

Hydrogen embrittlement (HE) phenomena and mechanisms

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Abstract: Mechanisms of hydrogen embrittlement in steels and other materials are described, and the evidence supporting various hypotheses, such as those based on hydride-formation, hydrogen-enhanced decohesion, hydrogen-enhanced localised plasticity, adsorption-induced dislocation-emission, and hydrogen-vacancy interactions, are summarised. The relative importance of these mechanisms for different fracture modes and materials are discussed based on detailed fractographic observations and critical experiments.

Key words: hydrogen-embrittlement, mechanisms, fractography, hydride embrittlement, hydrogen-enhanced decohesion, hydrogen-enhanced localised-plasticity, adsorption-induced dislocation-emission.

2.1 Introduction

The damaging effects of hydrogen in iron and steel were first recognised in the early 1870s, and the first tentative explanation, namely ‘hydrogen in interspaces impeding the movement of iron molecules’, was proposed at this time [1]. Since then, there have been intensive efforts to characterise and understand the phenomenon of hydrogen-embrittlement (HE) of materials in general, especially over the last 50 years as more advanced characterisation techniques became available. The present chapter describes the mechanisms of HE that are now considered to be viable, and summarises the evidence supporting them. The relative importance of these mechanisms for different fracture modes, which depends on the material, microstructure/strength, and testing conditions, is then discussed.

Mechanisms of HE are relevant to stress-corrosion cracking (SCC) (and corrosion-fatigue) in many materials since hydrogen is generated at crack tips in aqueous or moist-air environments. Mechanisms of SCC (with and without the involvement of hydrogen) are discussed in detail in Chapter 1, with reference to this chapter for more details regarding hydrogen effects. Before describing and discussing the mechanisms of HE, some background is provided regarding: (i) types of HE, (ii) the susceptibility of various materials to HE, (iii) sources of hydrogen, (iv) sites and traps of hydrogen

in materials, (v) hydrogen diffusion, (vi) measures of HE susceptibility, (vii) the main variables affecting HE, and (viii) the general characteristics of HE. Further details regarding these aspects, and original references, can be found in previous reviews, conference proceedings, and other compilations of papers on HE [2–14]. A chapter on ‘Metallographic and fractographic techniques for characterising and understanding hydrogen-assisted cracking’ [15] by the present author also provides additional information, albeit with a significant overlap with the present chapter in some areas.

2.1.1 Types of hydrogen embrittlement and terminology

There are a number of manifestations of HE, and various terminologies are used to describe different phenomena depending on the source of hydrogen and the type of damage produced. ‘Internal hydrogen embrittlement’ (IHE) involves concentration of pre-existing hydrogen in regions of high hydrostatic stress (applied or residual), resulting in cracking under sustained stresses well below the yield stress. ‘Hydrogen-environment embrittlement’ (HEE), on the other hand, involves sub-critical cracking of materials under sustained loads in hydrogen or hydrogen-sulphide gases. In hydride-forming materials containing high concentrations of hydrogen, embrittlement often involves formation and fracture of brittle hydrides at and ahead of cracks, and is termed ‘hydride-embrittlement’.

IHE, HEE, and hydride embrittlement are sometimes referred to simply as ‘hydrogen-assisted cracking’ (HAC) (with ‘internal’ or ‘environmental’ sometimes appropriately inserted). For HAC under cyclic loads, the term ‘hydrogen-assisted fatigue’ is sometimes used. Other terminologies for IHE are used in specific industries. For example, the term ‘hydrogen-assisted cold cracking’ (HACC) is often used in the welding industry (when welds crack after cooling to room temperature). In the oil and gas industry, the term ‘stress-oriented hydrogen-induced cracking’ is used when cracking has a ladder-like morphology due to cracking from elongated inclusions distributed along the rolling direction of plate. The term ‘environmental hydrogen embrittlement’ (EHE) is sometimes used when cracking occurs in cathodically protected structures.

Other forms of hydrogen damage are ‘blistering’ and ‘hydrogen-attack’. Blistering occurs when solute hydrogen re-combines to form high-pressure hydrogen gas at cracked inclusion/matrix interfaces near surfaces. The high pressure causes voids to expand by plastic deformation and cracking, causing surface swelling. Hydrogen-attack, also called ‘hydrogen-reaction embrittlement’, occurs when some materials such as steels and copper are exposed to hot hydrogen-bearing gases, leading to hydrogen diffusion to, and reaction with, carbides and oxides: High-pressure methane and steam, respectively, can then be produced, leading to internal voids and cracks.

Neither of these forms of hydrogen damage is considered further in this chapter.

2.1.2 Susceptibility of materials to HE

High-strength (and ultra-high-strength) martensitic steels with yield strengths greater than about 1400 MPa (Hardness > 38 on Rockwell C scale) are extremely susceptible to IHE, with solute hydrogen concentrations as little as 0.5–1 ppm (wt.) causing cracking. For ferritic steels with strengths less than about 750 MPa, relatively high hydrogen concentrations (~10 ppm) are often necessary for IHE to be significant. Titanium alloys with α - β microstructures are susceptible to IHE when hydrogen concentrations are greater than 100–200 ppm. Nickel alloys, aluminium alloys, (stable) austenitic steels, and copper alloys exhibit little (if any) susceptibility to IHE, and industrial problems due to IHE in these materials are rare. The susceptibilities of materials to HEE are generally similar to those for IHE, but high-strength nickel alloys seem to be an exception in that they can be very susceptible to HEE, but only slightly embrittled by internal hydrogen unless concentrations are high.

2.1.3 Sources of hydrogen

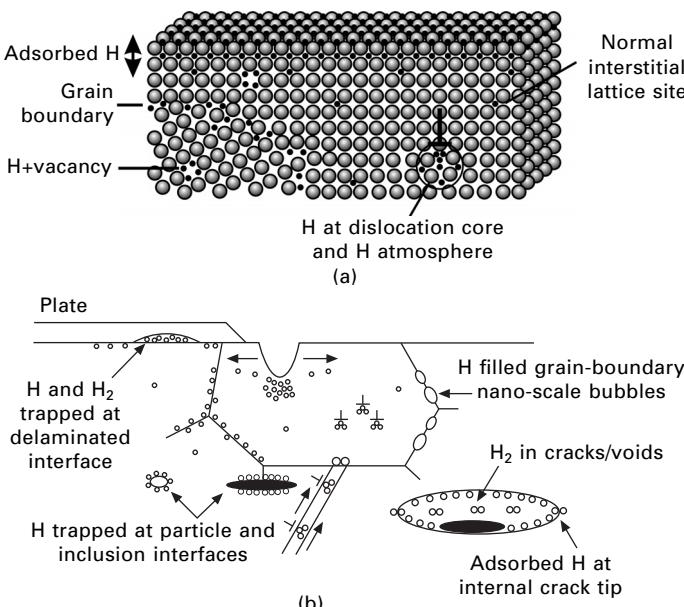
The main sources of hydrogen leading to IHE of high-strength steels are the solutions used to clean and apply (or re-apply) protective coatings. Electroplating solutions, especially if out-of-specification, are particularly prone to produce IHE. Other solutions include those used for pickling, phosphating, paint-stripping, and cathodic-cleaning. Welding (or melting/casting the original material) in moist atmospheres or with moisture in rust, fluxes, etc., has also led to a significant number of failures by IHE. Heat-treatment in hydrogen-bearing atmospheres can also lead to hydrogen uptake, as can applied cathodic-protection with impressed current devices or sacrificial anodes. Similarly, corrosion of sacrificial coatings during service can generate hydrogen, especially if coatings are porous.

High-pressure gaseous (and liquid) hydrogen have been used as a fuel source in the space industry for some time, and failures of steel tanks due to HEE first occurred in the 1960s [16]. Hydrogen gas and combustion/reaction products containing hydrogen are also encountered in the nuclear, chemical and other industries. The use of hydrogen as an energy source to replace fossil-fuels is projected to increase dramatically in the future, as climate-change and pollution become even more of a concern. Many more structures and components used for hydrogen-production, hydrogen-storage and hydrogen-transportation (e.g. pipelines), will therefore be exposed to hydrogen gas.

2.1.4 Sites and traps for hydrogen

Solute hydrogen occupies and diffuses between interstitial lattice sites in metals, and can be trapped to various degrees at other sites (i.e. occupy lower potential-energy sites relative to normal interstitial sites). These other sites, listed roughly in order of trapping strength, include: (i) some solute atoms, (ii) free surfaces and sites between the first few atomic layers beneath surfaces, (iii) mono-vacancies and vacancy clusters (which are present in concentrations well in excess of thermal equilibrium values because hydrogen reduces the vacancy formation energy), (iv) dislocation cores and strain fields, (v) grain boundaries (including prior-austenite grain boundaries in martensitic steels), (vi) precipitate/matrix interfaces and strain-fields around precipitates, (vii) inclusion/matrix interfaces, and (viii) voids and internal cracks (Fig. 2.1).

The high concentrations of hydrogen on or just beneath surfaces ('chemisorbed hydrogen')* will also be present at (non-atomically sharp)



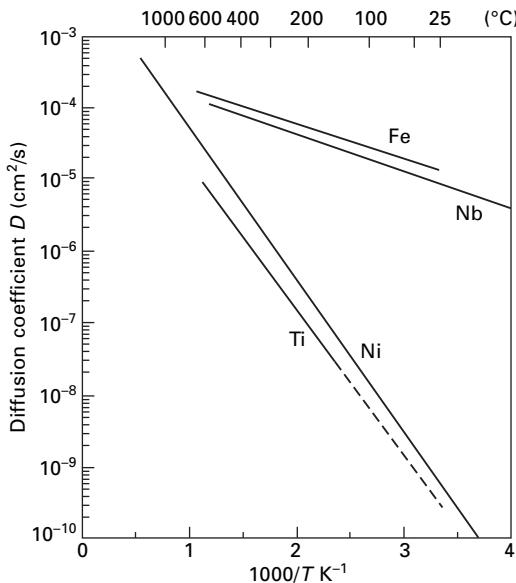
2.1 Schematic illustrations of sites and traps for hydrogen in materials (a) on the atomic scale (adapted from [12]), and (b) on a microscopic scale.

