture surfaces are entirely consistent with the AIDE mechanism. Moreover, the remarkable similarities between HE/SCC and LME show that an adsorption mechanism can produce these fracture-surface characteristics since only adsorption can occur for LME in the systems considered because

there is neither the time nor the tendency for interactions other than adsorption. Although the {100} <110> crystallography is the most common for cleavage-like cracking produced by HE, LME, and hydrogen-assisted SCC, cracking along other low-index planes such as {110} has also been observed. What determines which fracture plane occurs is not understood.

It can be argued that similar, relatively featureless fractures produced in different environments could occur by different mechanisms, and such arguments are reasonable when fracture surfaces are fairly featureless, e.g. smooth intergranular fracture surfaces could be produced by decohesion or dissolution. However, these arguments are much less convincing for cleavage-like fractures where the crystallographic fracture plane and direction, the active slip planes, and the *richly detailed* fracture-surface appearance are all the same. The observations for Ni single crystals cracked in hydrogen gas and liquid mercury are particularly striking since the detailed appearances of fracture surfaces depended on the crystal orientation with respect to the stress axis, but were the same for both environments for each orientation (Figs 18-20).

While the characteristics of cleavage-like fracture surfaces can be explained by an AIDE mechanism, it is difficult to envisage how a HELP mechanism involving just facilitating localised dislocation activity ahead of cracks could produce a change from non-crystallographic ductile fracture in inert environments to a cleavage-like fracture macroscopically along {100} planes in <110> directions in hydrogen-bearing environments. (The proponents of the HELP mechanism have not offered any explanation of how HELP might produce cleavage-like fracture.) Minor contributions from HELP, however, cannot be ruled out since, if dislocations emitted from crack tips (owing to AIDE) gathered hydrogen atmospheres (and atmospheres were present around other dislocations and obstacles ahead of crack tips), emitted dislocations may be able to move away from crack tips more readily (owing to HELP), so that subsequent dislocation emission was facilitated owing to lower back stresses. The nucleation of voids ahead of cracks could also be facilitated by HELP if plasticity was localised to greater extents than would be the case without the HELP effect.

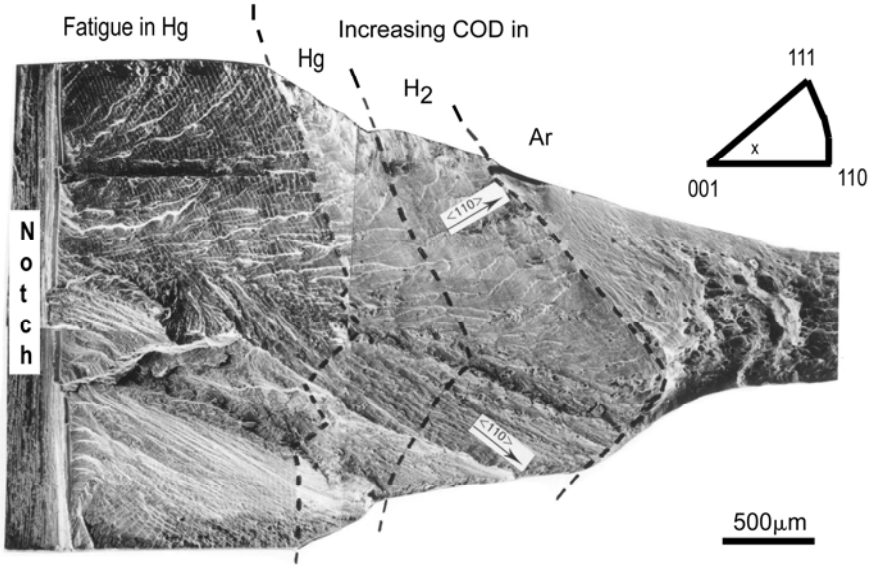

FIGURE 18 - Composite SEM of fracture surface of notched nickel single crystal (with a near-{100} orientation), fatigue pre-cracked in mercury, then cracked under monotonically increasing displacement producing crack velocities 0.5-1mm/s, first in mercury and then in gaseous hydrogen (101kPa), and finally in dry argon at 20^{o}C. Note that there is considerable lateral contraction at the sides of the specimen during cracking in mercury and hydrogen, indicative of very large strains, which are even larger for cracking in argon. (Lynch [21,23])

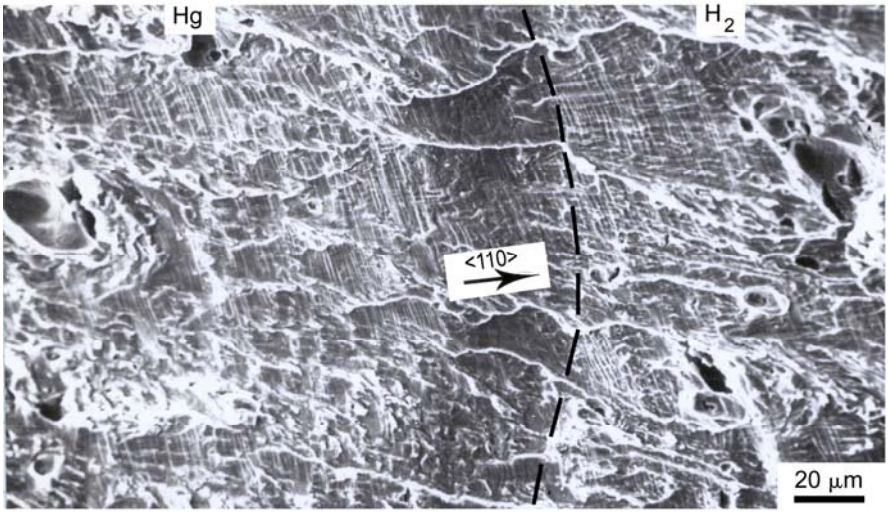

FIGURE 19 - SEM of fracture surface of junction between regions produced in mercury and hydrogen at a higher magnification than in the previous figure showing that features such as steps, tear ridges, slip lines, and isolated dimples are produced to the same extent in both environments. Note that the crack-tip-opening displacement was decreased slightly after evaporating mercury from cracks prior to cracking in hydrogen in order to produce a crack-front marking. (Lynch [21,23]) .

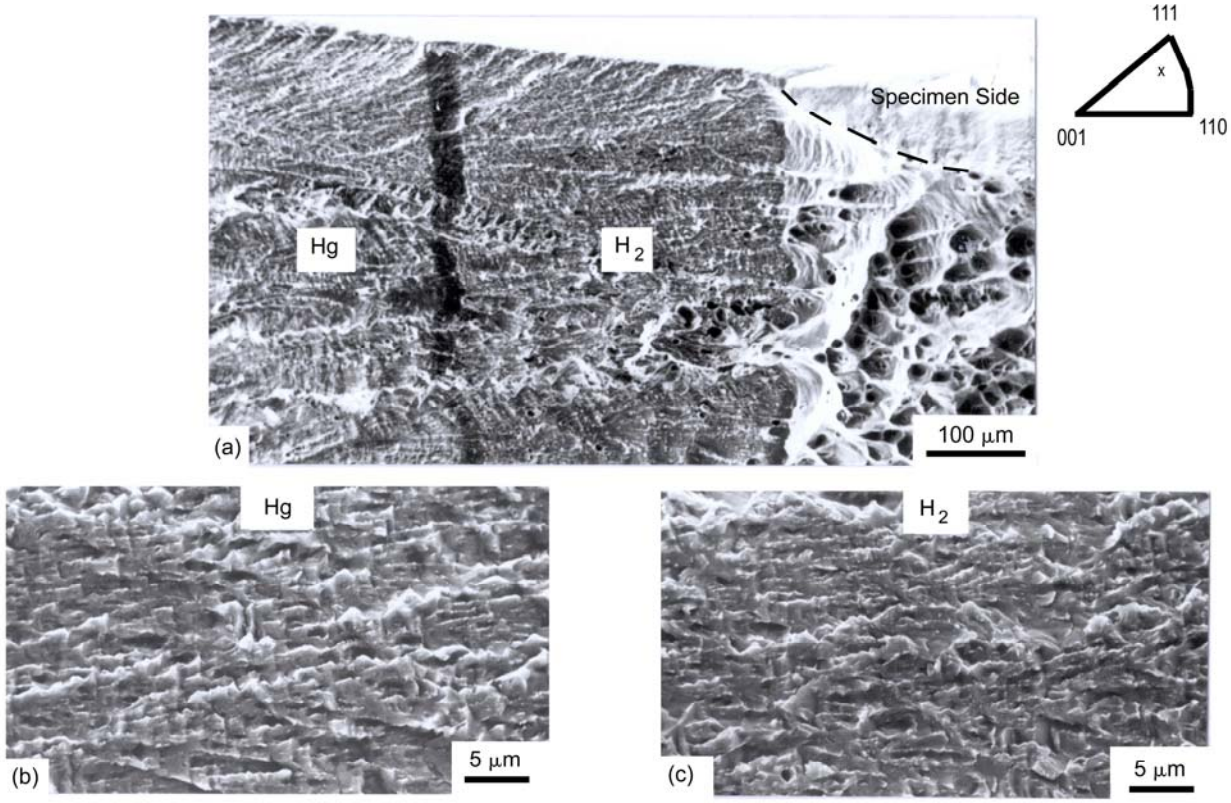

FIGURE 20 - (a) SEM of fracture surface of notched nickel single crystal (with a near-{111} orientation), fatigue pre-cracked in liquid mercury, then cracked under monotonically increasing displacements first in liquid mercury and then in gaseous hydrogen (101kPa), and finally in dry argon at 20°C (as described in the previous figure caption), again showing that the appearance after cracking in mercury and hydrogen are identical, although the appearance of fracture surfaces varies with crystal orientation: (b) and (c) SEM of areas produced in mercury and hydrogen at a higher magnification. (Lynch [21,23])

The characteristics of cleavage-like fracture surfaces described above are not only inconsistent with HELP but are also not compatible with HEDE playing a major role – given that large localised strains are associated with cracking, extensive slip occurs on planes intersecting crack tips, and there is evidence that crack growth occurs by a localised micro- (or nano-) void coalescence process. However, HEDE could play a minor role by facilitating void nucleation ahead of cracks by separation of particle-matrix interfaces weakened by trapped hydrogen. It is also conceivable that approximately equal proportions of AIDE and HEDE could occur in cases where strains are low and voids are not produced ahead of cracks. Thus, if stress-intensity factors required for each process were about the same, AIDE and HEDE could occur sequentially, with AIDE occurring until the back-stress from emitted dislocations increased somewhat so that HEDE then occurred, followed by AIDE again when the crack tip had moved away from the stress-field of dislocations previously emitted. Crack-growth increments by HEDE could maintain the <110> directions of crack growth produced by AIDE since the HEDE process might involve incipient shear movement of atoms rather than just tensile separation of atoms, as mentioned earlier. Schematic diagrams illustrating possible combinations of AIDE, HEDE, and HELP for cleavage-like cracking are illustrated in figure 21.

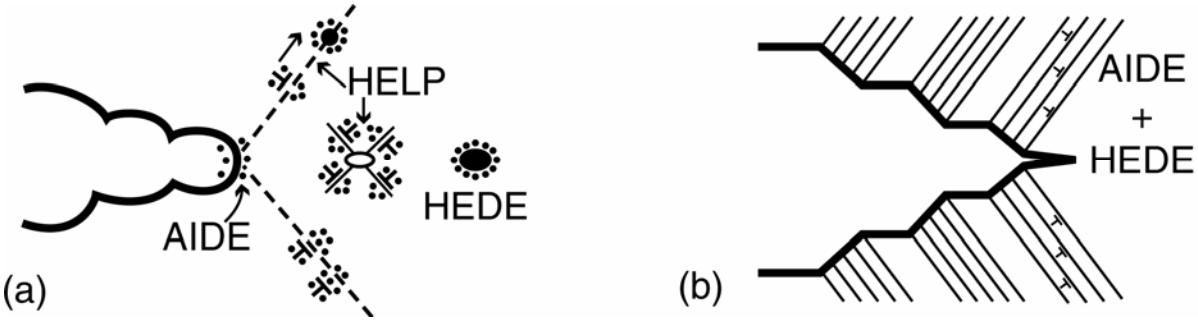

FIGURE 21 - Schematic diagrams illustrating hybrid mechanisms of hydrogen-assisted cracking: (a) AIDE with contributions from HELP and HEDE, and (b) AIDE alternating with HEDE. [25]

A characteristic of cleavage-like cracking not mentioned above, which at first sight appears to be more consistent with HEDE (or HELP) than AIDE is the crack-arrest markings (CAMs) sometimes observed on fracture surfaces (Fig. 22), which suggest that cracking occurs discontinuously with 0.1 to 1µm crack jumps. [89,95,96] Discontinuous cracking would be expected if HEDE or HELP occurred, with an increment of cracking occurring when a critical concentration of hydrogen built up over a critical distance ahead of cracks, followed by crack-arrest and blunting when cracks ran into a region of lower hydrogen concentration. However, discontinuous cracking might occur for other reasons and does not preclude an AIDE mechanism. In fact, CAMs have been observed on fracture surfaces produced by adsorption-induced LME. [97,98] Other possible explanations for CAMs for HE include (i) formation and intermittent fracture of ligaments behind the main crack tip which result in variations in the effective stress-intensity factor at crack tips, (ii) intermittent bursts of dislocation egress around cracks growing by AIDE owing to variations in the dislocation sub-structure ahead of cracks, and (iii) sequences of sudden coalescence of nano-voids when they reach a critical size and spacing, followed by crack-arrest, then nucleation and growth of voids ahead of the new crack tip. [98]

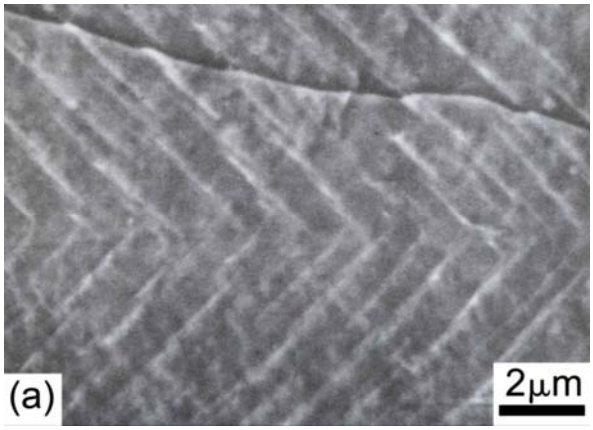

FIGURE 22 - SEM of cleavage-like fracture surface produced in an Fe-Si single crystal in gaseous hydrogen, showing crack-arrest markings. (Adapted from Chen and Gerberich [6,88,95])