*There is no generally accepted term that defines both surface and just sub-surface sites for hydrogen, although some papers do discuss 'chemisorption into sites below the surface' as well as hydrogen on the surface. In the context of HE mechanisms, hydrogen on crack-tip surfaces and hydrogen within a few atomic distances of crack tips are referred to as adsorbed hydrogen for convenience.

crack-tip surfaces. For HEE, hydrogen gas will dissociate and adsorb at crack-tips, while for IHE, solute hydrogen will diffuse to, and adsorb at, internal crack-tip surfaces. Solute hydrogen can also precipitate as hydrogen gas (sometimes resulting in high pressures) in voids and at delaminated non-porous plating/substrate interfaces, and can then be re-absorbed and diffuse under applied stresses. Hydrogen in normal interstitial lattice sites will concentrate ahead of notches and cracks where high hydrostatic stresses result in a slightly expanded lattice.

2.1.5 Hydrogen diffusion

Rates of hydrogen diffusion in pure metals at ambient temperatures depend especially on the crystal structure, with hydrogen-diffusion coefficients, D , generally 4 to 5 orders of magnitude higher for body-centred cubic (bcc) metals compared with face-centred cubic (fcc) and hexagonal close-packed (hcp) metals at 20°C (Fig. 2.2) [17, 18]. However, there are exceptions such as Pd (fcc) and Co (hcp) which have D values several orders of magnitude greater than most other fcc and hcp metals, presumably because quantum-effects override lattice-packing effects. For some metals, such as aluminium, D values quoted in the literature span 4 to 5 orders of magnitude at 20°C,



2.2 Hydrogen diffusion coefficients for Fe and Nb (bcc), Ni (fcc) and Ti (hcp) as a function of temperature (plotted as inverse absolute temperature) (data from [17, 18]).

possibly due to experimental difficulties related to controlling surface conditions (oxide films) that affect hydrogen ingress and egress [19].

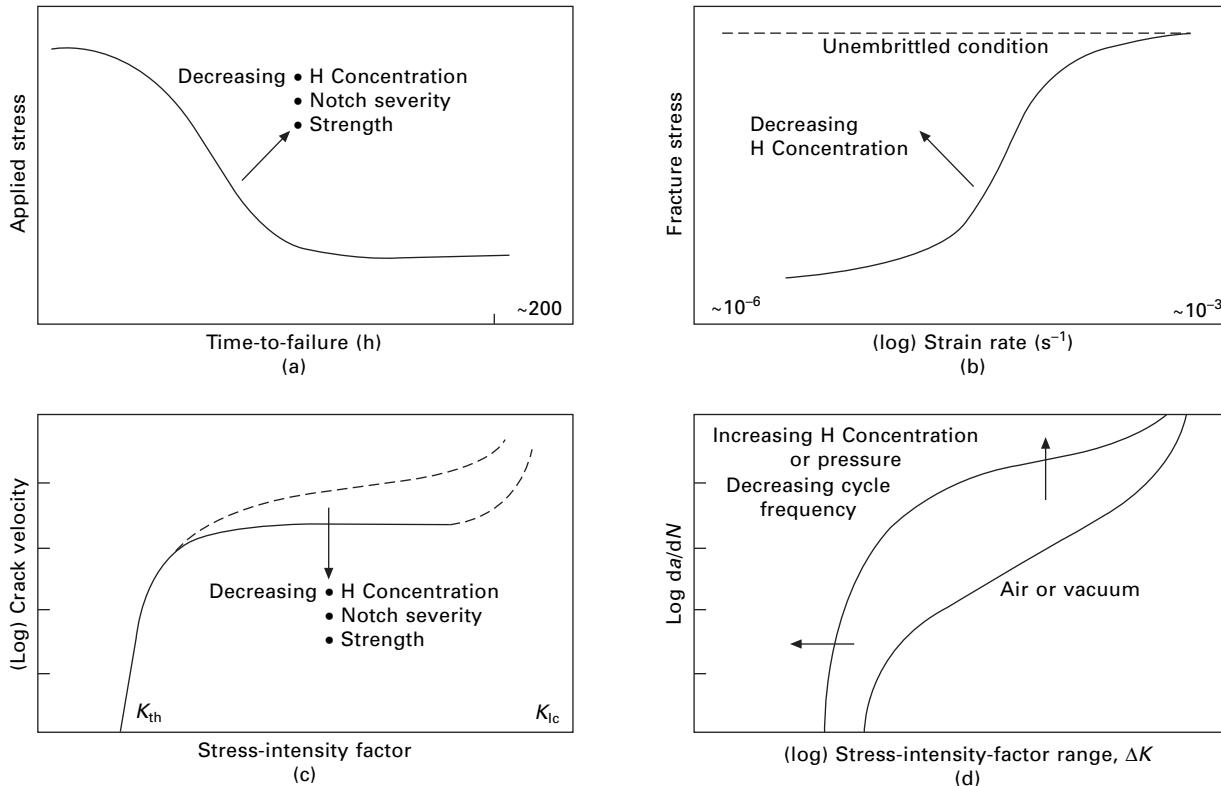
The hydrogen-diffusion distance $\sim(2Dt)^{1/2}$ in bcc iron with a D value $\sim 10^{-5}\text{cm}^2/\text{s}$ at 20°C is about $50\mu\text{m}$ in a time, t , of one second, whereas for nickel with a D value of $\sim 10^{-10}\text{cm}^2/\text{s}$, the corresponding distance is about $0.1\mu\text{m}$. In alloys with complex microstructures, effective D values at ambient temperatures decrease with increasing number and strength of traps. For ferritic steels, effective D values vary by 3 to 4 orders of magnitude at 20°C for different microstructures. Higher-strength steels tend to have lower effective D values owing to a larger volume fraction of carbide strengthening phases and a higher dislocation density.

Hydrogen-diffusion rates increase with increasing temperature, with a stronger dependence on temperature for most close-packed metals compared with bcc metals (Fig. 2.2). As the temperature is increased, hydrogen is released from deeper traps, and can diffuse to, and egress at, surfaces more readily. Thus, it is usual to minimise hydrogen contents in steels by ‘baking’ at elevated temperatures after processing and plating. For example, porous cadmium-plated high-strength steels are generally baked at 190°C for 23 h as soon as possible after plating. Optimum baking times and temperatures depend on the plating material, porosity, thickness, steel strength, and other factors that affect hydrogen egress.

Hydrogen diffuses through the lattice in response to gradients in (i) hydrogen concentration, (ii) temperature, and (iii) hydrostatic-stress fields (with the last factor being the most important in regard to IHE). Hydrogen can be transported more rapidly by mobile dislocations than by lattice diffusion when hydrogen is present at dislocation cores or as atmospheres around dislocations. Dislocation-transport of hydrogen may be important in moving hydrogen from grain interiors to grain boundaries, thereby promoting intergranular fracture. Hydrogen may also diffuse more rapidly along grain boundaries than through the lattice in some cases, but if there is a higher trap density at boundaries than elsewhere, then grain-boundary diffusion of hydrogen could be slower than through the lattice.

2.1.6 Testing procedures for assessing the degree of HE

A wide variety of parameters has been used to assess susceptibilities of materials to HE, and to determine the effects of variables on HE. Measures include (i) reductions in the strain to failure (elongation, reduction-of-area) and in the fracture stress of tensile specimens subjected to increasing loads, especially at low strain rates, (ii) delayed-failure times for tensile and C-ring specimens under sustained loads, and (iii) for hydride-containing material, reductions in fracture energies in impact tests (Fig. 2.3(a) and (b)). Fracture-



2.3 Schematic plots of measures of HE susceptibility: (a) time-to-failure (versus applied stress), (b) fracture stress (at low strain rates), (c) threshold stress-intensity factors and plateau velocities, and (d) relative rates of fatigue-crack growth (versus ΔK).

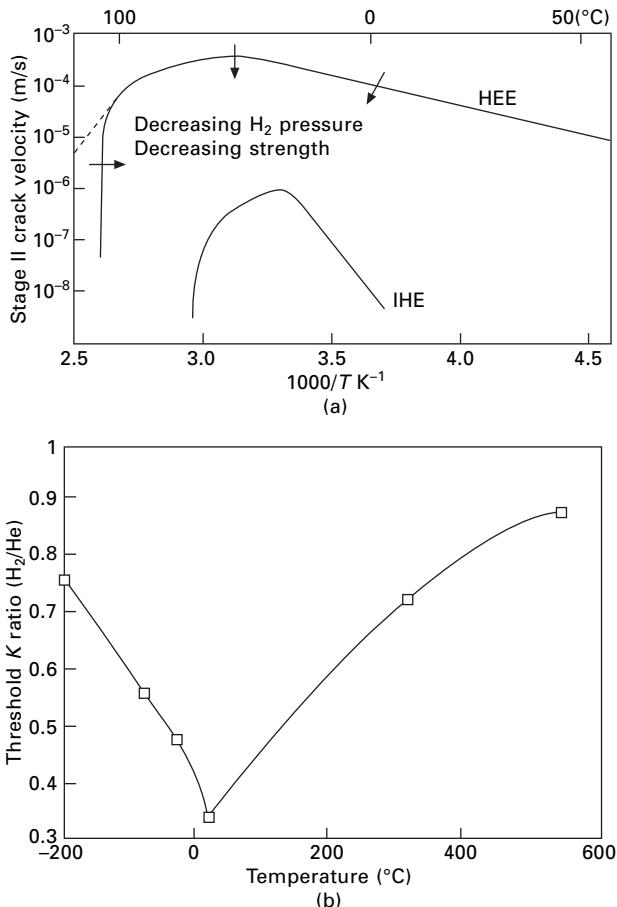
mechanics parameters, such as threshold stress-intensity factors ($K_{I\text{th}}$) and crack velocities at high K values for statically loaded specimens, are other common measures of susceptibility (Fig. 2.3(c)). For cyclic loading, ΔK threshold values and crack-growth rates per cycle compared with those in air (or vacuum) for hydrogen-free material provide measures of HE susceptibility (Fig. 2.3(d)).