Cleavage-like Cracking at High Velocities: In addition to the evidence above suggesting that AIDE predominates for cleavage-like cracking in fcc and bcc materials, observations that cracking in some fcc materials, with low hydrogen diffusivities, D, can occur at very high crack velocities, v, in hydrogen or aqueous environments in some circumstances indicate that adsorbed hydrogen alone can produce the characteristics observed. For pure nickel fatigue-pre-cracked single crystals tested in cantilever bending at 20˚C at high deflection rates (~50˚/s) in hydrogen gas (1 atmosphere), cleavage-like cracking at velocities of up to ~1mm/s has been observed. [21, 23] For a nickel-based superalloy single crystal (PWA 1480), which is strengthened by a high volume-fraction of γ' precipitates, sub-critical cracking in wedge-opening-load specimens in high-pressure hydrogen at 20˚C has been observed at crack velocities between 0.2 and 0.5mm/s for stress-intensity factors between 15 and 40MPa$\sqrt{m}$. [99] Fracture surfaces were not examined, but cleavage-like fractures along {100} planes have been reported in other studies of HE in PWA 1480. [100]

Analyses have indicated that significant hydrogen concentrations should not be present ahead of cracks for D/v ratios less than ~10^{-8}cm. [101,102] The hydrogen diffusivity at 20˚C for pure nickel is about 3 x 10^{-10}cm^2/s, and somewhat lower for Ni-based superalloys where trapping occurs. [103,104] Thus, D/v ratios are less than 10^{-8}cm for both materials. Transport of hydrogen by dislocations emitted from the crack tip (on inclined slip planes) is unlikely to occur at the high dislocation velocities associated with rapid crack growth, and even if it did, would be unlikely to result in hydrogen atmospheres around other dislocations and obstacles *directly* ahead of cracks. Thus, cracking at these high velocities is almost certainly the result of adsorbed hydrogen, i.e. hydrogen on the crack tip surface and, perhaps, within a few atomic distances of crack tips.

For fatigue pre-cracked precipitation-hardened Al-Zn-Mg single crystals tested by cantilever bending in water at 20°C at high deflection rates, cleavage-like cracking occurred at velocities of up to ~10mm/s (measured from high-speed cine films of the side surfaces of specimens) (Fig. 23). Published values of hydrogen diffusivities for Al-Zn-Mg (-Cu) alloys range from ~10^{-7} to ~10^{-10} cm^2/s [102] (with the wide range of values probably mainly associated with variability in surface conditions). For a crack velocity of 10mm/s, even using the highest D value, the D/v ratio is ~10^{-8}cm. Thus, hydrogen concentrations at distances of more than a few atomic distances ahead of cracks are likely to be insignificant, as discussed for Ni single crystals, so that an adsorption mechanism is probably responsible.

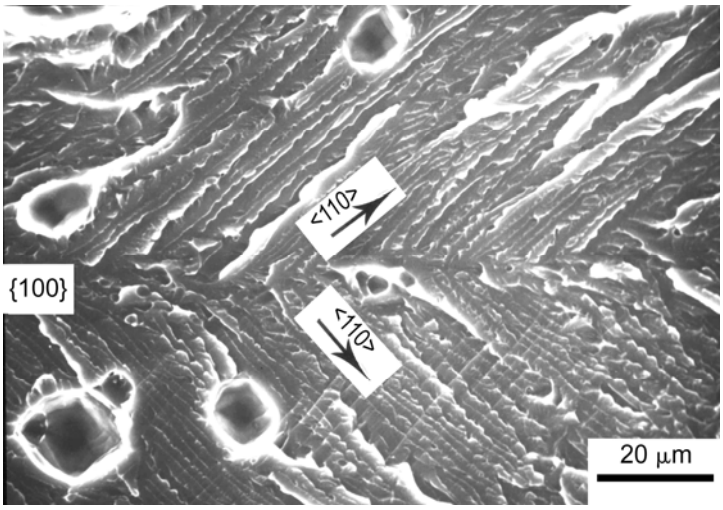

FIGURE 23 - SEM of cleavage-like fracture surface produced at high crack velocities (~10mm/s) in a fatigue pre-cracked, peak-aged Al-Zn-Mg single crystal tested by rapid cantilever bending in distilled water, showing herringbone pattern (and isolated large dimples), similar to that produced at lower velocities (by up to eight orders of magnitude) under sustained loading in water or moist air (Compare with figure 14(a)). (Lynch [18,23])

Fracture surfaces produced at high and low velocities in Ni and Al-Zn-Mg are similar, although more plasticity and larger crack-tip-opening angles are produced at high velocities, probably because surface coverages/concentrations of 'adsorbed' hydrogen at crack tips are lower at higher velocities so that smaller proportions of dislocation emission (versus dislocation egress) occur. HELP and HEDE could also make minor contributions to cracking at lower velocities when hydrogen has time to diffuse ahead of cracks, as previously discussed.

Effects of Hydrogen Pressure, Temperature, and Oxygen on Cleavage-like Cracking: Detailed analyses of the effects of hydrogen pressure and temperature on cleavage-like cracking in Ni (and Fe-Si) single crystals suggest that the embrittlement site is extremely close to crack tips (within about eight atomic distances). [105-107] Thus, this analysis does not support the HELP mechanism. However, given some uncertainties in the analysis, it is not really inconsistent with an 'adsorption' mechanism, where 'adsorption' is considered to include not only hydrogen on the surface but also hydrogen trapped within about three atomic distances of crack tips. Cleavage-like cracking has been observed for HE in nickel, not only in the temperature and strain-rate regime where HELP can occur, but also at temperatures (< -80^{o}C) and strain-rates where hydrogen diffusion is not sufficiently rapid for hydrogen atmospheres to keep up with dislocation movement. [108] Thus, HE under the latter conditions (which produces similar fracture-surface characteristics as those observed at higher temperatures) cannot be explained in terms of HELP, but could involve AIDE or HEDE.

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 suggest that cracking is due to a surface or very-near surface effect. [105-107] It was estimated that solute hydrogen (as atmospheres around dislocations) would be present for about 1μm 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 probably have continued 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.

Cleavage-like Fractures in Hydrogen-Charged Material: Tests on hydrogen-charged nickel single crystals (in air) also suggest that cleavage-like cracking is associated with adsorbed hydrogen rather than solute hydrogen since hydrogen-charged specimens are ductile (except, it appears, when adsorbed hydrogen is present at internal cracks or voids). Thus, fracture surfaces of fatigue pre-cracked, hydrogen-charged specimens exhibited large, deep dimples and stretched areas, with only isolated cleavage-like areas observed around large dimples (arising from voids nucleated from large isolated particles ahead of cracks) (Fig. 24). The cleavage-like areas can be explained by AIDE occurring when hydrogen has diffused or been transported by dislocations to voids to produce a sufficiently high concentration of hydrogen on (or within a few atomic distances of) the void surface. [21,23] Similar cleavage-like islands around dimples have also been observed on fracture surfaces of hydrogen-charged mild steel, and a similar explanation is probably applicable. [109-111]

For Al-Zn-Mg single crystals, electrochemically charged with hydrogen by straining un-notched tensile specimens in an aqueous environment, and then dried, notched, and fatigue pre-cracked prior to testing at slow strain rates in *dry* air, fracture surfaces exhibited large, deep dimples, with no signs of cleavage-like cracking (Fig. 25). [23] Thus, it appears that solute hydrogen does not facilitate transgranular cracking in aluminium alloys. Hydrogen could diffuse to internal voids, as for Ni and steels, but re-surfaced hydrogen would recombine and form hydrogen gas, which is more stable than dissociated hydrogen on Al surfaces so that there would be insufficient 'adsorbed' hydrogen at internal voids to produce AIDE. Cleavage-like cracking has been reported in hydrogen-charged Al alloy polycrystalline specimens (with cleavage-like areas usually initiating from intergranular cracks). [112] However, tests were not carried out in *dry* air, so that moisture in the air (or residual liquid in corrosion pits or products) could result in hydrogen production and adsorption at crack tips during testing.

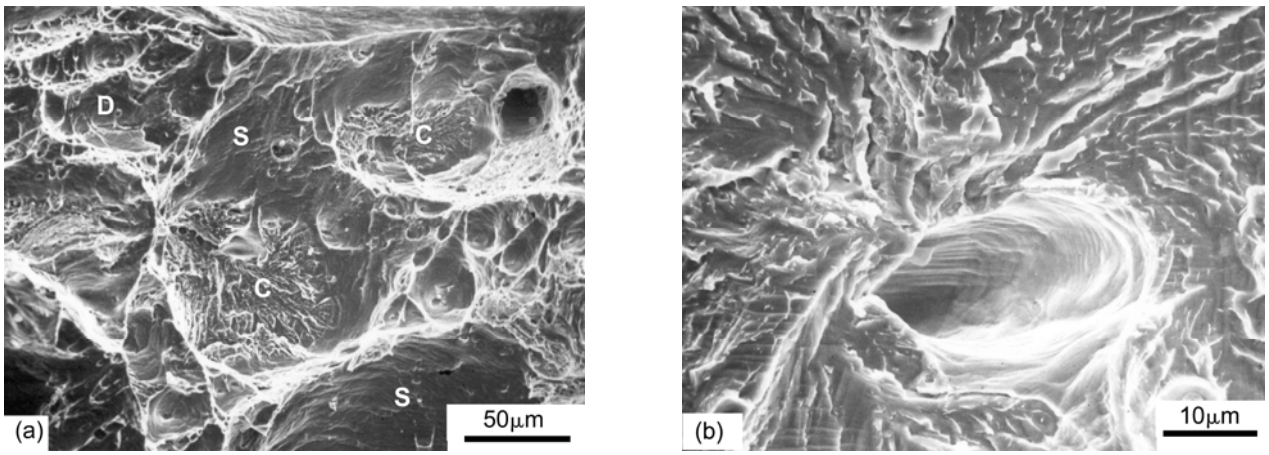

FIGURE 24 - SEM of fracture surface produced in a hydrogen-charged nickel single crystal (0.45 at.% H) tested in air at low cracking velocities (10^{-4}mm/s), showing (a) mostly ductile behaviour with dimples (D) and stretched areas (S), plus isolated cleavage-like islands (C), and (b) detailed appearance of cleavage-like region surrounding a deep dimple. (Lynch [21,23])

Ductile fracture has also been observed in a β-titanium alloy with high hydrogen concentrations (H/M ~0.2) suggesting that solute hydrogen at such levels is also innocuous in this material. However, increasing the hydrogen concentration to higher levels resulted in an abrupt transition to cleavage-like cracking, with the transitions occurring at an H/M value of ~0.21 at 25°C, and somewhat lower values at -25°C (Fig. 26). [12,113] A HELP mechanism was discounted because *in-situ* TEM observations of stressed thin foils showed that hydrogen

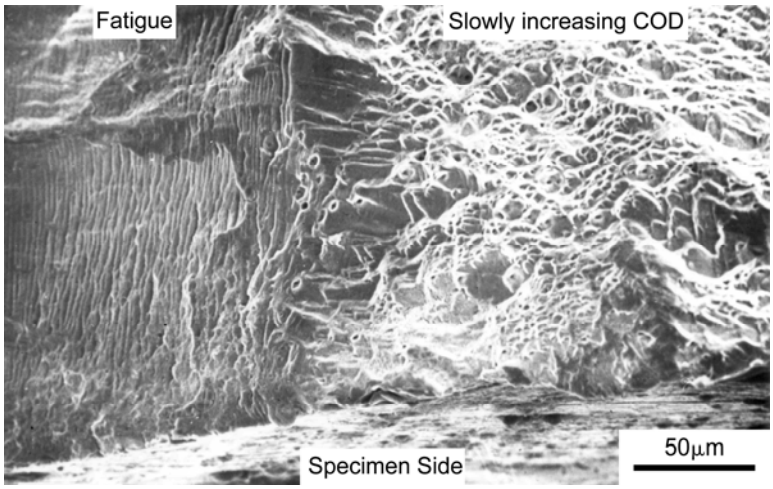

FIGURE 25 - SEM of fracture surface of produced by fatigue pre-cracking and then by slowly increasing crack-tip-opening displacement by cantilever bending at a deflection rate ~0.0006°/s in dry air for a hydrogen-charged under-aged Al-Zn-Mg alloy, showing ductile fatigue striations and dimples. The specimen was electrolytically charged with hydrogen for 4h in a 3.5NaCl + 250mg/l Na_2AsO_2 solution at 20°C at -1.6V (vs. SCE) while being simultaneously strained ~2% in tension at a slow strain rate (~10^{-5}/s) prior to notching, pre-cracking, and testing. (Lynch [23])

increased dislocation activity to similar extents both above and below the critical concentration for bulk embrittlement. A hydride mechanism was also discounted because detailed examination of specimens did not show any evidence of hydride formation. An AIDE mechanism was also ruled out because it was thought that adsorbed hydrogen would not be present at crack tips. It was therefore proposed [12,113] (largely by default) that HEDE occurred when a critical hydrogen concentration was reached ahead of crack tips. However, no *high-resolution* fractography was reported so that it was not clear whether fracture surfaces were consistent with a HEDE mechanism. In fact, the observations that were made suggested that significant plasticity occurred during fracture.

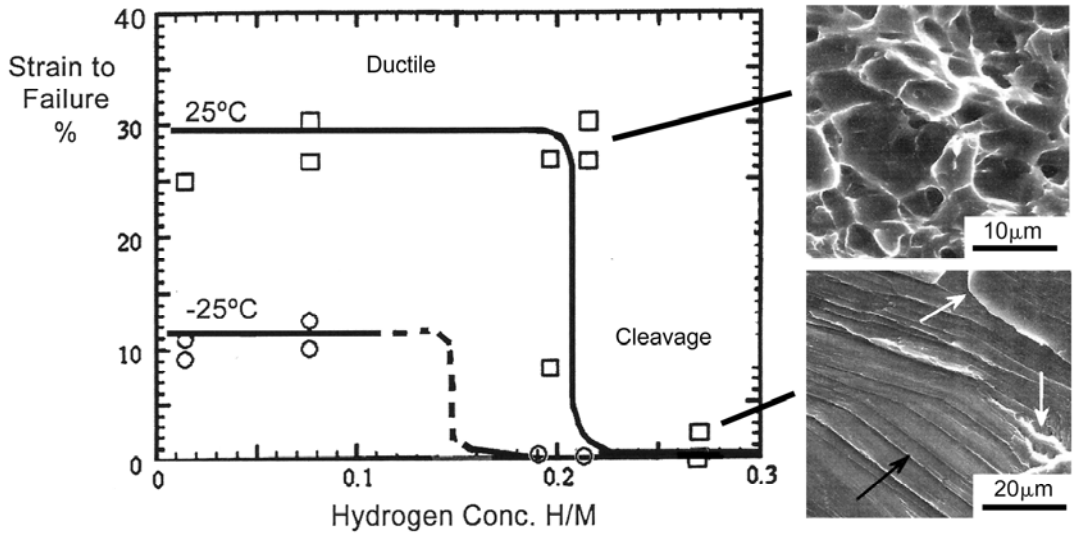

Figure 26 - Plot of strain to failure versus hydrogen concentration for β-titanium alloy tensile specimens tested in air at a strain rate of $10^{-5}s^{-1}$, showing sharp, temperature-dependent transitions associated with changes from ductile dimpled fracture to cleavage-like fracture, as shown in the accompanying SEMs. (Adapted from Teter et al. [12,113])

An alternative explanation for the temperature-dependant ductile-to-brittle transitions in the β titanium alloy could be that a surface (crack-tip) phase-transition occurs above a critical hydrogen concentration such that dislocation emission is facilitated and a localised micro/ nano-void-coalescence process occurs. Phase transitions at plane surfaces, which depend on temperature and composition of 'surface' layers, are a well established phenomenon, and phase diagrams are available for some systems. As discussed in an earlier section, surface-phase transitions (reconstructions) should also occur at crack-tip surfaces during crack growth, and should influence dislocation emission. For materials such as β-titanium with very high concentrations of hydrogen, diffusion of hydrogen to crack tips is probably unnecessary for embrittlement to occur, although re-arrangement of hydrogen in sub-surface 'adsorption' sites and re-surfacing of hydrogen during crack growth might be involved.

Cleavage-like cracking has also been observed in a hydrogen-charged 316 stainless steel (where strain-induced martensite is not likely to be formed at crack tips) (Fig. 27). [114] It appears that cracking, which occurred at high strain-rates, was not initiated at internal voids (as in nickel), and probably did not involve significant diffusion during testing. Thus, a HEDE mechanism or a dislocation-emission/localised plasticity mechanism owing to a crack-tip surface-phase change, as suggested for β-titanium, could possibly apply in this case.

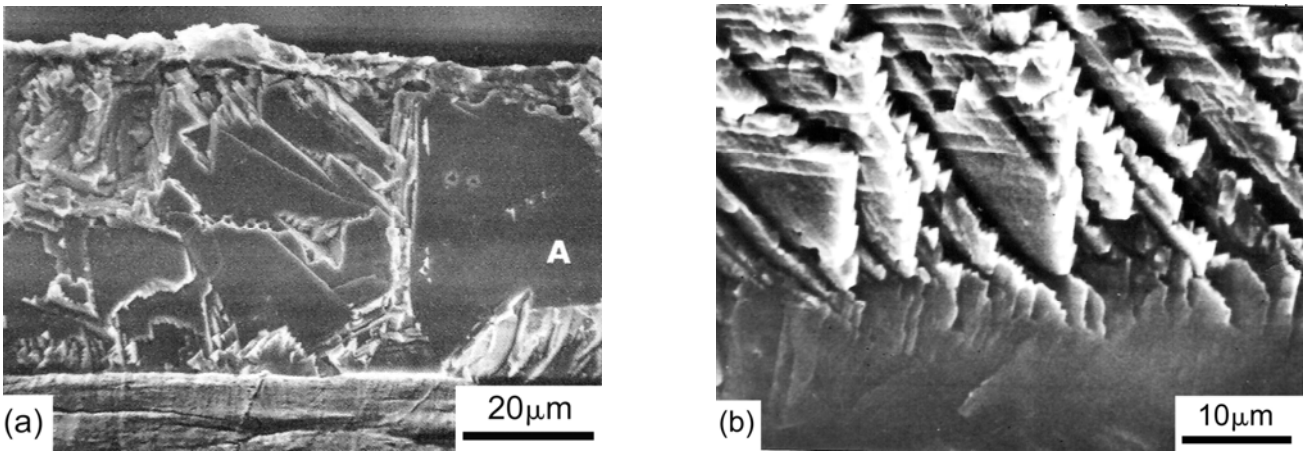

FIGURE 27 - SEM of fracture surface of thin (0.1mm) hydrogen-charged 316 stainless steel tensile specimens tested at high strain rates (~1mm/s), showing cleavage-like fracture (a) at low magnification, and (b) at a higher magnification. (Adapted from Hanninen et al. [114])

Cleavage-like Cracking in HCP Materials

Some of the observations that support an adsorption mechanism for fcc and bcc materials have also been made for cleavage-like SCC in magnesium and hcp titanium alloys (under conditions where hydrides do not form). For example, the appearance and crystallography of cleavage-like fractures produced by SCC are essentially identical to those produced by adsorption-induced LME (Figs 28,29). In addition, cleavage-like cracking at high velocities (~0.1mm/s for Ti alloys and ~50mm/s for Mg) in aqueous environments has been observed under certain conditions. [22-24] Fracture planes are parallel to basal planes for both Mg and Ti alloys, and also sometimes 10 -15^{o} away from basal planes for Ti alloys. [115]

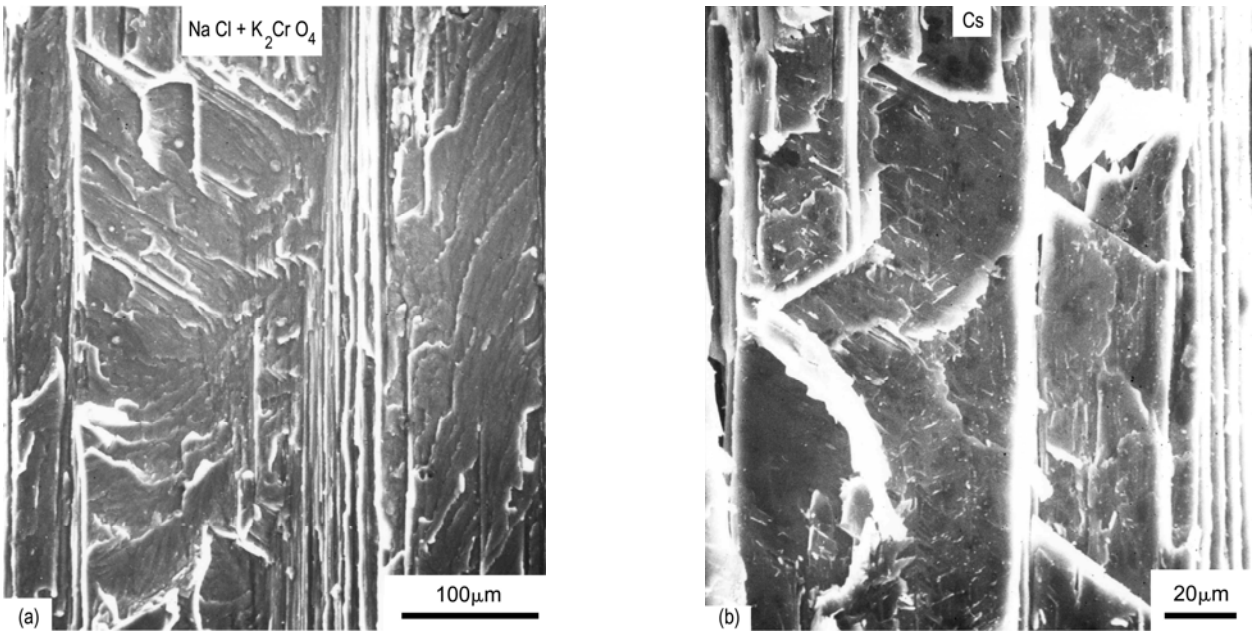

FIGURE 28 - SEM of cleavage-like {0001} fracture surfaces for pure magnesium produced by (a) slow crack growth (~10^{-3}mm/s) in a NaCl + K_2CrO_4 solution at 20°C, and (b) rapid crack growth in liquid caesium at 30°C. (Lynch [22,23])

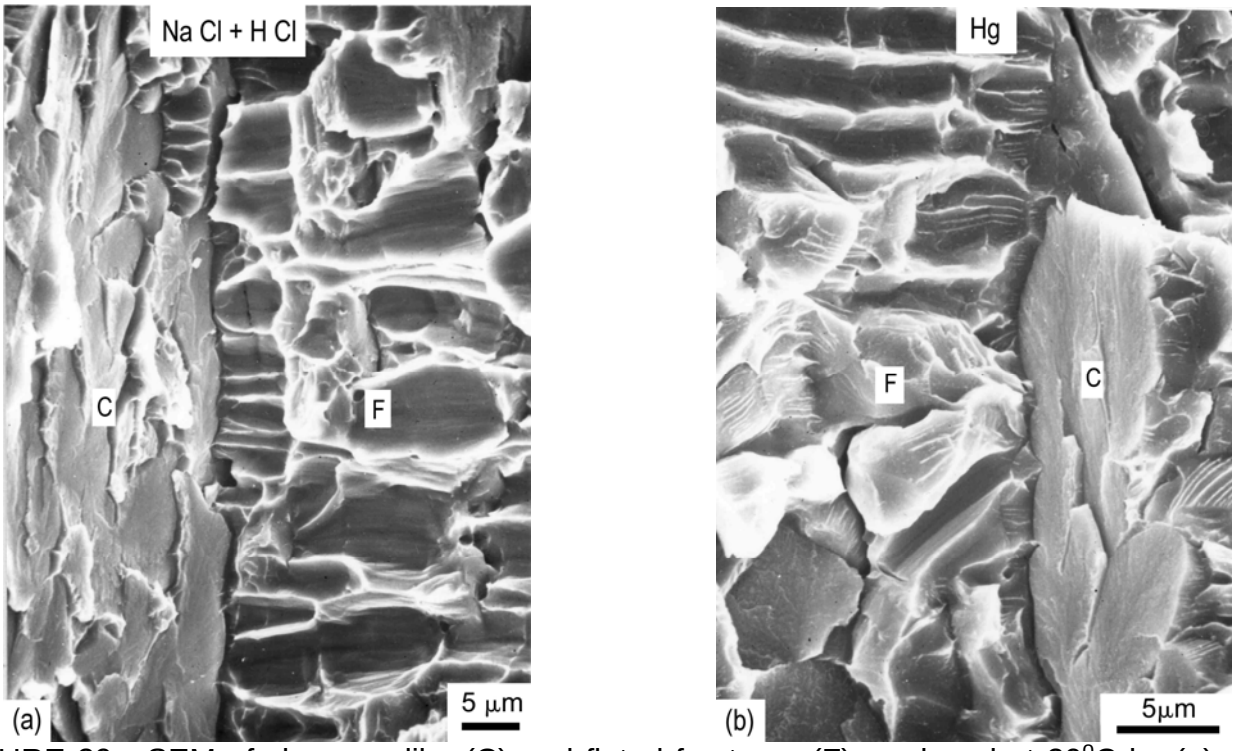

FIGURE 29 - SEM of cleavage-like (C) and fluted fractures (F) produced at 20°C by (a) slow crack growth in an aqueous environment, and (b) rapid crack growth in liquid mercury, in a Ti6%Al4%V alloy (Lynch [23])

The remarkably high SCC velocities observed for Mg were produced in very large-grained pure Mg under the conditions described for rapid SCC in Al-Zn-Mg single crystals, viz. fatigue pre-cracked specimens tested in cantilever bending at high deflection rates, while much lower velocities were produced under sustained loading conditions. D/v ratios at high velocities for

the Ti alloys are ~10^{-8}cm, but are not known for magnesium since there appears to be no reliable data for hydrogen diffusion rates in pure Mg at room temperature. However, D values required for significant hydrogen diffusion ahead of cracks at 50mm/s seem unlikely for a close-packed hcp lattice. Thus, a mechanism of cracking at high velocities based on adsorbed hydrogen is highly probable, and seems likely at low velocities as well since fracture surfaces produced by SCC were similar at high and low velocities, except for more post-fracture corrosion at the lower velocities.

TEM of replicas of fracture surfaces for Ti alloys revealed numerous tear ridges and perhaps small, shallow dimples similar to those observed for the fcc and bcc materials (Fig. 30(a)). The characteristics of cleavage-like fracture surfaces in Mg were somewhat different from those in Ti alloys in that there were fewer tear ridges and more 'tongue-like' features associated with twinning (Fig. 30(b)). TEM of replicas of fracture surfaces of Mg (produced at high velocities such that little corrosion occurred after fracture) revealed that the areas between the tongues were not completely featureless (as indicated by SEM), but whether the fine-scale markings are 'nano-dimples' is questionable owing to their extremely fine scale.