Testing procedures for checking whether or not batches of steel components have been embrittled by plating processes are detailed in various standards [8]. For example, notched tensile specimens of a susceptible high-strength steel are considered to be not significantly embrittled if specimens survive 200 h at a sustained load of 75% of the notched tensile strength. Components subject to the same process conditions are then deemed to be safe to use. (It is worth noting that specimens are not usually tested for longer than 200 h and, when they are, failures do occasionally occur at longer times.) For notched tensile specimens subjected to slow strain rates ($2 \times 10^{-4}\text{s}^{-1}$), achieving a fracture stress of greater than ~75% of the notched tensile strength indicates that similarly processed components are not significantly embrittled by hydrogen.

2.1.7 Main variables affecting HE

Important variables include stress/stress-intensity factors, hydrogen content or pressure, temperature, strain-rate (or rise-time/cycle-frequency for fatigue), and alloy-strength/microstructure/impurity level (Fig. 2.3). As would be expected, increasing hydrogen contents (for IHE) and increasing hydrogen-gas pressures (for HEE) result in increasing susceptibility, although there can be a threshold hydrogen concentration for embrittlement and there is sometimes little change in the degree of embrittlement with increasing hydrogen pressure once a certain critical ‘saturation’ level is reached. Susceptibility to HE is often greatest around ambient temperature and gradually decreases with decreasing temperature in Ni alloys and steels, with susceptibility decreasing more steeply for IHE than for HEE for high-strength steels (Fig. 2.4). Susceptibility decreases precipitously above a critical temperature (often less than 100°C) for both IHE and HEE in some steels. Strain rate (during tensile tests) is another important variable, with the extent of HE decreasing with increasing strain rate. HE is usually not observed under impact loading unless high hydrogen (and impurity) concentrations are present at grain boundaries, or unless hydrides are present.

The susceptibility of most materials to HE increases with increasing strength providing that differences in microstructure are not too large, e.g. for tempered martensitic steels with strengths greater than about 900 MPa. However, microstructure can sometimes override the effects of strength, and HE susceptibility can sometimes increase with decreasing strength



2.4 Effects of temperature on susceptibility to HE: (a) sustained-load crack-growth rates versus $1/T$ for IHE and HEE of high-strength steels [13, 20, 21], and (b) ratio of threshold stress-intensity factor for Inconel 718 in high-pressure hydrogen (34.5 MPa) compared with inert (helium) environment as a function of temperature [16].

below ~ 800 MPa due to coarsening of spheroidised carbide microstructures. Other important microstructural features that influence HE susceptibility of steels include grain size, amount of retained austenite, and the type of martensite (with twinned martensite being much more susceptible than lath martensite).

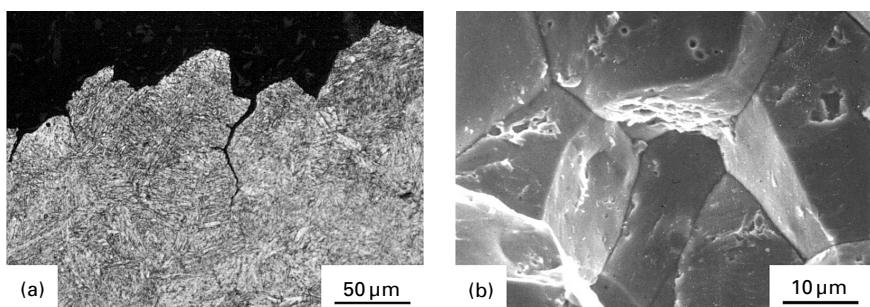
Materials with higher impurity contents can be more susceptible (for a given strength) owing to impurity segregation to grain boundaries or increase in size or number of inclusions. Thus, plots of HE susceptibility versus strength, without considering microstructure, can exhibit considerable scatter, especially for lower strength steels. In principle, microstructures with strong

traps (such as inclusions) that are easily fractured should be particularly susceptible to IHE since these traps are not only associated with high hydrogen concentrations but also act as crack-initiation sites. On the other hand, numerous moderate-to-strong traps, such as some small precipitates that do not easily initiate cracks, should inhibit hydrogen diffusion to crack-initiation sites, thereby increasing resistance to IHE.

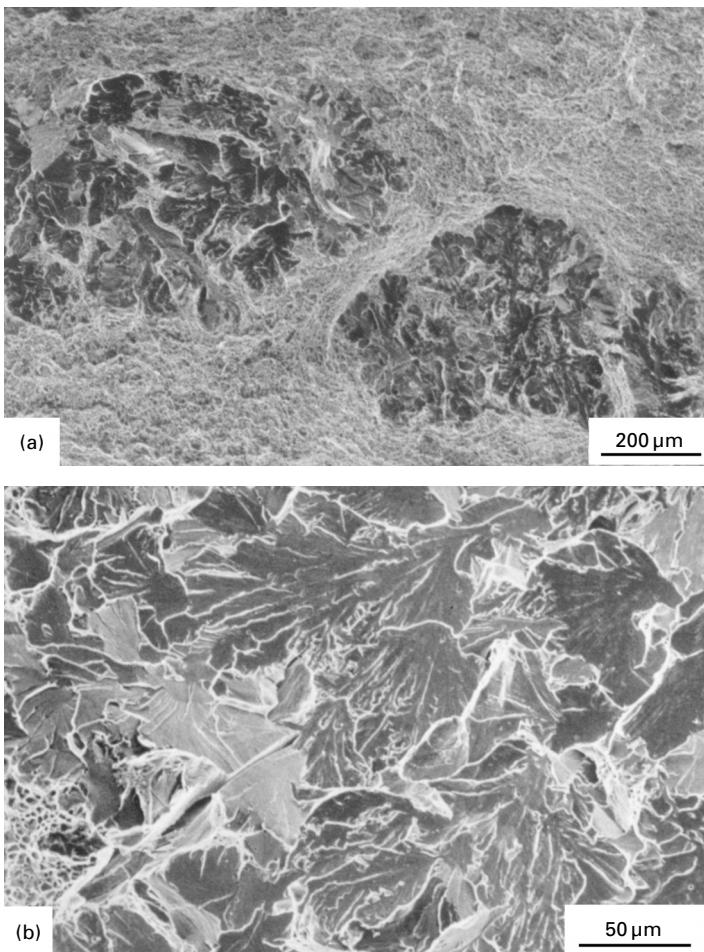
2.1.8 Characteristics of HE

Cracking produced by HE is associated with little or no macroscopic deformation, but does generally exhibit signs of localised plasticity. Fracture surfaces are generally bright (unless atmospheric corrosion occurs after cracking), and are usually faceted due to cracking along grain boundaries or along low-index crystallographic cleavage planes. For high-strength steels, cracking usually occurs along prior-austenite grain boundaries for normal levels of metalloid-impurity segregation at boundaries (Fig. 2.5), but can occur along martensite–lath interfaces in high-purity steels.

IHE initiates at or very close to surfaces (or at electroplate–steel interfaces) for high-strength steels, whereas IHE for low-strength steels can initiate well below the surface. In the latter case, ‘fish-eyes’ or ‘flakes’ with a bright, faceted appearance, surrounded by either ductile overload fractures or fatigue fractures are observed (Fig. 2.6). Further details of the metallographic and fractographic characteristics of IHE and HEE are discussed in subsequent sections of this chapter, especially with regard to whether or not the various proposed mechanisms of HE are consistent with the observations.



2.5 (a) Metallographic section through fracture surface showing cracking along prior-austenite grain boundaries of the tempered-martensite structure, and (b) SEM of fracture surface of a high-strength steel showing brittle intergranular facets.



2.6 SEMs of fracture surface of hydrogen-charged medium-strength steel showing (a) fisheyes – bright, faceted, cleavage-like areas surrounded by dimpled areas, and (b) cleavage-like areas at a higher magnification.

2.2 Proposed mechanisms of hydrogen embrittlement (HE) and supporting evidence

2.2.1 Hydride formation and fracture

Description

A mechanism based on the formation and fracture of hydrides at crack tips was first proposed by Westlake in 1969 [22]. The basic mechanism is thought to involve repeated sequences of: (i) hydrogen diffusion to regions of high hydrostatic 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. 2.7).

A hydride mechanism only occurs in the temperature and strain-rate regime where hydrogen has time to diffuse to regions ahead of crack tips, and only at temperatures where the hydride phase is stable (and brittle) [23, 24]. When hydrogen is present as solute, embrittlement is not observed, and tensile specimens sometimes undergo considerable plastic strain before hydrides are nucleated and brittle fracture occurs. Variations to the hydride mechanism illustrated in Fig. 2.7 may occur in some circumstances, e.g. (i) pre-existing hydrides may be present, and may dissolve and reorient so that hydride plates are perpendicular to the tensile stress axis, (ii) hydrides may dissolve after fracture owing to relaxations of hydrostatic stresses, and (iii) ductile tearing may occur between discrete, closely spaced hydrides. HE in some hydride-forming materials can, however, also occur in the absence of hydrides by other mechanisms described in subsequent sections.