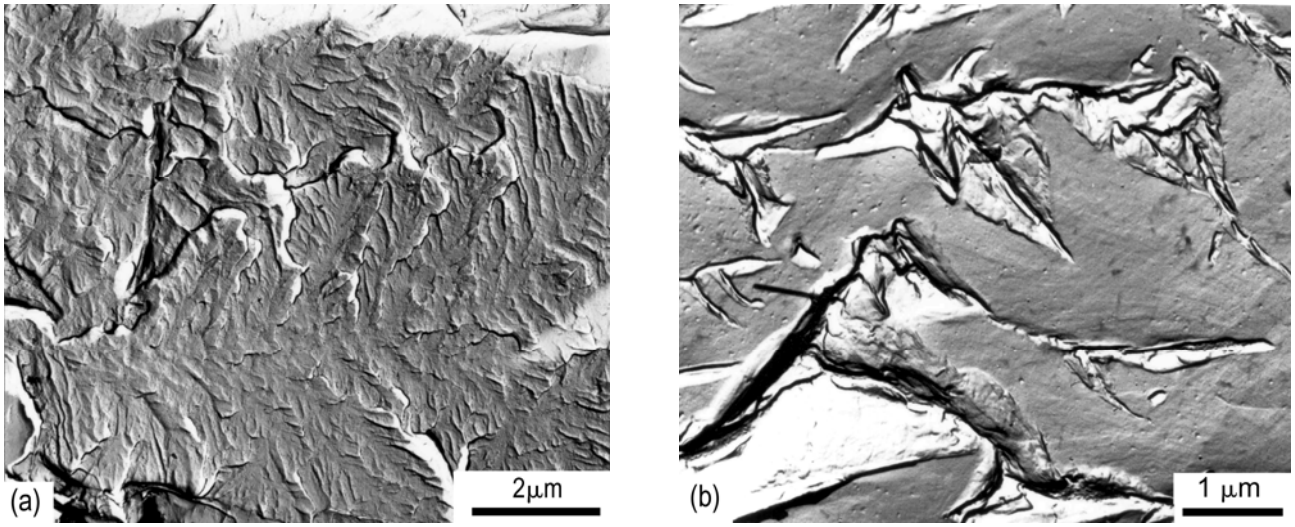

FIGURE 30 - TEM of cleavage-like fracture surfaces produced by SCC of (a)Ti6%Al4%V alloy showing numerous tear ridges, and (b) pure Mg showing 'tongues' associated with twins, and very fine markings between them. (Lynch [22,23])

The similarities between SCC and LME, the cracking at high velocities under some conditions, and the detailed appearance of fracture surfaces are consistent with an adsorption mechanism for Ti and Mg alloys, as discussed for fcc and bcc materials, but it is not clear whether AIDE of HEDE or combinations of these processes is involved. Also as discussed previously for fcc and bcc materials, it is difficult to account for cleavage-like cracking by a HELP mechanism. It is not clear why SCC sometimes occurs along basal planes and sometimes 10 to 15^{o} from basal planes for Ti alloys, but it is noteworthy that both fracture-plane orientations can also be produced by adsorption-induced LME.

Transgranular Fluted Fractures in HCP Materials

Fluted fracture surfaces, usually in addition to cleavage-like fractures, are produced by SCC and LME in some hcp metals, with the relative extents depending on grain orientations with respect to the applied stress. Fast fracture in inert environments can also produce fluted

fracture surfaces when there are limited slip systems active. Fluting results from a microvoid-coalescence process involving nucleation of long, tubular voids at slip-band intersections ahead of cracks, followed by coalescence of voids by slip on the same systems as involved in nucleation. Thus, elongated dimples (flutes) aligned in specific crystallographic directions are observed on macroscopically brittle, faceted fracture surfaces (Fig.31). In some cases, smaller, more equiaxed dimples are present within larger, elongated dimples.

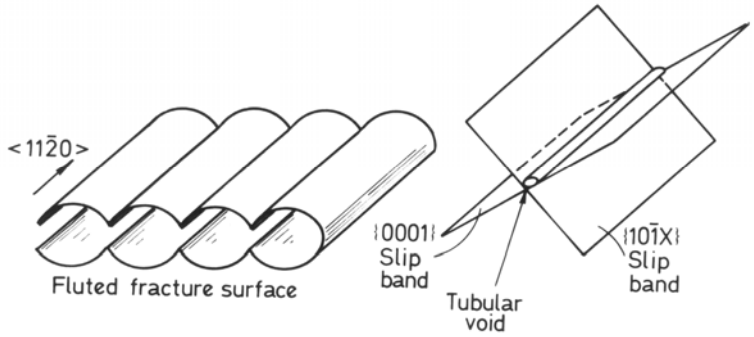

FIGURE 31 - Schematic diagram illustrating formation of fluted fracture surfaces, involving formation of tubular voids at slip-band intersections ahead of cracks.

Crack-growth in pure Mg (with very large grains) illustrates how the fluting process is influenced by the testing environment. Tests in aqueous environments and then in dry air (within the same grain) showed that flutes were much shallower and apparently smaller after fracture in the aqueous environment (Fig. 32). [22,23] The effect was more pronounced at lower SCC velocities, but was quite marked even at crack velocities of ~10 mm/s (produced as described earlier for cleavage-like cracking). Crack growth in liquid-alkali metal environments also produced finer-scale flutes than those resulting from fracture in air, with the fracture-surface appearance and crystallography essentially the same as those after slow crack growth in aqueous environments (Fig. 33).

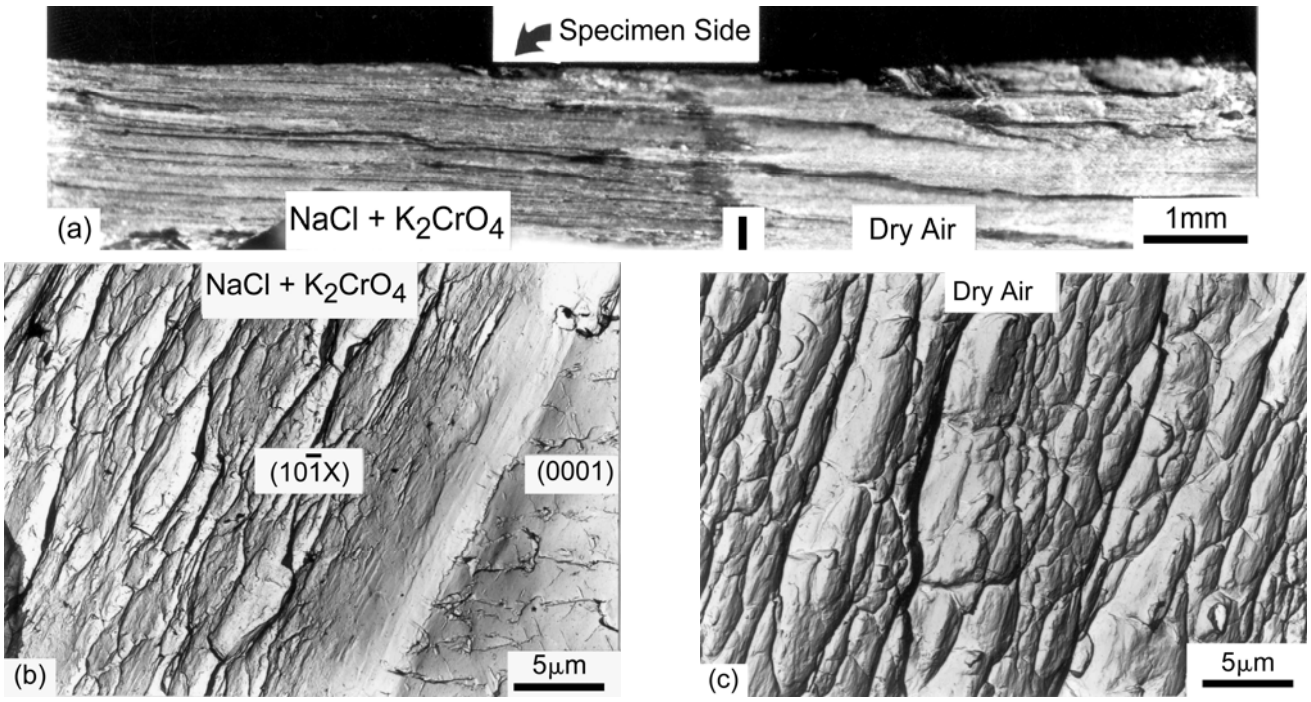

FIGURE 32 - (a) Optical micrograph and (b),(c) TEM of replicas of fracture surface of pure Mg ‘single crystal’ showing transition from shallow flutes (plus some secondary cracking) to large, deep flutes produced by changing the environment from a salt solution to dry air. (Lynch [22,23])

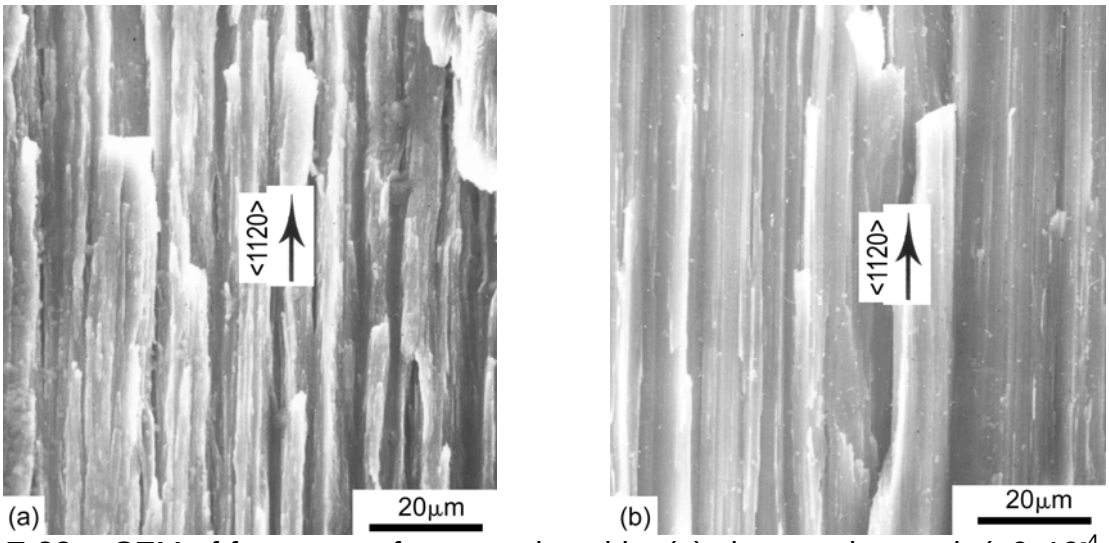

FIGURE 33 - SEM of fracture surfaces produced by (a) slow crack growth (~$6x10^{-4}$mm/s) in a salt solution at 20°C, and (b) rapid crack growth (~10mm/s) in liquid sodium at 120°C, for pure Mg, showing fluted fracture surfaces. (Lynch [22,23])

SCC and LME of Ti and Zr alloys also produce fluted (and cleavage-like) areas on fracture surfaces, whereas fast fracture in air produced more equi-axed dimples – presumably because strains were higher and more slip systems operated. All the observations regarding fluting are consistent with an AIDE mechanism for SCC and LME since crack growth clearly occurs by a more localised microvoid-coalescence process in embrittling environments than in air. HEDE clearly cannot be a major contributor, although HEDE could perhaps somehow be involved in void nucleation at slip-band intersections. HELP could also be a contributor to SCC at low velocities where hydrogen has time to diffuse ahead of cracks, since HELP might localise slip into narrower bands thereby possibly leading to higher stresses at slip-band intersections and easier void nucleation. However, the similarities between SCC and LME, and the occurrence of SCC at high velocities show, as for cleavage-like cracking, that adsorption alone can account for the effects observed without any contribution from other processes.

Dimpled 'Transgranular' Fractures in Steels

Sub-critical cracking of high-strength martensitic steels in gaseous hydrogen can produce completely dimpled transgranular fractures (with respect to prior-austenite grain boundaries but not necessarily with respect to martensite-lath boundaries) for certain steel compositions and heat treatments. It was such an observation that led Beachem [10] to challenge the then widely accepted decohesion theory, and propose that solute hydrogen facilitated dislocation activity ahead of cracks so that a more-localised microvoid-coalescence process occurred. Lynch subsequently confirmed that fracture surfaces produced by sub-critical cracking in gaseous hydrogen were completely dimpled for some heat-treatments and, moreover, showed that sub-critical cracking in liquid mercury could also produce completely dimpled fractures. [19,23] Furthermore, the dimples produced by HE and LME were shallower and appeared smaller than those produced by fast fracture in air (Fig. 34). (Comparison of dimple sizes is difficult because small, stretched dimples *within* large deep dimples are present on overload fracture surfaces, and the small, stretched dimples are sometimes difficult to resolve.) Lower strains to fracture and differences in dimple size (generally smaller and with a smaller depth-to-width ratio) have also been observed in hydrogen-charged steels compared with uncharged steels after tensile testing. [9,116,117]

The fact that adsorption-induced LME can produce the same dimpled fracture-surface appearance as HE indicates that solute hydrogen need not necessarily be involved, and that an AIDE mechanism could account for the observations, as discussed for cleavage-like and fluted fracture surfaces. However, since hydrogen can diffuse rapidly in steels, so that hydrogen will be present ahead of cracks, a combination of the AIDE, HEDE, HELP mechanisms could possibly be involved. Thus, HEDE could facilitate void nucleation by hydrogen-induced weakening of particle-matrix interfaces, and HELP could localise deformation so that void coalescence occurred with less crack blunting. Contributions of HEDE and HELP are, however, likely to be minor since void-nucleation at particle-matrix interfaces probably occurs fairly readily in the absence of hydrogen. For internal hydrogen embrittlement, an enhancement of void growth owing to high pressures of hydrogen within them is another possibility.

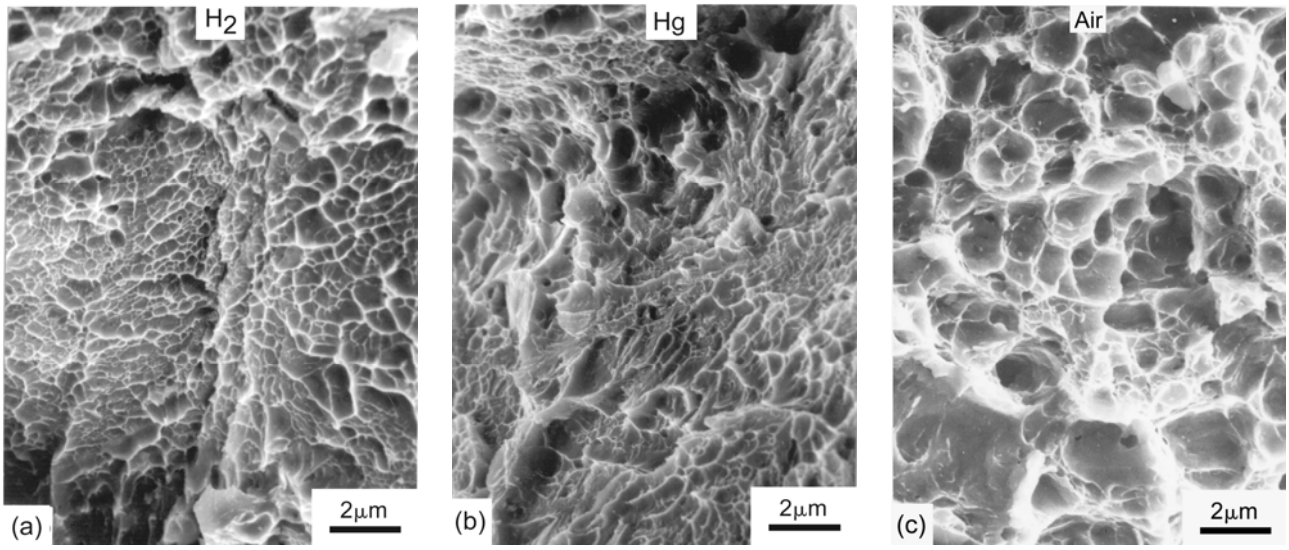

FIGURE 34 - SEM of transgranular fracture surfaces of D6aC steel (290ºC temper) resulting from (a) sub-critical cracking in gaseous hydrogen (1 atmosphere), (b) sub-critical cracking in liquid mercury, and (c) overload in air, at 20ºC, showing shallower dimples after LME and HEE compared with overload fracture. (Lynch [19,23])

Dimpled Intergranular Fractures

For some high-strength steels and heat-treatment conditions, small, shallow dimples are observed on intergranular fracture surfaces produced by both HE and LME, whereas relatively large, deep dimples are produced on transgranular fractures produced in air (Fig. 35). [19,23] Using the same arguments as discussed for dimpled transgranular fractures, the observations can best be explained by an AIDE mechanism predominating. Intergranular fractures rather than transgranular fractures due to AIDE may occur for several reasons. Firstly, bonding across grain boundaries may be already weakened by segregation of metalloid impurities (for the heat treatments where intergranular HE occurs), and additional (or synergistic) weakening of interatomic bonds by ‘adsorbed’ hydrogen or adsorbed mercury atoms could favour dislocation emission from intergranular cracks rather than transgranular cracks. Secondly, grain-boundary/crack-tip intersections could act as sites for preferential adsorption even in the absence of impurity segregation. Thirdly, grain boundaries are strong traps for hydrogen and possibly rapid diffusion paths, and tend to have more numerous and larger carbides than elsewhere, so that nucleation and growth of intergranular voids are likely to be favoured at grain boundaries.

Dimpled intergranular fractures are also occasionally produced by hydrogen-induced SCC in some materials (including steels). Examples of transitions from dimpled intergranular fractures in aqueous environments to dimpled intergranular fracture in dry air for an Al-Zn-Mg alloy and for pure Mg (Figs 36,37) illustrate how dimples (or flutes) are shallower and smaller after cracking in aqueous environments. [20,22] For the pure Mg, the change in the scale of the dimples/flutes was apparent even at intergranular crack velocities in aqueous environments as high as 50mm/s – mirroring the behaviour of transgranular fluted fractures. Similar shallow dimples/flutes to those produced by cracking in aqueous environments have been observed after cracking in liquid-metal environments in these materials. Thus, an AIDE mechanism is capable of accounting for the observations, although minor contributions from HEDE and HELP cannot be discounted, as discussed for the previous fracture modes. HEDE may play a more dominant role for brittle intergranular fractures, as discussed in the next section.

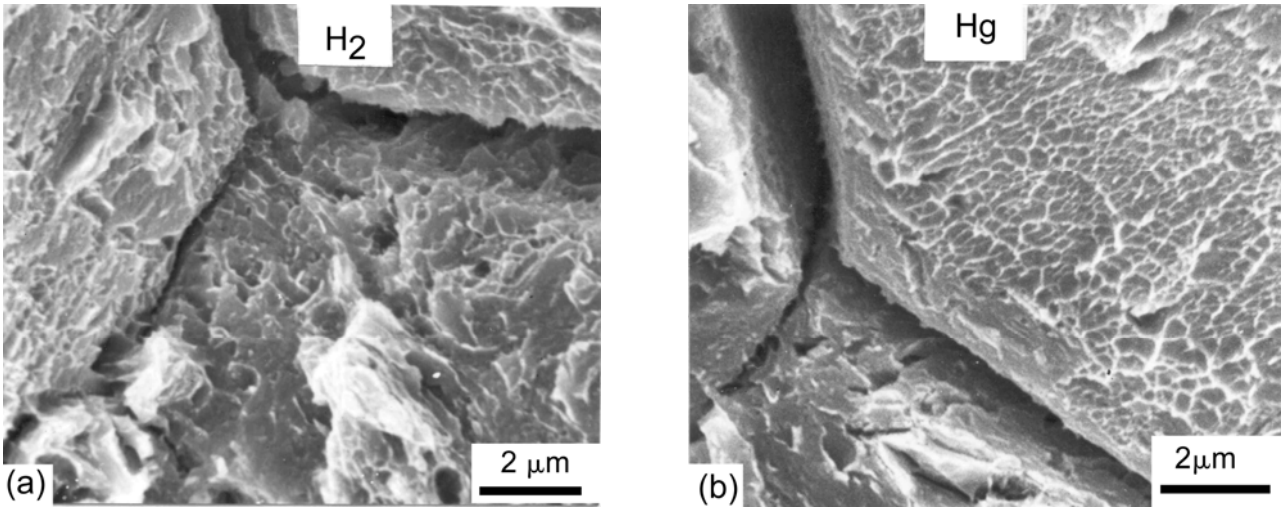

FIGURE 35 - SEM of fracture surface produced by (a) slow crack growth in gaseous hydrogen, and (b) rapid crack growth in liquid mercury, at 20°C in a high-strength martensitic steel (tempered at 650°C), showing dimpled intergranular facets. (Lynch [19,23])

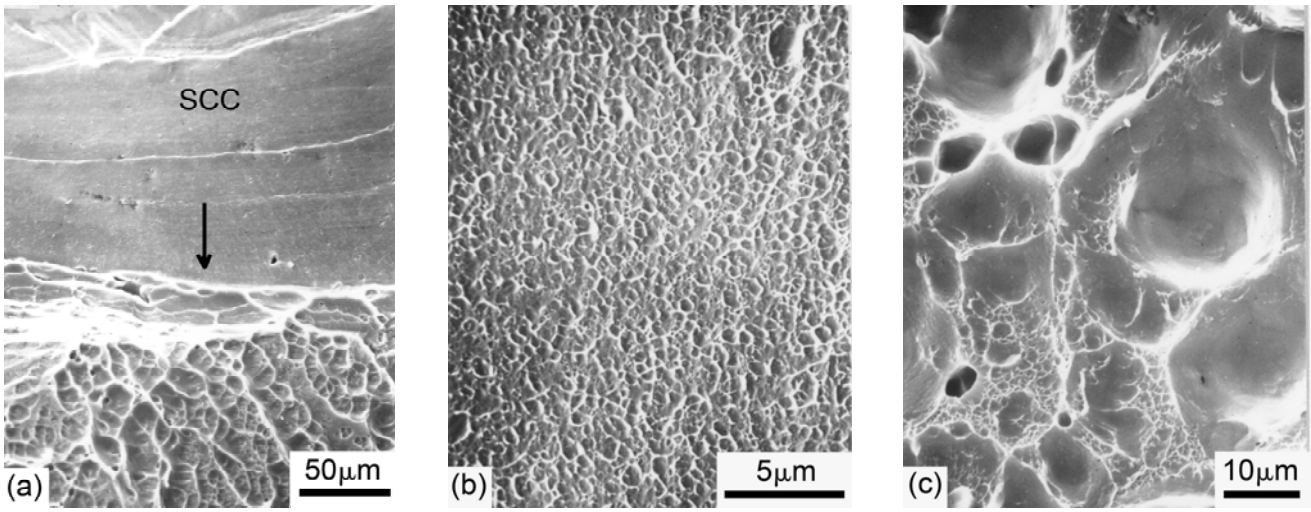

FIGURE 36 - SEM of intergranular fracture surface showing (a) transition from SCC to fast fracture in dry air in an Al-Zn-Mg bi-crystal (with a wide PFZ adjacent to the grain boundary), and (b),(c) each area at a higher magnification, showing small, shallow dimples for SCC and large, deep dimples sometimes containing smaller ones for fast fracture in dry air. (Lynch [20])

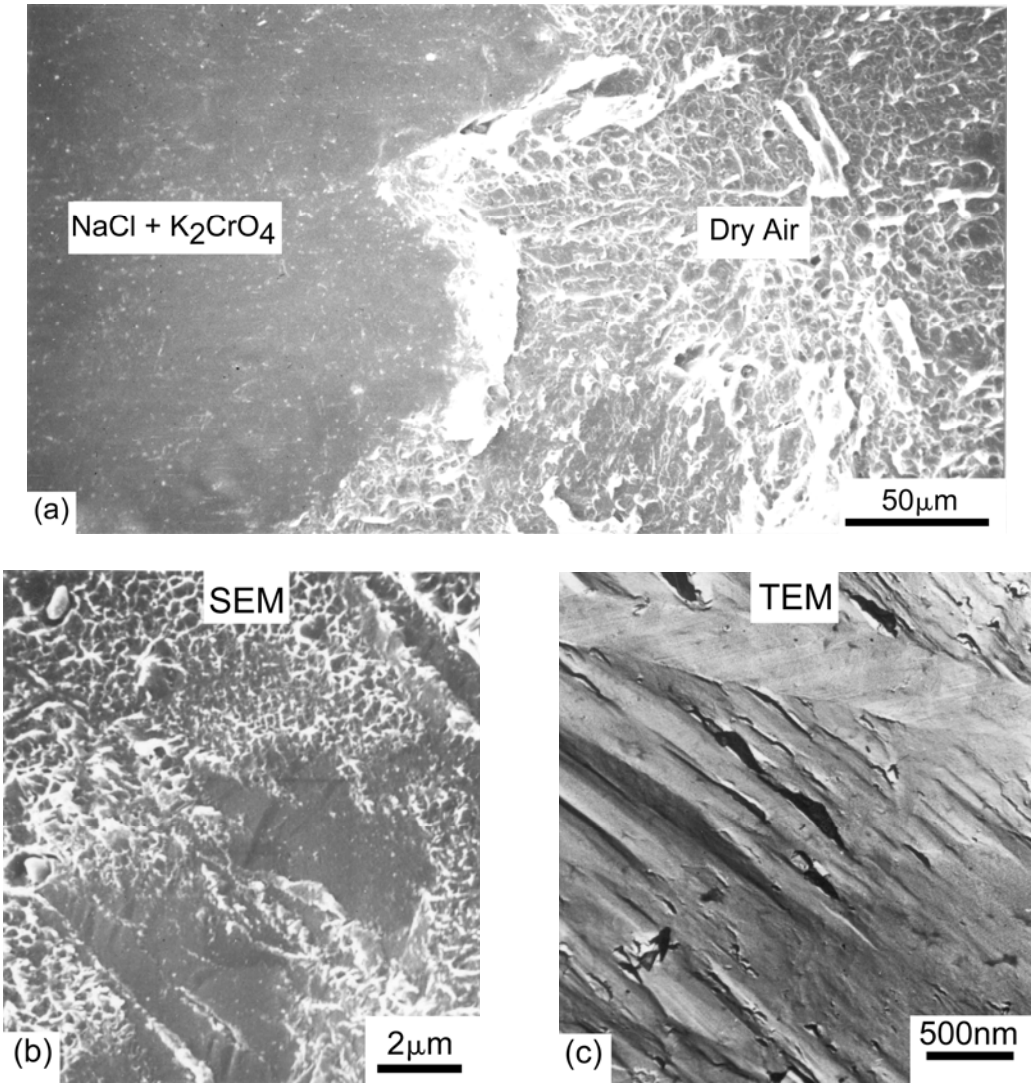

FIGURE 37 - (a) SEM of intergranular fracture surface showing transition from fast fracture in a salt solution to fast fracture in dry air in a Mg bi-crystal, and (b),(c) smooth area at a higher magnification, showing small, shallow dimples and flutes. (Lynch [22])

Brittle Intergranular Fractures

"Brittle" intergranular fractures are much more commonly observed than other fracture modes for environmentally assisted cracking in a wide variety of materials. They are relatively featureless compared with dimpled intergranular fractures, but do sometimes show signs of localised plasticity such as tear ridges, and isolated dimples (Fig. 38). Such fractures are usually considered to be consistent with a HEDE mechanism, with the ridges and isolated dimples explained by tearing of ligaments of material between 'decohered' material. This may well often be the case, but the possibility that featureless areas (observed by SEM) are produced by a nano-void coalescence process, on such a fine scale that small, shallow dimples are not resolved, cannot be discounted, especially as fine details can sometimes be resolved by TEM of replicas of fracture surfaces (Fig. 39). Numerous slip lines are also sometimes observed on brittle intergranular fracture surfaces, indicating significant plastic zones are present around cracks (Fig. 40).