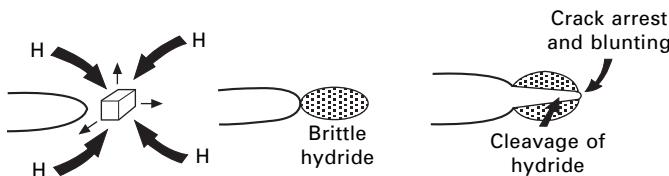
Supporting evidence

A hydride mechanism is generally accepted for HE of certain materials such as V, Zr, Nb, Ta, and Ti [23, 24] since (i) there is a strong thermodynamic driving force for hydride formation, (ii) hydrides are known to be brittle, (iii) hydrides have been observed on both halves of cleavage-like fracture surfaces, (iv) the process has been directly observed in hydrogen-charged thin foils by high-voltage transmission-electron microscopy (TEM), and (v) crack-arrest markings (CAMs) have been observed on fracture surfaces of these materials, consistent with the discontinuous cracking process illustrated in Fig. 2.7.

2.2.2 Hydrogen-enhanced decohesion (HEDE)

Description

A decohesion theory was first proposed in 1926 by Pfeil [25], who proposed that ‘hydrogen decreased the cohesion across cubic cleavage planes’ (and grain

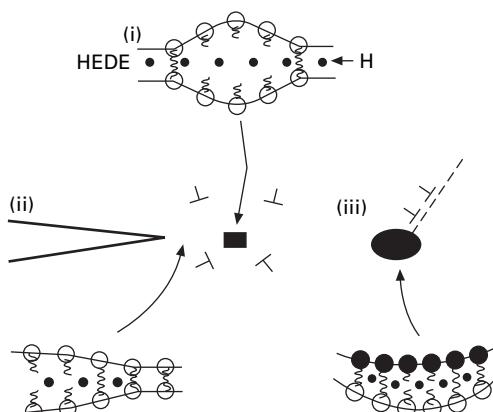


2.7 Schematic diagram illustrating sub-critical crack growth involving hydrogen diffusion to hydrostatically stressed regions, then formation and fracture of a brittle hydride at a crack tip.

boundaries). In 1959 Troiano [26] suggested that weakening of interatomic bonds (in iron) was due to donation of the hydrogen 1s electron to the unfilled 3d shell of the iron atoms. The decohesion hypothesis – involving charge-transfer and weakening of interatomic bonds so that tensile separation of atoms (decohesion) occurred in preference to slip – was subsequently quantitatively developed by Oriani [27] and others [13, 28–30]. Decohesion is usually envisaged as a simple, sequential tensile separation of atoms when a critical crack-tip-opening displacement (CTOD) (approximately 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 CTOD to be achieved [31].

Some dislocation activity may accompany decohesion, and may locally increase stresses at decohesion sites, but should be fairly limited so that atomically sharp crack tips are not continually blunted. High concentrations of hydrogen and the decohesion event could occur at a variety of locations, namely: (i) at atomically sharp crack tips due to adsorbed hydrogen, (ii) several tens of nanometres ahead of cracks where dislocation shielding effects result in a tensile-stress maximum, (iii) positions of maximum hydrostatic stress (several micrometres in high-strength steels), and (iv) particle–matrix interfaces ahead of cracks (Fig. 2.8).

Very high elastic stresses are probably required to produce sufficiently high concentrations of hydrogen in interstitial lattice sites ahead of crack tips to produce decohesion, and whether such stresses can be achieved, e.g. due to strain-gradient hardening [13], is debatable. Decohesion at grain boundaries



2.8 Schematic diagrams illustrating the HEDE mechanism, involving tensile separation of atoms owing to weakening of interatomic bonds by (i) hydrogen in the lattice (ii) adsorbed hydrogen and (iii) hydrogen at particle–matrix interfaces [32].

could occur at or ahead of crack tips due to hydrogen trapped at specific sites, and may occur as a result of bond weakening by both hydrogen and metalloid-impurity segregation. Hydrogen diffusion to the aforementioned sites is required for both IHE and HEE, except for cases where hydrogen adsorption at tips of external cracks is solely responsible for HEE.

Supporting evidence

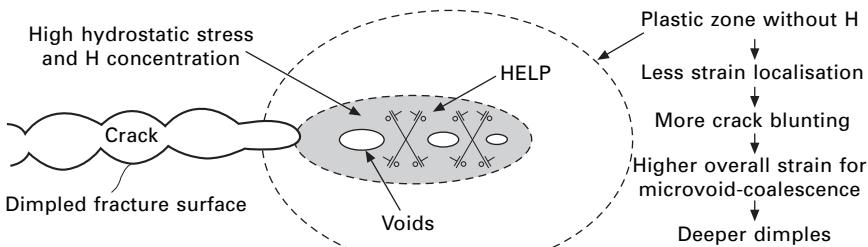
High hydrogen concentrations have been observed at grain boundaries and particle–matrix interfaces by various techniques, and quantum-mechanical calculations support the concept of weakening of interatomic bonds by hydrogen leading to HEDE, particularly if slip planes around crack tips are not favourably oriented for slip [33, 34]. Direct experimental evidence of HEDE is, however, difficult to obtain since there are no techniques for directly observing events on the atomic scale at crack tips in bulk material. Perhaps the most direct experimental evidence that hydrogen can weaken interatomic bonds is the easier field-evaporation of surface atoms observed during field-ion microscopy when hydrogen is used as the imaging gas [35].

A featureless fracture surface sometimes observed by SEM at high magnifications is often taken as evidence that decohesion has occurred [13], but it is debatable whether SEM is able to resolve sufficiently small, shallow dimples that crack growth by very localised plasticity can be ruled out. However, TEM of fractured thin foils shows that atomically brittle intergranular fracture can occur in materials with segregated impurities at grain boundaries [36], e.g. S in Ni, and atomistic calculations indicate that such impurities can, like hydrogen, weaken interatomic bonds [37, 38]. Thus, it would not be surprising if hydrogen segregated at grain boundaries and other interfaces also resulted in decohesion, especially if hydrogen and impurity elements were both present.

2.2.3 Hydrogen-enhanced localised plasticity (HELP)

Description

In 1972 Beachem [39] was the first to suggest, partly on the basis of fractographic observations, that HAC occurred because solute hydrogen facilitated the movement of dislocations. This idea was subsequently promoted by Birnbaum, Sofronis, Robertson, and co-workers from the 1980s onwards [23, 24, 40, 41]. It was proposed that, since hydrogen concentrations were localised near crack tips due to hydrostatic stresses or entry of hydrogen at crack tips, deformation was localised near crack tips as a result of solute hydrogen facilitating dislocation activity. It was argued that sub-critical crack growth should then occur by a more localised microvoid-coalescence (MVC) process than that which would occur in inert environments (Fig. 2.9).



2.9 Schematic diagram illustrating the HELP mechanism, involving a microvoid-coalescence process, with plasticity localised and facilitated in regions of high hydrogen concentrations.

Hydrogen diffusion to local regions ahead of crack tips is obviously required for operation of the HELP mechanism for both IHE and HEE. Crack paths could be transgranular or intergranular depending on whether locally high hydrogen concentrations were present within grain interiors or adjacent to grain boundaries.

Supporting evidence

The idea that solute hydrogen facilitates dislocation activity is supported by: (i) elasticity theory, (ii) atomistic calculations, (iii) *in-situ* transmission-electron microscopy observations of dislocations in thin foils exposed to hydrogen gas, (iv) softening and strain localisation in bulk specimens under some conditions, (v) comparisons of slip-line characteristics in hydrogen-charged compared with hydrogen-free specimens, and (vi) nano-indentation tests.

Elasticity theory

Linear-elastic and finite-element calculations indicate that dislocations are ‘shielded’ from the full force of repulsive interactions between dislocations and obstacles (including other dislocations) when hydrogen is present [23, 24, 40, 41]. This is thought to arise due to ‘re-configuration’ of hydrogen atmospheres around dislocations as they approach and pass obstacles during deformation providing, of course, that hydrogen atmospheres can keep up with dislocations. Edge dislocations should be more effectively shielded than screw dislocations since the dilatational stress-field around edge dislocations promotes hydrogen atmospheres around them.

Atomistic calculations

Atomistic simulations indicate that hydrogen lowers the dislocation-core energy, and thereby reduces the Peierls stress for dislocation movement

(in Al) by more than an order of magnitude [42]. This effect occurred for edge, screw and mixed dislocations, although the effect of hydrogen on the binding energy depended on the dislocation character such that cross-slip was inhibited and slip-planarity was promoted. These effects were thought likely to be applicable to other metals besides aluminium, and that the effect of hydrogen on the core energies of dislocations could act in conjunction with hydrogen effects on elastic interactions between dislocations [42].

In-situ TEM observations

Direct observations of hydrogen-induced increases in dislocation activity have been made using high-voltage TEM, where hydrogen gas is introduced into an environmental cell around thin foils subjected to stress [43]. 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 to 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 upon the introduction of hydrogen.

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 hydrogen-free specimens tested in air. However, the influence of hydrogen on stress-strain curves depends on the material, its purity, strain rate, temperature, and other variables, and hardening is observed in some circumstances. The degree of softening, when it occurs, is usually quite small, e.g. ~10% in hydrogen-charged aluminium and nickel, but is sometimes large, e.g. in hydrogen-charged pure iron single crystals at low temperatures and low strain rates [3, 23, 24, 40, 41, 44].

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 hydrogen-free specimens. 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 [23, 24, 44–51]. 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.

Nano-indentation experiments

Besides observations of the effects of hydrogen on slip characteristics around indentations, 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 [52]. 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). 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.

Fractographic observations and direct TEM observations of HAC

Fractographic observations, showing smaller, shallow dimples on fracture surfaces after HAC than after fast fracture in air, are often taken as evidence for HELP, and were what prompted Beachem to first propose this mechanism, as already mentioned. Direct observations of HAC in thicker regions of thin foils by high-voltage TEM also show that cracking occurs by a localised nano-void coalescence process [53]. However, such observations could also be explained by an adsorption-induced dislocation-emission mechanism (AIDE) (or a combination of AIDE and HELP), as discussed in the next section.