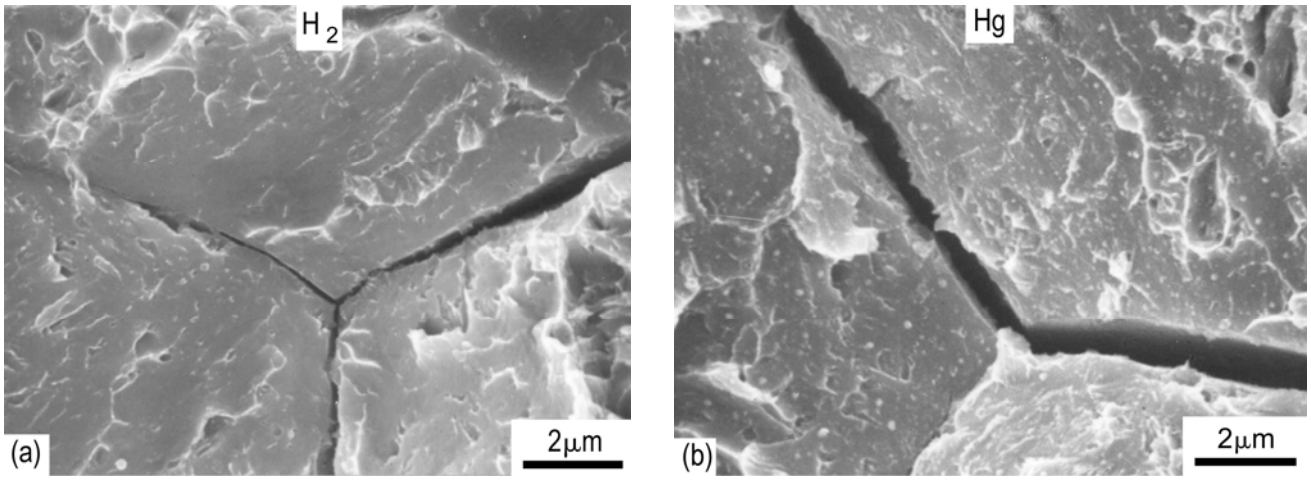

FIGURE 38 - SEM of fracture surfaces produced by (a) slow crack growth in gaseous hydrogen, and (b) rapid crack growth in liquid mercury, in a high-strength martenstic steel (tempered at 550^{o}C), showing 'brittle' intergranular facets exhibiting tear ridges and isolated dimples. (Lynch [19,23])

FIGURE 39 - TEM of replica of fracture surface produced by slow crack growth in gaseous hydrogen, showing very fine details on apparently smooth areas shown in the previous figure. (Lynch [19,23])

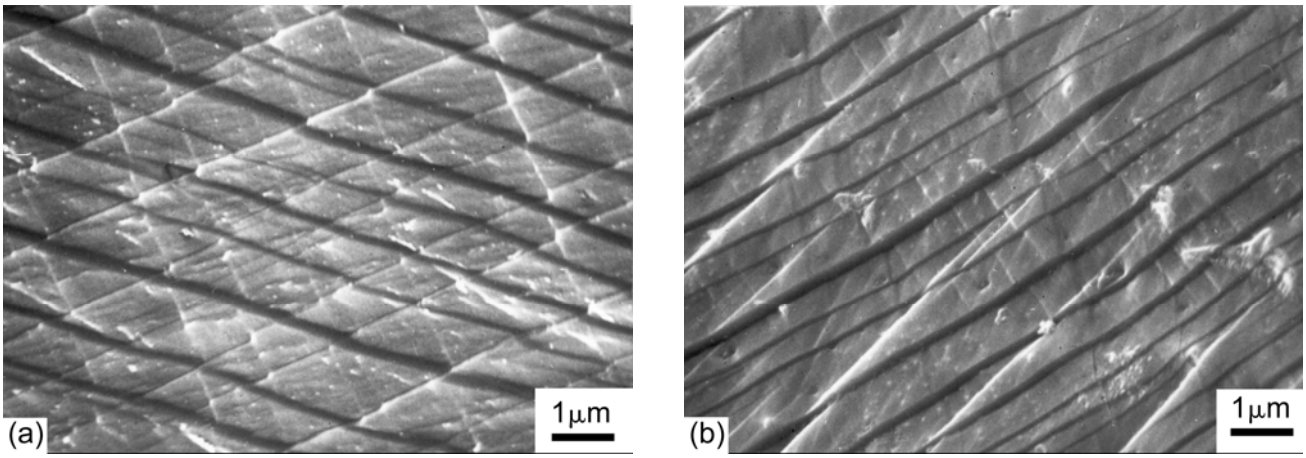

FIGURE 40 - SEM of intergranular facet produced by (a) slow crack growth in hydrogen-charged nickel, and (b) rapid crack growth for nickel in liquid mercury, showing numerous slip traces. (Lynch [21,23])

For high-strength steels and nickel, sub-critical cracking by HEDE most likely predominates when there are high levels of impurity segregation at grain boundaries (where fast fracture can occur by decohesion owing to just metalloid impurities.) HEDE could occur in preference to AIDE for grain boundaries where slip systems at tips of intergranular cracks are not favourably oriented for dislocation emission from cracks. The decohesion sites could be exactly at crack tips, at particle/matrix interfaces, and just ahead of crack tips at specific grain boundary structural units that have a high affinity for impurities or hydrogen (or both). The case for a crack-tip-surface site, for HE of steels, is supported by the similarities between HE and LME, and in this regard, it is worth noting that the fracture path and appearance produced by HE (in hydrogen gas) and LME (in liquid mercury) for a D6aC steel depended on the heat-treatment (tempering temperature), but were similar after cracking in these environments for each heat-treatment (Fig. 41).

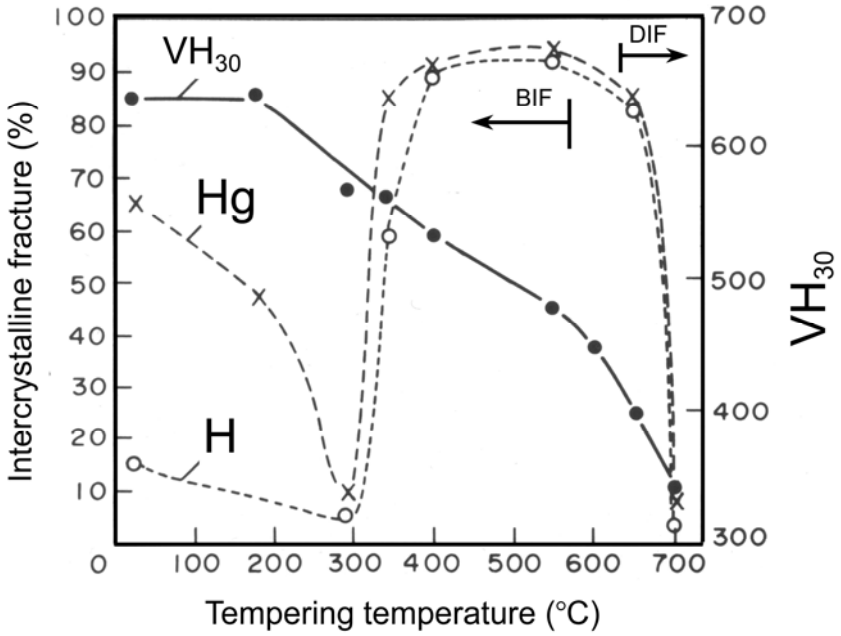

FIGURE 41 - Plot of proportion of intergranular fracture for HE (in gaseous hydrogen) and LME (in liquid mercury) in a D6aC steel as a function of the steel tempering temperature (for a given tempering time of 2h) showing similar extents and types of intergranular fracture for mercury and hydrogen environments, except for low tempering temperatures. (Variation of hardness with tempering temperature is also shown.) (Lynch [19])

For hydrogen-charged 4340 steel (cadmium-plated to minimise hydrogen effusion) tested in air – giving mixed brittle intergranular plus dimpled transgranular fractures, there was an abrupt decrease in crack velocity with increasing temperature over the range of 50-70^{o}C, with no cracking occurring above about 70^{o}C. [118] Hydrogen atmospheres around dislocations and obstacles would not be expected to disperse until higher temperatures (~200^{o}C) [12-14], so that HELP should have been effective at 70^{o}C and should have produced embrittlement if the process were a significant one. The effect of temperature can, however, be explained in terms of HEDE (or AIDE) since observations of surfaces have shown that the concentration of embrittling adsorbed hydrogen can decrease sharply with increasing temperature in the range where crack velocities decrease sharply. [39-43] A similar temperature-dependence is observed for steels cracked in hydrogen gas, although the activation energy is different in the low-temperature regime (Fig. 42). [9,119]

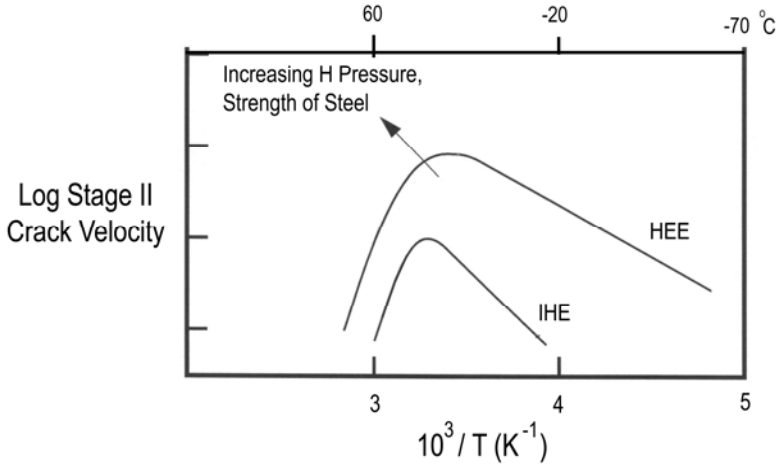

Figure 42 - Schematic plots of stage-II sub-critical crack-growth rate versus inverse of absolute temperature for IHE (a cadmium-plated hydrogen-charged 4340 steel with 4ppm H) and HEE (in gaseous hydrogen) for high-strength steels showing abrupt decreases in crack velocity above a critical temperature. (From data in [118,119])

For some Al alloys, intergranular fracture surfaces produced by SCC exhibit relatively featureless facets except for particles and crack-arrest markings (Fig. 43), which suggests that discontinuous cracking by a HEDE mechanism occurs. However, as discussed for cleavage-like cracking, other explanations besides an accumulation of a critical concentration of hydrogen ahead of cracks over a critical distance could possibly give rise to CAMs. In addition, a very localised AIDE/MVC process on a scale not resolved by SEM could occur rather than (or in addition to) HEDE, especially considering that crack growth occurs at grain boundaries with a soft precipitate-free zone adjacent to them.

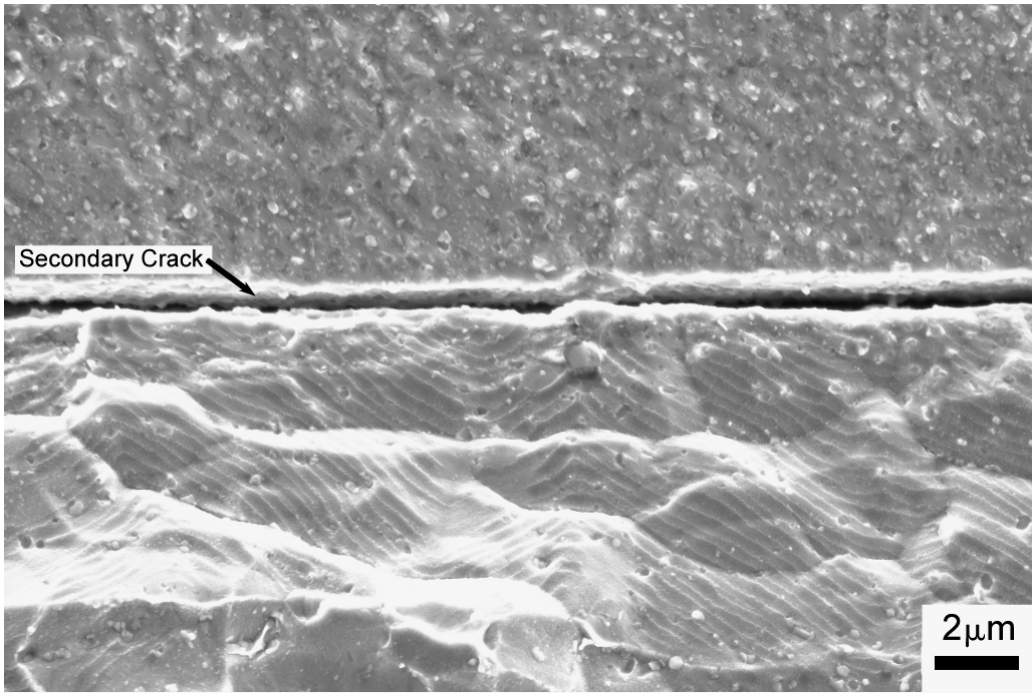

FIGURE 43 - SEM of fracture surface of intergranular fracture surface produced by slow crack growth in moist air for a 7079-T651 aluminium alloy, showing particles (or sites of particles) but no evidence of dimples, along with crack-arrest markings in regions with partially recrystallised grains (lower part of micrograph). (Knight and Lynch [120])

Slip-Band Fractures

Hydrogen-assisted cracking along slip bands, while much less common than cleavage-like and intergranular cracking, is sometimes observed in materials where there is an inherent tendency for planar slip, e.g. in stainless steels and nickel-based superalloys (Fig. 44). [121-123] In some cases, slip-band fractures occur only in hydrogen-charged specimens, while in other cases, slip-band fractures occur in hydrogen-free specimens as well as hydrogen-charged specimens, with the latter exhibiting lower strains to failure. Small, shallow dimples are observed on fracture surfaces indicating that cracking occurs by a localised microvoid–coalescence process along slip bands.

Slip bands appear to be more sharply defined (less diffuse) in hydrogen-charged specimens than in uncharged specimens in some materials, and the HELP mechanism is probably significant in promoting more planar slip as a result of edge dislocations being more effectively shielded by hydrogen atmospheres than screw dislocations so that the tendency for cross-slip is reduced. Reductions in stacking-fault energy due to solute hydrogen could also reduce the tendency for cross-slip, but such reductions are thought to be small. Greater slip planarity would increase the strains within slip bands leading to void initiation at lower overall strains.