2.2.4 Adsorption-induced dislocation emission (AIDE)

Description

The AIDE mechanism was first proposed by Lynch in 1976 and further developed in subsequent papers [32, 54–56]. Theories of HE based on

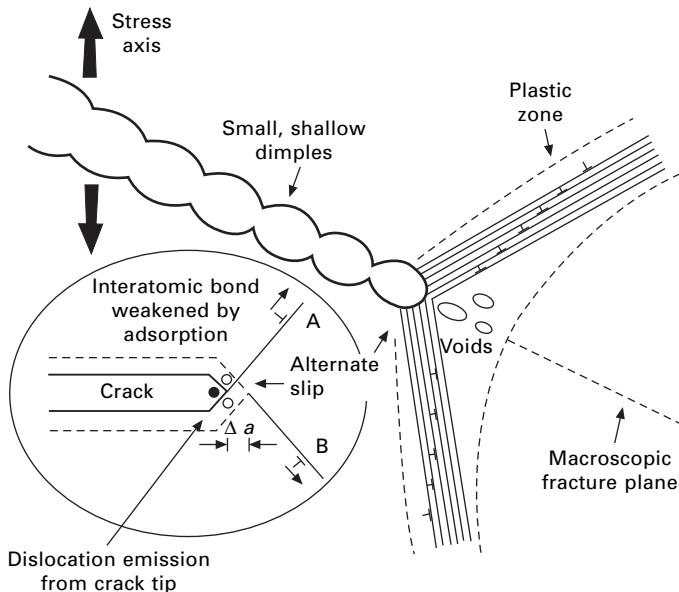
adsorbed hydrogen had been suggested earlier by others, such as Petch in 1956 [57], but were couched in thermodynamic terms, e.g. surface-energy reductions, rather than in mechanistic terms. In 1975 Clum [58] was the first to suggest, based on field-ion microscopy observations, that adsorption (of hydrogen) might facilitate dislocation nucleation at surfaces. However, he did not indicate how such a process could lead to embrittlement.

The AIDE mechanism is, in some respects, more complex than the HEDE or HELP mechanisms and, hence, requires a lengthier explanation. For the AIDE model, the term ‘dislocation-emission’ encompasses both nucleation and subsequent movement of dislocations away from crack tip, and it is important to note that it is the nucleation stage that is critical and facilitated by adsorption. Once nucleated, dislocations can readily move away from the crack tip under the applied stress. The nucleation stage involves the simultaneous formation of a dislocation core and surface step by co-operative shearing of atoms (breaking and re-forming of interatomic bonds) over several atomic distances. Thus, weakening of interatomic bonds over several atomic distances by ‘adsorbed’ hydrogen can facilitate the process.

In the AIDE model, crack growth under sustained or monotonically increasing stresses occurs not only by dislocation emission from crack tips, but also involves nucleation and growth of microvoids (or nano-voids) ahead of crack tips. Nucleation and growth of voids at second-phase particles, slip-band intersections, or other sites in the plastic zone ahead of cracks occurs because stresses required for dislocation emission are sufficiently high that some general dislocation activity occurs ahead of cracks. Void formation contributes to crack growth, and also serves to re-sharpen crack tips and results in small crack-tip-opening angles. However, crack growth primarily occurs by dislocation emission from crack tips (Fig. 2.10).

For IHE, hydrogen diffusion to, and adsorption at, internal crack tips or voids is necessary for AIDE, while diffusion is not essential for HEE – just dissociation of hydrogen molecules and adsorption at external crack tips is required. However, hydrogen diffusion to voids ahead of cracks may occur during HEE, resulting in AIDE at tips of voids as well at the external crack tip. Dislocation transport as well as lattice diffusion could be involved in some circumstances. For IHE, if internal crack tips break through to the external surface, hydrogen adsorption would be inhibited by preferential adsorption of oxygen (from air environments), but could still occur at tips of voids just ahead of crack tips.

To understand why facilitating dislocation emission from crack tips results in embrittlement, it is necessary to consider how crack growth occurs in inert (non-embrittling) environments for ductile materials. Ductile crack growth appears to occur predominantly by egress of dislocations, nucleated from sources in the plastic zone ahead of cracks, with little or no emission of dislocations occurring from crack tips. Dislocation emission from crack

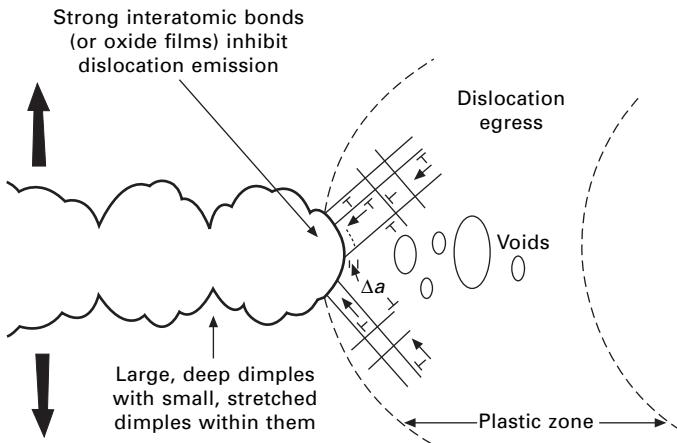


2.10 Schematic diagram illustrating the adsorption-induced dislocation emission (AIDE) mechanism for HEC, which involves crack growth by alternate-slip (for transgranular paths) from crack tips, facilitating coalescence of cracks with voids formed in the plastic zone ahead of cracks [55].

tips is probably difficult in inert or air environments because interatomic bonding at crack tips is intrinsically strong or because strong bonds are formed between oxygen and substrate bonds, respectively.

When dislocation egress around crack tips predominates, only a small proportion of dislocations emanating from near-crack-tip sources exactly intersect crack tips to produce crack advance – most 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, 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 small voids (nucleated from smaller particles or other sites at higher strains) between large voids (Fig. 2.11).

When hydrogen adsorption weakens interatomic bonds and thereby promotes dislocation emission from crack tips, a greater proportion of 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. The dimples



2.11 Schematic diagram illustrating ductile crack growth involving coalescence of cracks with voids by egress of dislocations nucleated from near-crack-tip sources [55].

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 were active in fcc or 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 location of void nuclei ahead of cracks.

Background and supporting evidence

As detailed in the following, an AIDE mechanism for IHE and HEE in some materials is supported by: (i) the presence of high concentrations of hydrogen adsorbed on surfaces (and within a few atomic distances of surfaces), (ii) surface-science observations, (iii) atomistic modelling, (iv) observations of HE at 'high' crack velocities relative to hydrogen diffusivities, (v) metallographic

and fractographic observations, including remarkable similarities between HE and LME, and (vi) other miscellaneous observations.

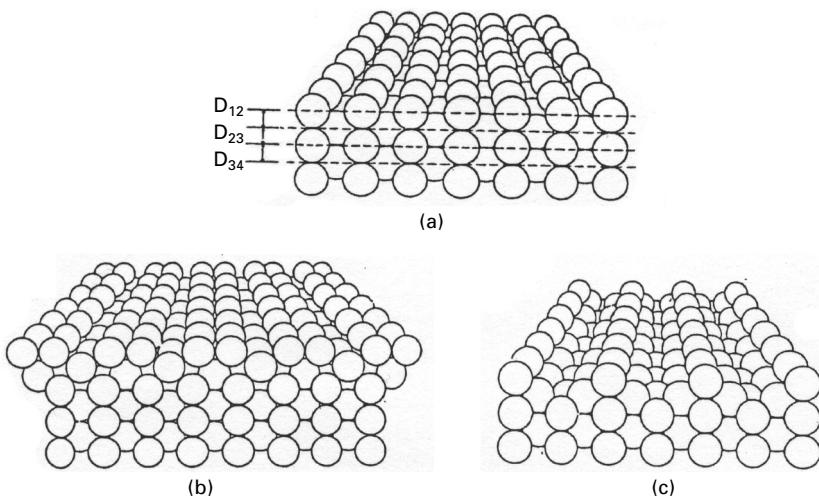
Hydrogen adsorbed at surfaces

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 [12, 59–62]. Thus, much higher hydrogen concentrations would be expected at (crack-tip) surface sites and just sub-surface sites than at normal interstitial lattice sites (Fig. 2.1). 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. 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 and HEDE mechanisms.)

Surface-science observations

For clean, stress-free metal surfaces (without adsorbates or films), surface-lattice ‘relaxations’ or ‘reconstructions’ are observed, i.e. the lattice spacings or lattice structure within several atomic distances of surfaces are different from those in the bulk [63–67]. These surface-lattice perturbations occur essentially because atoms at the surface have fewer neighbours than those in the bulk and, hence, electron-charge is redistributed. Thus, it is not surprising that electron-charge transfer owing to adsorption of hydrogen and other environmental atoms often affects the extent and nature of the perturbations. These changes can sometimes produce buckling or rumpling of the surface, involving lateral or vertical shear movements of atoms (Fig. 2.12). The exact effect of adsorption depends on variables such as the adsorbed species, surface-crystallography, surface-coverage of adsorbed species and temperature. Generalisations are difficult to make because such a diversity of effects has been observed, and an understanding of all these effects is far from complete.

When crack tips are not atomically sharp but have a finite radius, surface-lattice perturbations (and modifications thereof by adsorption) should occur at crack tips during sub-critical crack growth. Indeed, the phenomenon of adsorption-induced LME, involving sub-critical cracking at velocities of the



2.12 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) [65].

order of 100 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 and effects of adsorption are probably significantly different from those at plane surfaces. For example, there may be insufficient time to achieve an equilibrium state during crack growth, and high elastic (and plastic) strains and crack-tip curvature are likely to have significant effects.