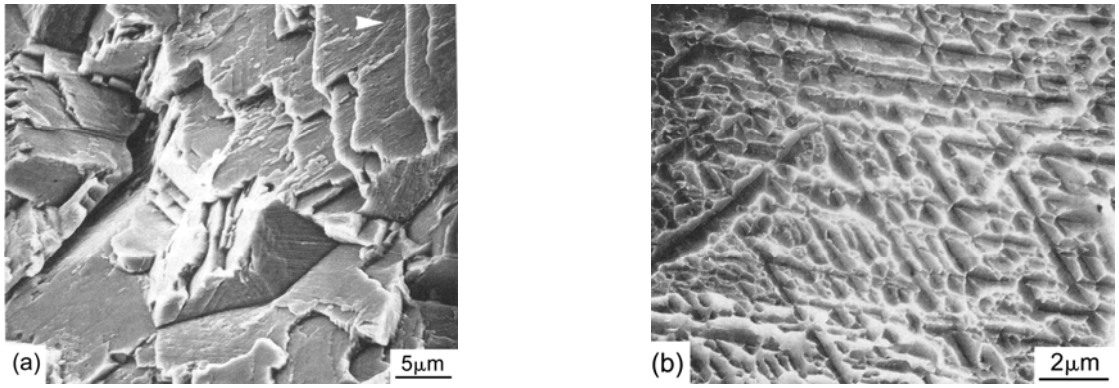

FIGURE 44 - SEM of slip-band fracture surfaces produced by slow sub-critical crack growth in hydrogen-charged IN 718 nickel-base alloy, showing (a) general morphology, and (b) dimples and slip traces. (Adapted from Hicks and Altstetter [121])

Void-initiation appears to occur at slip-band intersections and at precipitates, and HEDE at precipitate-matrix interfaces could be involved. Once voids were initiated, dislocations egressing at voids would dump their hydrogen atmospheres resulting in voids filled with gaseous hydrogen. Hydrogen adsorption (AIDE) and pressure effects could then occur at voids to facilitate opening and growth of voids along the primary slip bands. Once a significant number of voids were initiated along a slip band, shear localisation would intensify resulting in more voids, and the localisation process would become autocatalytic. Void coalescence would then occur rapidly and contributions from hydrogen effects would probably not be significant.

Fractures along slip bands on a sub-microscopic scale are sometimes observed on cleavage-like fracture surfaces produced by SCC, with crack growth occurring alternately along different {111} slip planes such that fracture planes are macroscopically parallel to {100} or {110} planes (Fig. 45). [124,125] Various explanations have been proposed to account for such observations, such as a corrosion-enhanced localised-plasticity mechanism [125], involving: (i) film-formation and fracture at the crack tip, (ii) localised dissolution along a {111} plane intersecting the crack tip, (iii) enhanced plasticity along the {111} plane owing to HELP, (iv) dislocation pile-ups

against obstacles such as Lomer-Cottrell locks, (v) cleavage (nucleated at the head of the pile-up) along the {111} plane back towards the main crack tip, and (vi) repetition of the above sequence on a differently inclined slip plane (Fig. 46). However, it is not clear why slip on other planes intersecting crack tips should not relieve the pile-up stresses.

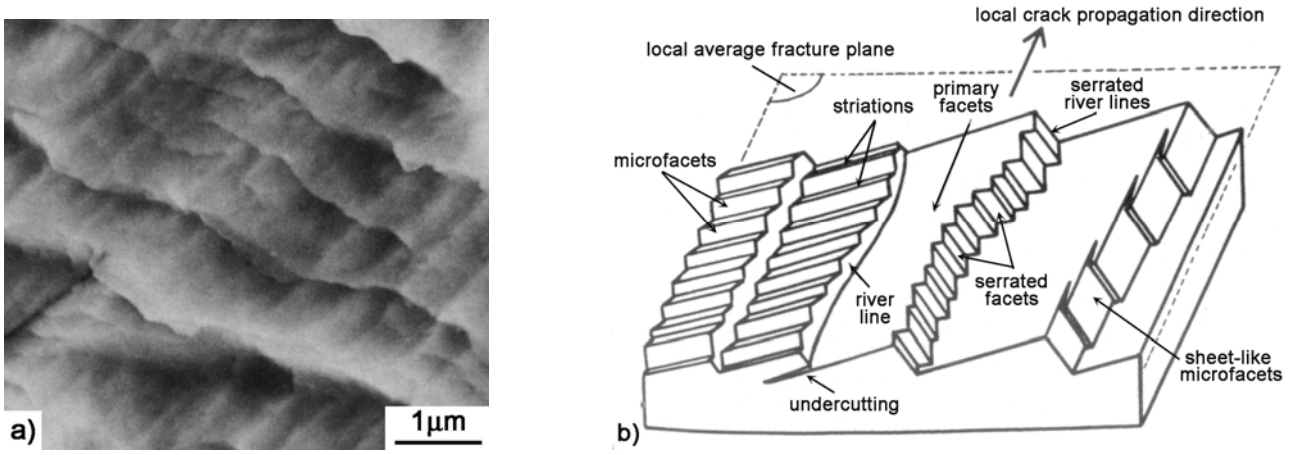

FIGURE 45 - (a) SEM of SCC fracture surface of a stainless steel showing alternate {111} microfacets, and (b) schematic diagram showing common characteristics of some cleavage-like SCC fracture surfaces. (Adapted from Dickson et al.[124])

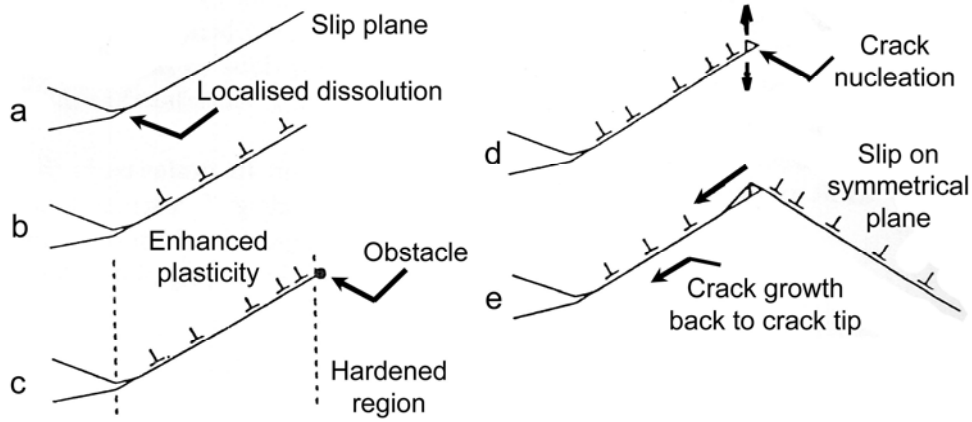

FIGURE 46 - Schematic diagram illustrating corrosion-enhanced localised-plasticity mechanism for SCC along alternating {111} slip planes. (Adapted from Magnin et al.[125])

Environmentally Assisted Fatigue Fractures

Fatigue crack growth for many materials in hydrogen, aqueous, and liquid-metal environments often produces cleavage-like or intergranular fracture surfaces similar to those produced by monotonically increasing or sustained loading, except for the presence of brittle fatigue striations. Striations are produced because slip during the unloading part of the stress cycle deforms part of the fracture surface produced during the preceding loading part of the cycle, and results in re-sharpening at the crack tip. Mechanisms of crack advance during loading are probably essentially the same as those that occur during monotonic loading, with AIDE, HEDE, or HELP resulting in larger crack-growth increments per cycle for a given crack-tip opening displacement in hydrogen-bearing environments than in inert environments. Void formation ahead of cracks, however, appears to occur to lesser extents for cyclic loading (especially at lower ΔK) and is not essential for an AIDE mechanism for fatigue where re-sharpening of crack tips occurs during unloading.

For transgranular hydrogen-assisted fatigue (producing cleavage-like facets), the arguments supporting an AIDE mechanism discussed previously for cleavage-like cracking are mostly applicable. In fact, many of the experiments carried out under monotonically increasing loads or sustained loads have also been performed under cyclic loading with similar results. For example, there are remarkable similarities between the appearance of fatigue fracture surfaces produced in hydrogen-bearing environments and those produced in liquid-metal environments, with those for nickel single crystals being particularly striking, in that the same spacing of brittle striations and the same crystallographic fracture planes and directions were produced in gaseous hydrogen and in liquid mercury (Fig. 47). The extent of slip on the side surfaces of specimens was also the same after fatigue in hydrogen and in mercury, with extensive slip on planes intersecting crack tips. In comparison, fatigue in inert environments produced ductile striations on 'non-crystallographic' planes, and plastic zones around cracks were more diffuse.

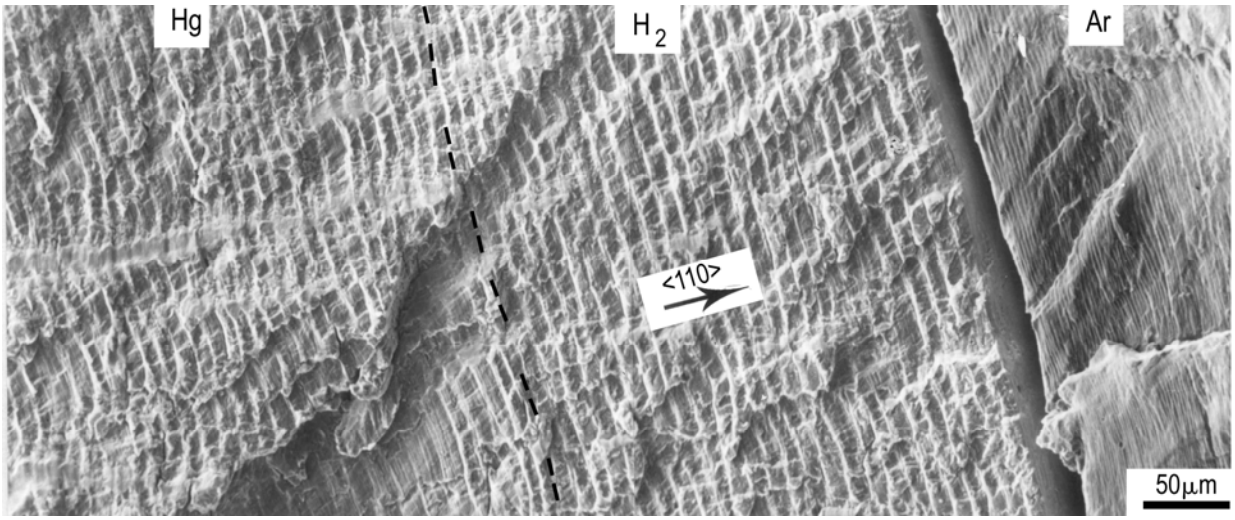

FIGURE 47 - SEM of fracture surface produced in a nickel single crystal by fatigue crack growth (1Hz, 20^{o}C) in liquid mercury and then, after completely evaporating mercury from the crack, in gaseous hydrogen (101kPa), and then in argon, showing similarly spaced 'brittle' striations on a {100} fracture plane after cracking in mercury and hydrogen, and 'ductile' striations on 'non-crystallographic' fracture planes after cracking in argon. (Specimens tested separately in mercury and hydrogen also produced essentially the same fracture-surface appearance, and hence there was no doubt that mercury was evaporated from cracks prior to continuing cracking in hydrogen!) (Lynch [23])

Ductile striations were also observed on fracture surfaces after fatigue crack growth in hydrogen-charged nickel and hydrogen-charged Al-Zn-Mg single crystals tested in dry air, and the striation spacings were the same as in uncharged specimens (Fig. 48) [126], supporting the view that solute hydrogen (HELP) plays little or no role in facilitating crack growth in these (and probably other) materials. An embrittlement site that is very close to crack tips is also supported by abrupt changes in striation spacing and appearance when the environment, electrochemical potential, cycle frequency, temperature, and other variables are changed. For example, changing the electrochemical potential during fatigue of a 7075 aluminium alloy in a salt solution produced abrupt transitions from ductile to brittle striations (and vice versa) as well as an abrupt change in the fracture plane (Fig. 49). [127]

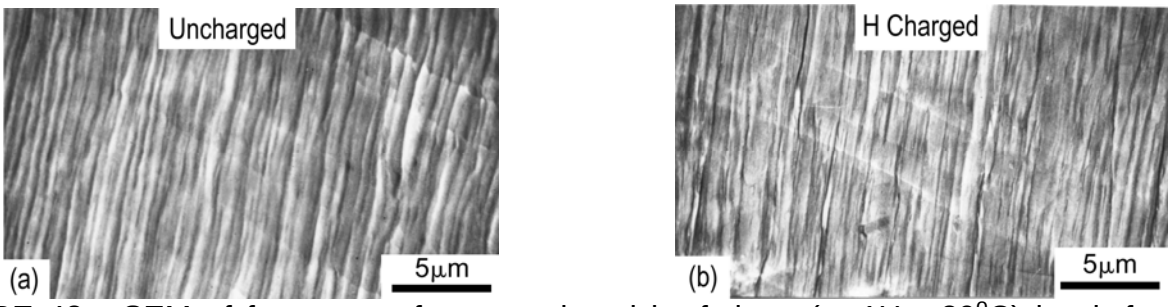

FIGURE 48 - SEM of fracture surfaces produced by fatigue (at 1Hz, 20°C) in air for nickel single crystals (a) uncharged, and (b) hydrogen-charged (0.45at.%H), showing similarly spaced 'ductile' striations for both conditions. (Lynch [126])

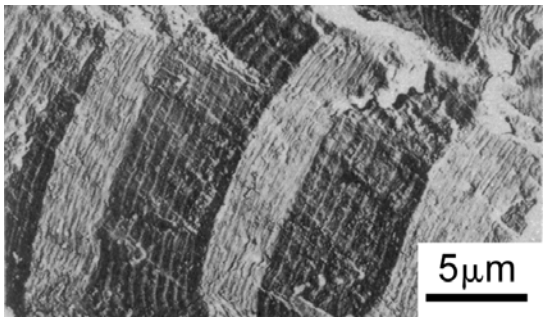

FIGURE 49 - TEM of replica of corrosion fracture surface of a 7075 Al alloy showing abrupt changes from ductile to brittle striations (and vice versa), produced at cathodic and anodic potentials, respectively. (Adapted from Pelloux [127])

For Al-Zn-Mg single crystals, increasing the temperature during fatigue crack growth in distilled water resulted in abrupt decreases in the spacing of brittle striations, whereas increases in striation spacings were observed with increasing temperature for fatigue crack growth in NaCl solutions (Fig. 50). [128] Differences in adsorption kinetics (which are not well understood) leading to differences in hydrogen concentrations at surface (and just sub-surface sites) are probably involved. Another observation for Al-Zn-Mg single crystals, which supports an adsorption mechanism for corrosion fatigue is that fatigue crack growth at high ΔK and at high cycle frequencies (24Hz) in water results in {100} <110> cleavage-like facets exhibiting brittle striations with a spacing ~0.2mm – such that crack velocities during loading must have been ~10mm/s. As discussed for cleavage-like cracking at similarly high velocities during rapid monotonic loading, hydrogen should not have time to diffuse ahead of cracks, and only adsorbed species should be present at crack tips.