Crack-tip surface-lattice perturbations/interatomic-bond strengths would be expected to influence dislocation nucleation from crack tips because the nucleation 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 perturbations (and weak adsorbate–substrate and weak adsorbate–adsorbate bonding) should favour emission of dislocations. (Adsorbate–substrate and adsorbate–adsorbate bonds as well as metal–metal bonds have to be sheared.) Conversely, large crack-tip lattice perturbations (or strong adsorbate–substrate bonding) would be expected to inhibit dislocation emission.

Atomistic modelling

Atomistic calculations of crack growth in nickel using the embedded-atom method indicate that adsorbed hydrogen facilitates dislocation emission from crack tips, providing that slip planes are favourably oriented with respect

to the crack plane [33, 34]. Another study showed that dislocations (in Al) should be emitted more easily when hydrogen is present due to lowering of the unstable stacking-fault energy [42]. Theoretical calculations also suggest that dislocation emission from crack tips could be affected by adsorption-induced changes to surface stresses (which are linked to the surface lattice perturbations being restrained by the sub-surface lattice) [68, 69]. 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 [70].

Observations of HEE at low D/v ratios

Analyses have shown that hydrogen should not diffuse ahead of cracks (for more than a few atomic distances) for D/v ratios of less than $\sim 10^{-8}$ cm, were D is the hydrogen diffusivity and v is the crack velocity [19, 71]. HEE in nickel can occur at crack velocities such that D/v ratios are less than 10^{-8} cm [54, 55], which suggests that adsorption is responsible and, since considerable localised plasticity occurs, that AIDE rather than HEDE predominates. Dislocation-transport of hydrogen directly ahead of crack tips was considered to be unlikely for the particular circumstances involved. More details are provided in a subsequent section.

Metallographic and fractographic observations

Remarkably similar (dimpled) fracture surfaces produced by HE and LME in some materials suggest that the AIDE mechanism is responsible. For LME, only adsorption occurs at crack tips in many systems because crack growth occurs so rapidly (up to 200 mm/s) that there is no time (or tendency) for other interactions to occur [54, 55]. Details of the close similarities between HE and LME are shown in subsequent sections for specific materials, where the pros and cons of AIDE, HELP and HEDE mechanisms are discussed in detail. Other observations supporting an adsorption mechanism for some fracture modes are also discussed in more detail in subsequent sections.

2.2.5 Hybrid mechanisms and possible role of vacancies

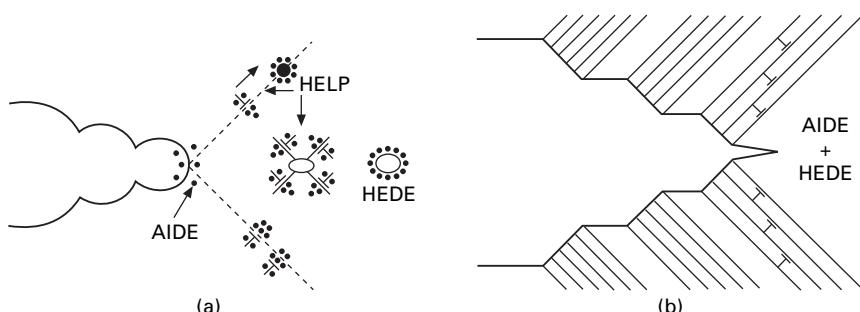
Combinations of AIDE, HELP, and HEDE mechanisms could, of course, occur in many cases, with the relative importance depending on the fracture mode, which depends on the material and other variables [32]. For example, dislocations nucleated from crack tips (due to AIDE) may move away from crack tips more readily due to HELP, thereby decreasing the back-stress on subsequent dislocation emission. For crack growth predominantly by AIDE, void-nucleation ahead of cracks could be promoted at slip-band intersections

by HELP or by HEDE at particle–matrix interfaces (Fig. 2.13(a)). AIDE and HEDE could also 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 (Fig. 2.13(b)). Such a process could produce small crack-tip-opening angles without void formation ahead of cracks [10, 32].

As well as AIDE and HELP possibly acting conjointly to localise plasticity, additional strain-localisation could occur due to hydrogen–vacancy interactions. Vacancy effects probably play only a secondary role, although there has been a somewhat radical suggestion that HE may be primarily the result of a high concentration of vacancies ahead of cracks, due to hydrogen-induced reductions in the vacancy-formation energy, rather than hydrogen effects *per se* [72]. A high concentration of vacancies ahead of cracks could occur not only due to high hydrogen concentrations at regions of high triaxial stress but also because hydrogen stabilises vacancies produced by dislocation–dislocation interactions [73]. Vacancy agglomeration could lead to nano-void formation [74], and autocatalytic void-growth and coalescence might occur if the number or size of nano-voids reached a critical level. Vacancies could also facilitate dislocation-climb and cross-slip, and reduce strain-hardening, thereby promoting strain localisation, possibly in conjunction with hydrogen-induced slip-localisation due to AIDE or HELP.

2.3 Relative contributions of various mechanisms for different fracture modes

The likelihood that different mechanisms predominate for different fracture modes (in non-hydride forming materials) is discussed in the following. The characteristics of various fracture modes are described in detail, followed by



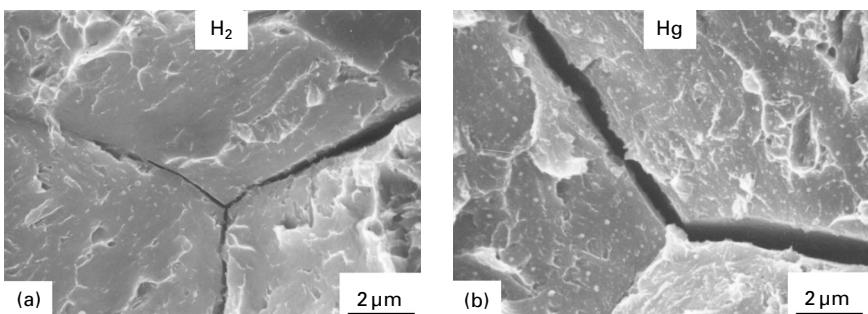
2.13 Schematic diagrams illustrating hybrid mechanisms of hydrogen-assisted cracking: (a) AIDE with contributions from HELP and HEDE, and (b) AIDE alternating with HEDE [32].

a discussion of how well different mechanisms account for the observations. Intergranular fracture produced by HE in high-strength steels and other materials is considered first since this is the most common fracture mode. Transgranular fractures in high-strength steels are then discussed, followed by consideration of cleavage-like fractures, and slip-band fractures.

2.3.1 Intergranular fracture in high-strength steels and other materials

Intergranular fracture along prior-austenite grain boundaries is the most common fracture mode for IHE, HEE and LME of high-strength steels. For normal metalloid-impurity contents, especially in steels tempered in the range where impurity segregation is prone to occur, SEM indicates that intergranular fracture surfaces are featureless in areas between ridges and isolated dimples (Fig. 2.14). However, in some cases, the relatively smooth areas appear to be dimpled on a very fine scale when they are examined by TEM of replicas (Fig. 2.15). TEM resolves small, shallow features better than SEM, providing that replicas are shadowed at low angles ($10\text{--}15^\circ$), and examined at low kV at high tilt angles ($\sim 30^\circ$) [54].

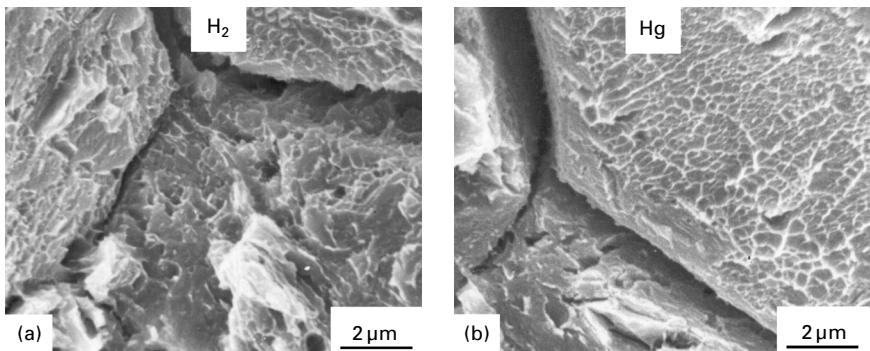
In other cases, e.g. for high-strength steels tempered at high temperatures, SEM (and TEM) show that intergranular facets produced by HEE and LME are completely covered by well-defined dimples (Fig. 2.16). Such observations lend credibility to the possibility that apparently smooth areas observed by SEM for other heat-treatments could be dimpled on a scale not resolved by SEM. The dimples on fracture surfaces produced by HE appeared to be smaller and shallower than those produced by fast fracture in air (where transgranular fracture generally occurred). Comparison of dimple sizes is,



2.14 SEM of fracture surfaces produced by sub-critical cracking ($v \sim 10^{-5} \text{ m/s}$) in (a) gaseous hydrogen (101 kPa), and (b) liquid mercury, at 20°C for a high-strength martensitic steel (tempered at 550°C), showing 'brittle' intergranular facets exhibiting tear ridges and isolated dimples [54].



2.15 TEM of replica of fracture surface produced by slow crack growth in gaseous hydrogen (101 kPa) for a high-strength martensitic steel (tempered at 550°C), showing fine details between tear ridges [54].



2.16 SEM of fracture surface produced by sub-critical cracking ($v \sim 10^{-5}$ m/s) in (a) gaseous hydrogen (101 kPa), and (b) in liquid mercury, at 20°C in a high-strength martensitic steel (tempered at 650°C), showing dimpled intergranular facets [54].

however, difficult since the large, deep dimples produced by fracture in the absence of hydrogen contain small, stretched dimples that are often difficult to resolve.