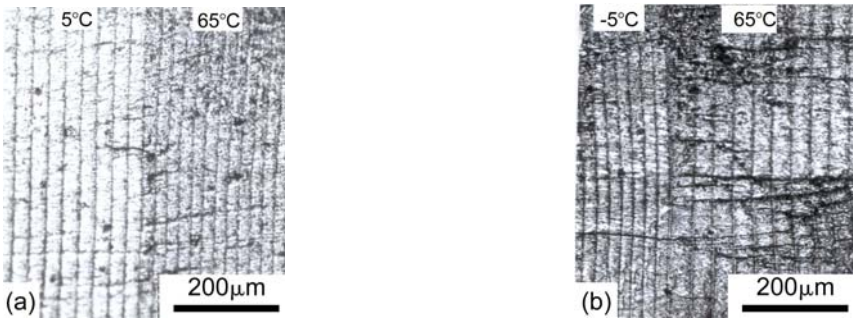

FIGURE 50 - SEM of fatigue fracture surfaces of Al-Zn-Mg single crystals tested at 1Hz (a) in distilled water at 5°C then at 65°C, and (b) in 3.5%NaCl solution at -5°C then at 65°C, showing abrupt changes in the spacing of brittle striations with changes in temperature, with opposite effects of temperature on striation spacing for the two different environments. (Lynch [128])

GENERAL COMMENTS AND SUGGESTIONS FOR FUTURE WORK

The conclusion that HE and hydrogen-assisted SCC involving localised plasticity predominately occur by AIDE for many fracture modes is at odds with the more general popularity of HELP for explaining these phenomena regardless of the fracture mode. The widespread acceptance of HELP seems to stem from (i) the diverse and convincing evidence that the phenomenon does occur, (ii) observations that hydrogen-assisted fractures are dimpled or associated with significant localised plasticity, and (iii) the fact that hydrogen can diffuse rapidly in many materials so that solute hydrogen is present ahead of cracks in most circumstances. However, these facts should not be linked without critically examining whether (i) the magnitude of the HELP effect at crack tips is sufficiently large to significantly promote sub-critical cracking, and (ii) HELP is consistent with all the other observations.

Mechanisms of HE and SCC must be able to account, in particular, for (i) the detailed fracture characteristics and crystallography, and (ii) the effects of temperature, crack-tip strain rate, hydrogen pressure, and other variables. A mechanism based predominantly on HELP cannot account for these observations for many common fracture modes and, considering the evidence overall, it appears that HELP only plays a dominant role in initiating slip-band fractures. In most circumstances, HELP is probably too small to have much effect on sub-critical crack growth. The absence of any embrittlement when only solute hydrogen is present ahead of crack tips (without adsorbed hydrogen at internal cracks/voids) in some materials supports such a view.

The HEDE mechanism also has many adherents because essentially featureless fracture surfaces are often observed using scanning-electron microscopy (SEM). However, as already mentioned, it is debatable whether SEM (even when instruments with field-emission guns are used) is capable of resolving sufficiently shallow dimples to conclude that atomically brittle decohesion, rather than an extremely localised plasticity process, has occurred when fracture surfaces are featureless. The fact that dimples could be as small as ~20nm diameter, with the cusps separating them perhaps only ~4nm high, needs to be borne in mind. The additional secondary electron emission from such cusps may not be sufficiently above background levels for them to be resolved. The quoted resolution of ~2nm for some latest-generation microscopes is usually based on the resolution of high-emissivity gold particles on a low-emissivity support, and is not relevant to the resolution of features on fracture surfaces. Thus, HEDE could be much less common than generally supposed, although probably does dominate for brittle intergranular fractures when high concentrations of other embrittling impurities are present at grain boundaries.

The popularity of solute-hydrogen based mechanisms possibly also arises because adsorption mechanisms have often been discounted for various reasons. For example, early adsorption mechanisms were based on surface-energy reductions, and it was argued that, since significant localised plasticity usually occurred, the overall fracture energy (dominated by a plastic-work term) would not be significantly reduced by decreasing the surface energy. Such an argument is clearly not applicable to an AIDE mechanism since this process reduces the plastic strains required for crack growth by increasing the proportion of dislocations that produce crack growth. Since AIDE facilitates the coalescence of cracks with voids ahead of them, voids do not grow to the same extent as they would in an inert environment – a point that has eluded some workers who have objected to an AIDE/MVC mechanism on the grounds that the range of influence of adsorption is only a few atomic distances and, hence, should not

affect voids ahead of crack tips.

The suggestion that embrittlement results from *easier* dislocation emission from crack tips is also contrary to the predictions of most criteria for ductile versus brittle behaviour. For example, the widely-cited Rice-Thomson (R-T) criterion [129] based on the competition between decohesion and dislocation-emission assumes that, if dislocation emission occurs at a lower stress than decohesion, then ductile fracture will ensue. However, the R-T criterion, and variants of it, do not address whether macroscopically ductile behaviour will occur, but simply whether crack growth occurs by decohesion or dislocation activity. Such criteria are therefore not relevant to transitions from macroscopically brittle (but microscopically ductile) fracture to a more macroscopically ductile fracture, which are often observed on changing from a hydrogen-bearing environment to an inert environment.

An adsorption mechanism has also sometimes been discounted because not all adsorbed species produce embrittlement. However, only weakly adsorbed species such as hydrogen and some metal atoms, e.g. mercury on particular metals, are likely to result in weakened metal-metal bonds *and* weak metal-adsorbate bonds, and thereby facilitate dislocation emission. Strongly adsorbing species such as oxygen form strong bonds with most metals, with oxygen atoms sometimes incorporated into the topmost layer of surface atoms. Dislocation emission would involve shearing these strong metal-oxygen bonds, making emission difficult. Thus, the fact that oxygen does not promote cracking, but rather inhibits HE, does not cast doubt on an AIDE mechanism for HE. A good understanding of why only some weakly adsorbing metal species produce embrittlement is, however, lacking. For example, liquid lithium and sodium but not potassium embrittle nickel. [21] Explanations probably lie in the subtleties of the effects of adsorption on the surface-lattice perturbations discussed earlier.

In summary, objections that have been raised to an adsorption mechanism for HE and hydrogen-assisted SCC in the past are not applicable to an AIDE model, for which there is compelling evidence – with the similarities between HE/SCC and LME being particularly persuasive. The ability of an AIDE mechanism to account for the detailed appearance of many fracture modes is vitally important. There are, nevertheless, many aspects of the adsorption and dislocation-emission processes that are not well understood and, undoubtedly, there are other processes such as film-formation and dissolution that also play an important role in many cases of hydrogen-assisted SCC. There are also some materials and environments where hydrogen is not involved in SCC, and film-formation and dissolution (and possibly associated effects such as vacancy injection) are solely involved. [130] The AIDE mechanism is therefore not claimed to be a universal mechanism of environmentally assisted cracking, as critics have sometimes suggested.

The relative importance of AIDE and HEDE for some ‘brittle’ fracture modes obviously requires further investigation. In particular, further work is necessary to determine whether or not the fine details often observed on ‘brittle’ fracture surfaces by TEM (but not by SEM) are the result of nano-void formation ahead of cracks. Atomistic modelling of crack growth does show such nano-voids in some cases [131], but whether such modelling is sufficiently realistic is debatable. Fractographic studies using scanning-tunnelling microscopy (STM) and atomic-force microscopy (AFM) on ‘brittle’ fracture surfaces would be worthwhile, and it would be interesting to compare images obtained using STM/AFM with TEM of replicas and SEM, ideally for the same areas of fracture surfaces. Examining matching areas of opposite fracture surfaces would also help in deducing crack-tip processes. Other high-resolution techniques such as

thin-foil TEM of partially cracked specimens, as has been carried out for some stress-corrosion cracks [132], would also be valuable.

Further quantum-mechanical based atomistic and multi-scale modelling of HE and LME are also clearly merited. For example, it would be particularly interesting to compare the influence of adsorbed hydrogen and adsorbed mercury using such techniques, given the remarkably similar effects of hydrogen and mercury on crack growth for a number of materials such as nickel and steels. One possible explanation for these similarities could be that the adsorbate-substrate charge-transfer process is similar, with each adsorbed hydrogen atom and adsorbed mercury atom contributing one 's' and two 's' electrons from their outermost shells, respectively, but with twice as many hydrogen atoms as mercury atoms contributing owing to their differences in size. However, the details are probably far more complex, and quantum-mechanical calculations, preferably for strained/stepped crack-tip surfaces, are needed.

Realistically modelling the effects of adsorption on dislocation emission is challenging because the process depends not only on the structure and bonding at crack tips, but also on a number of other parameters [e.g. 133-135] such as: (i) stress-mode, and the extent of 'shear-softening' due to tensile stresses across slip planes, (ii) whether emission occurs 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, (iii) the crack-tip radius and core-width of nucleating dislocations, (iv) the shape of the emitted dislocation loop, and whether full or partial dislocations are involved, and (v) 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.

The debate regarding mechanisms of HE in this review has focussed on the relative merits of HELP, HEDE, and AIDE for various fracture modes since these mechanisms have the most support. There is, however, emerging evidence from experimental and theoretical studies that hydrogen-vacancy interactions may also be important in some circumstances. [136-138] High vacancy concentrations, far in excess of equilibrium values, may occur ahead of crack tips when high concentrations of hydrogen are present because hydrogen reduces the energy of formation of vacancies and stabilises vacancies produced by dislocation activity (such as dragging of jogs). Vacancy condensation into small clusters probably occurs quite rapidly (owing to steep concentration gradients and pipe diffusion of vacancies along dislocations), and modelling studies suggest that vacancy clusters might form chains along specific crystallographic planes and directions, e.g. {100} planes and <110> directions in fcc metals. It has further been proposed that such aligned clusters could promote fracture along these planes. [117]

Hydrogen-enhanced vacancy concentrations and clustering, by themselves, cannot account for many of the characteristics of HE, but aligned vacancy clusters could possibly make a significant contribution to crack growth by the AIDE/void-coalescence process (for cleavage-like and some other fracture modes) and to the HELP/void-coalescence process (for slip-band cracking) by facilitating nano-void nucleation ahead of cracks. Another possibility, not previously considered, is that high concentrations of hydrogen-vacancy complexes within a few atomic distances of crack tips could facilitate dislocation emission to a greater extent than that owing to 'adsorbed' hydrogen alone. Further studies of the possible role of vacancies near crack tips in facilitating fracture are clearly merited.

CONCLUSIONS

1. There are four mechanisms of hydrogen-assisted cracking for which there is significant experimental and theoretical support, viz:

   (i) repeated formation and fracture of brittle hydrides at crack tips,

   (ii) adsorption-induced dislocation-emission (AIDE) (involving hydrogen at crack-tip surfaces and within a few atomic distances of crack/void tips),

   (iii) hydrogen-enhanced localised-plasticity (HELP) (involving hydrogen atmospheres around dislocations and obstacles in the plastic zone ahead of cracks), and

   (iv) hydrogen-enhanced decohesion (HEDE) (involving hydrogen adsorbed at crack tips, and hydrogen segregated at grain boundaries and at particle-matrix interfaces).

2. There is also emerging evidence that hydrogen-vacancy complexes and vacancy clusters may play some role in the above processes and, for hydrogen-assisted SCC, film formation and dissolution at crack tips could complicate matters.

3. The four mechanisms of cracking listed above may occur conjointly in some circumstances, although one will usually dominate. The dominant mechanism depends on the fracture path and fracture mode which, in turn, depend on the material, microstructure, environment, temperature, stress-intensity factor, and other variables.

4. The formation and fracture of brittle hydrides at crack tips, producing cleavage-like fracture surfaces, is a well-established mechanism of embrittlement for many hydride-forming materials such as Zr, Nb, and V.

5. The AIDE mechanism probably predominates for cleavage-like fractures in non-hydride forming materials such as Fe, Ni, and Al alloys, and for dimpled intergranular and transgranular fractures in steels and some other materials. Fluted fractures produced by SCC in some hcp metals such as Ti and Mg alloys are probably also the result of AIDE.

6. The HEDE mechanism probably predominates for brittle intergranular fractures (where SEM shows essentially flat facets) when high hydrogen concentrations in conjunction with segregated embrittling impurity are present at grain boundaries. An AIDE mechanism cannot be discounted in some cases, however, since it is debatable whether the resolution of SEM is sufficient to rule out the presence of very shallow dimples produced by a nano-void coalescence process.

7. The HELP mechanism contributes to the initiation of slip-band fractures in, for example, Ni-base superalloys and stainless steels, by localising slip, but probably plays only a minor role (if any) for other fracture modes.

8. An ‘adsorption’ mechanism (involving hydrogen within a few atomic distances of crack tips) for cleavage-like and some other fracture modes in Fe, Ni, Al, Mg, and Ti alloys is supported by:

   (i) remarkable similarities in fracture path, fracture-surface appearance, and crystallography between HE/SCC and adsorption-induced LME,

(ii) observations that cracking can occur at high crack velocities in materials with low hydrogen diffusivities in some circumstances,

(iii) the effects of hydrogen pressure, temperature, and oxygen additions to hydrogen-gas environments, on the kinetics of cracking, and

(iv) the absence of embrittlement in some hydrogen-charged materials.

9. Further work is obviously required on many aspects of embrittlement, but quantum-mechanical based modelling on the effects of adsorption of hydrogen and metal atoms on dislocation emission from crack tips is particularly warranted.

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