For completely dimpled fractures, AIDE or HELP mechanisms rather than HEDE are most likely to be primarily responsible for facilitating and localising microvoid-coalescence processes. The AIDE mechanism probably predominates because higher hydrogen concentrations are likely to be present

exactly at grain boundaries than adjacent to grain boundaries. The essentially identical, dimpled intergranular fracture mode produced by adsorption-induced LME (Fig. 2.16) as produced for HEE (for the same steel and the same heat-treatment condition) also supports an AIDE mechanism.

For intergranular fractures where it is debatable whether or not dimples are present, either an AIDE/MVC process operates on such a fine scale that dimples are difficult to resolve or a HEDE process occurs. It is also possible that both processes occur, with some grain-boundary structures and metalloid-impurity contents locally favouring HEDE and other grain-boundary structures and compositions favouring AIDE. A combined process is reasonable since both HEDE and AIDE are based on hydrogen-induced weakening of interatomic bonds. The same considerations regarding AIDE, HELP and HEDE mechanisms, as discussed for the high-strength steels, also apply to intergranular fracture in other materials.

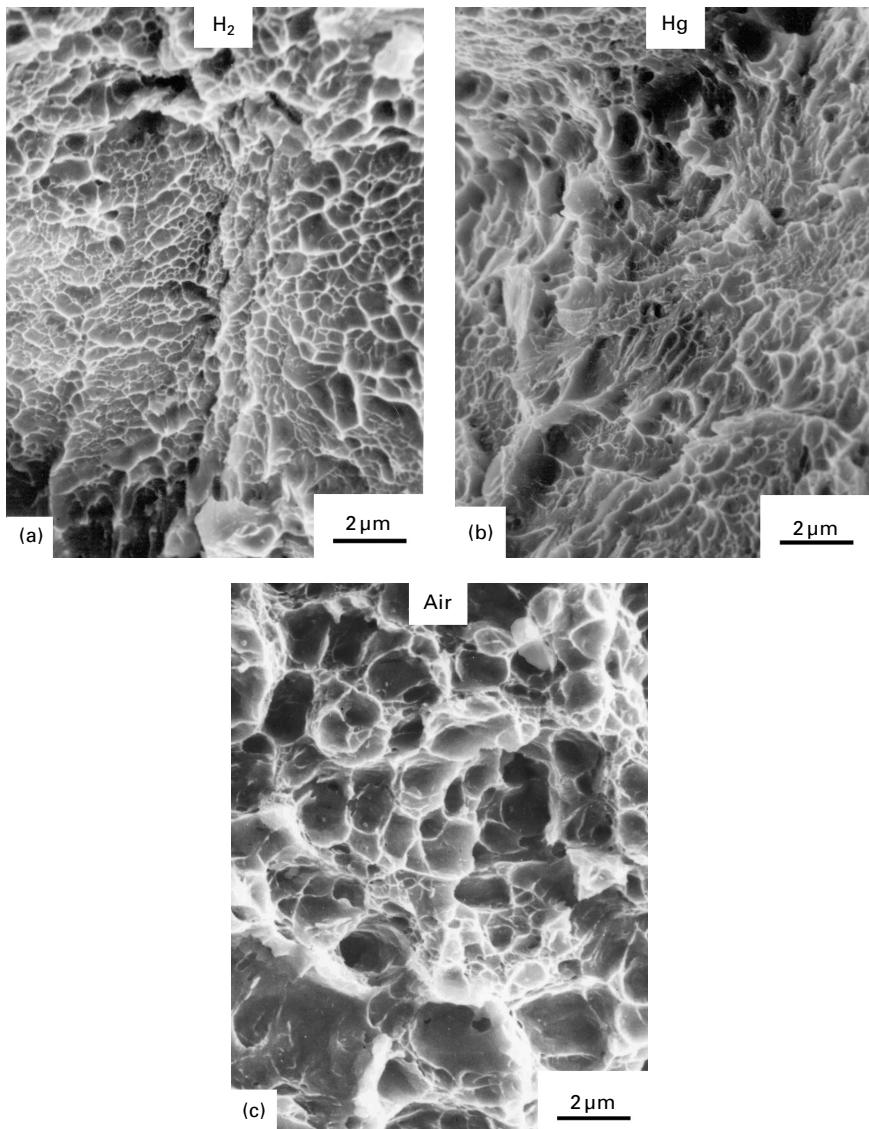
2.3.2 Transgranular dimpled fracture in high-strength steels and other materials

For high-strength martensitic steels with low levels of metalloid impurities, especially at tempering temperatures that do not promote metalloid-impurity segregation to prior-austenite grain boundaries, HEE can produce completely dimpled transgranular fractures [54]. (Crack-paths were transgranular with respect to prior-austenite grain boundaries, but sometimes followed martensite-site lath boundaries.) Dimples appeared to be smaller and were shallower than those produced by fast fracture in air, as discussed for dimpled intergranular fractures. Transgranular dimpled fracture surfaces essentially identical to those produced by HEE were observed for adsorption-induced LME (for the same steel and tempering temperature) (Fig. 2.17) [54]. Lower strains-to-fracture and differences in dimple size (generally smaller and with a smaller depth-to-width ratio) have also been observed in other (lower strength) hydrogen-charged steels compared with hydrogen-free steels after tensile testing [75]. The HEE and LME comparisons suggest that an AIDE mechanism most likely predominates, with possible contributions from HELP and HEDE (and vacancy effects), as discussed in previous sections.

2.3.3 Cleavage-like fractures

Hydrogen-induced cleavage-like fractures (involving slow, stable crack growth) are less common than intergranular fractures, but have been extensively studied, especially in single crystals (e.g. Ni, Fe, Fe-Si), on the basis that it should be easier to elucidate the mechanisms of HE in such materials than in materials with more complex microstructures [10, 54, 55, 76–80].

For Ni single crystals, cleavage-like fractures have been observed after



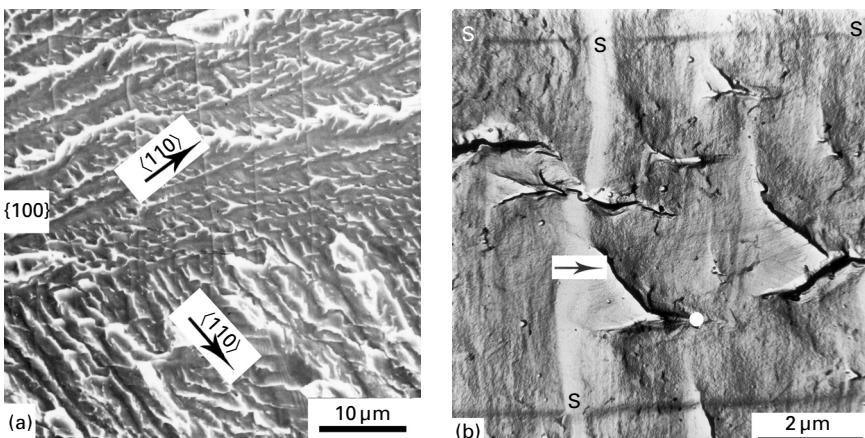
2.17 SEM of transgranular fracture surfaces of martensitic steel (290°C temper) resulting from slow crack growth in (a) gaseous hydrogen (101 kPa), (b) liquid mercury, and (c) overload in air, at 20°C, showing shallower dimples after LME and HEE compared with overload fracture [54].

crack growth in notched and fatigue pre-cracked specimens tested in tension or cantilever-bending in gaseous hydrogen [10, 54, 55, 76]. Increasing deflection rates in cantilever bending increased rates of crack growth, and cleavage-like

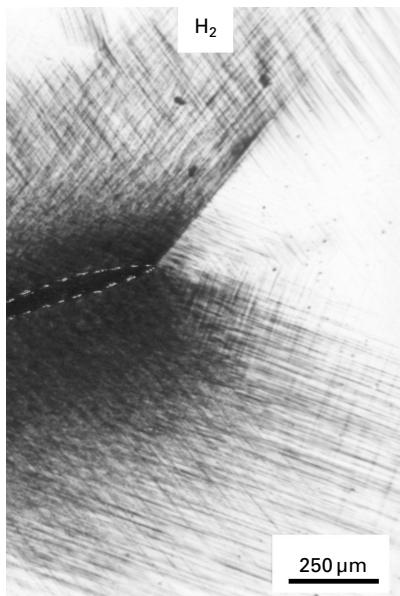
fracture surfaces were observed even at crack velocities of up to 0.5 mm/s [54, 55]. Fracture planes were generally near {100}, although significant deviations occurred for specimen orientations where {100} planes were at large angles to the tensile-stress axis, especially at high deflection rates. Crack-growth directions on {100} planes were near $\langle 110 \rangle$, and Y-shaped tear ridges, isolated large dimples, and coarse slip lines were observed on fracture surfaces (Fig. 2.18(a)). TEM of replicas showed that the regions between the tear ridges and large dimples had a rumpled appearance due to fine slip markings and (possibly) nano-scale dimples (Fig. 2.18(b)). Extensive slip on {111} planes intersecting crack tips was observed on the side surfaces of specimens (Fig. 2.19).

For iron and iron-silicon single crystals, cleavage-like fractures, generally along {100} planes, have been observed after HEE and IHE of Fe and Fe-Si single crystals under conditions where ductile fracture would occur in the absence of hydrogen [77–79]. Cracking often occurred in two different crystallographic directions ($\langle 112 \rangle$ in Fe and $\langle 110 \rangle$ in Fe-Si) in adjacent regions, resulting in a herringbone pattern of steps and tear ridges. Fracture surfaces also sometimes exhibited regularly spaced crack-arrest markings (CAMs) ($\sim 1 \mu\text{m}$ apart) (Fig. 2.20).

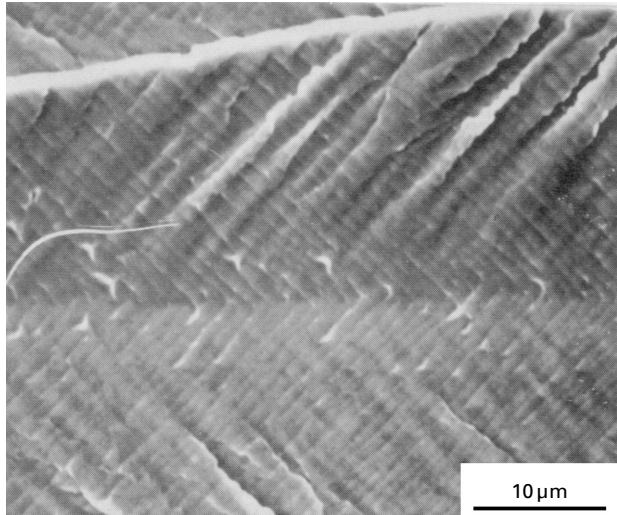
Slip on {111} or {112} planes intersecting crack fronts was observed on the side surfaces of specimens (and in the interior for Fe-Si after sectioning and etching). Other evidence that cleavage-like fracture surfaces are associated with locally high strains includes diffuse electron-channelling patterns (and electron back-scattered diffraction patterns), and high dislocation densities



2.18 Cleavage-like fracture surfaces in a nickel single crystal cracked in gaseous hydrogen (101 kPa) at 20°C ($v \sim 10^{-3} \text{ mm/s}$): (a) SEM showing tear ridges and steps forming a herringbone pattern, and (b) TEM of secondary-carbon replica showing fine details between the tear ridges and coarse slip lines (S-S) [54].



2.19 Optical micrograph showing slip around crack tip after fatigue crack growth of nickel single crystal in hydrogen gas (101 kPa) at 20°C. The slip distribution was similar, but more extensive, after cracking under monotonically increasing displacements [54].



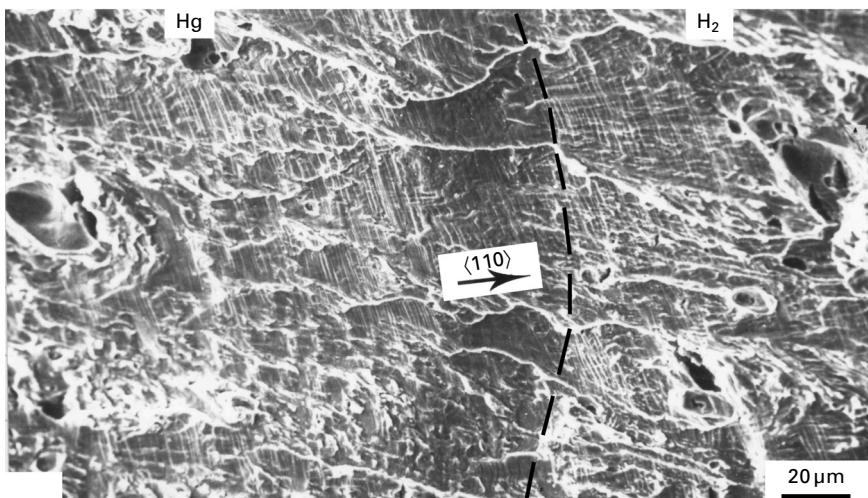
2.20 SEM of cleavage-like fracture surface produced in an Fe-Si single crystal in gaseous hydrogen, showing crack-arrest markings [77].

observed just beneath fracture surfaces by TEM [28, 77]. Fracture surfaces were also rumpled on a fine scale, which was particularly apparent when replicas were examined by TEM [54]. Hydrogen-induced cleavage-like cracking has been observed in Fe at temperatures ranging from -100°C to 20°C , and occurred regardless of whether hydrogen resulted in hardening (at lower temperatures) or softening (at higher temperatures) [80].

The fact that cleavage-like fracture surfaces could be produced in nickel single crystals at velocities as high as 0.5 mm/s at 20°C suggests that ‘adsorbed’ hydrogen, by itself, can produce such fractures since D/v ratios are $\sim 10^{-8}\text{ cm}$. As already mentioned, this is the value below which hydrogen should not have time to diffuse more than one or two atomic distances ahead of cracks. Detailed analyses of the effects of hydrogen-gas pressure and temperature on slow crack growth in nickel single crystals also suggest that the embrittlement site is close (within about eight atomic distances) to crack tips [10, 76]. Assuming some uncertainties in the analyses, this is not inconsistent with an adsorption mechanism, where adsorption is considered to include not only hydrogen on the surface but also hydrogen trapped within a few atomic distances of the crack tip. Observations that cleavage-like cracking in iron-silicon single crystals in gaseous hydrogen can be arrested almost immediately (within 1s) of adding oxygen to the environment also suggest that cracking is due to a surface or very near-surface effect rather than HELP in the plastic zone ahead of cracks [10, 76].

Similarities between fractures produced by HEE and adsorption-induced LME in Fe-Si and Ni single crystals (Figs 2.21 and 2.22) also support an adsorption mechanism for cleavage-like cracking. These similarities are even more striking than those described in the previous section for high-strength steels. For Ni single crystals, partially cracking specimens in liquid mercury, evaporating the mercury, then continuing crack growth in hydrogen gas (at $v \sim 0.1\text{--}0.5\text{ mm/s}$ in both mercury and hydrogen), showed that there were essentially no differences in the detailed fracture-surface appearance and crystallography (Fig. 2.21). Moreover, the detailed appearance and crystallography depended somewhat on the crystal orientation with respect to the stress-axis, but was the same in mercury and hydrogen environments for each orientation. The extent and distribution of slip lines on the side surfaces of specimens were also the same for cracking in mercury and hydrogen [54, 55].

Since plastic strains are locally high, with extensive slip on planes intersecting crack fronts, and there is evidence of void formation ahead of cracks, at least in some cases, it appears that an AIDE/MVC mechanism rather than an adsorption-induced decohesion mechanism predominates. However, it has been suggested that crack growth involves sequences of alternate-slip and decohesion (as shown in Fig. 2.13(b)) on the basis that dimples were not apparent on fracture surfaces [10, 76]. Comments made

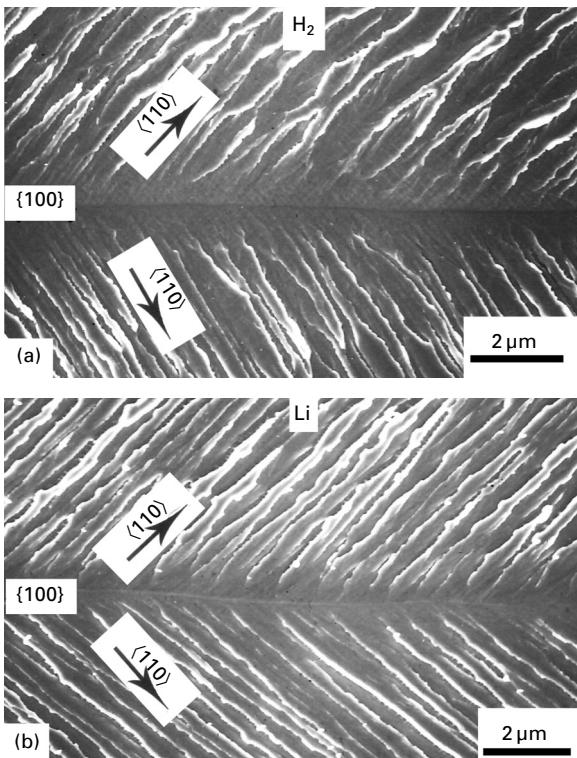


2.21 SEM of fracture surface around the junction (dotted line) between regions produced in mercury and gaseous hydrogen (101kPa) at 20°C, showing steps, tear ridges, slip lines and isolated dimples for both environments. Note that the crack-tip-opening displacement was decreased slightly after evaporating mercury from cracks prior to cracking in hydrogen in order to produce a crack-front marking [54, 55]. (Note also that tests on separate specimens resulted in the same fracture characteristics in mercury and hydrogen.)

regarding the difficulty of resolving very small, shallow dimples on fracture surfaces made previously are, however, relevant here, and further work is required to resolve this issue.

Aside from evidence discussed above showing that an adsorption mechanism can account for cleavage-like fractures, it is difficult to envisage how a HELP mechanism could explain the fractographic observations. Thus, just facilitating and localising dislocation activity ahead of cracks would not be expected to produce a change from a non-crystallographic ductile fracture in inert environments to a cleavage-like fracture macroscopically along low-index planes in specific directions in hydrogen environments. On the other hand, the fracture characteristics are exactly what one would expect for an AIDE (or AIDE plus HEDE) mechanism. However, minor contributions from HELP (and vacancy effects) cannot be discounted at crack velocities where hydrogen can diffuse ahead of cracks, as discussed in Section 2.2.5.

A characteristic of cleavage-like cracking which at first sight appears to be more consistent with HEDE (or HELP) than AIDE are the crack-arrest markings sometimes observed on fracture surfaces, which suggest that cracking occurs discontinuously with ~1 μm crack jumps. Discontinuous cracking can be explained by a HEDE or HELP mechanism in terms of an



2.22 SEM of cleavage-like $\{100\}$ fracture surfaces produced in Fe2.6%Si single crystals by (a) slow crack growth ($\sim 10^{-3}$ mm/s) in gaseous hydrogen (101 kPa) at 25°C, and (b) rapid crack growth (>1 mm/s) in liquid lithium at 210°C, showing herringbone pattern of steps owing to crack growth in two $\langle 110 \rangle$ directions in adjacent regions [54, 55].

increment of cracking occurring when a critical concentration of hydrogen is built up over a critical distance ahead of cracks, followed by crack-arrest and blunting when cracks run into a region of lower hydrogen concentration. However, discontinuous cracking could occur for other reasons [81], and does not preclude an AIDE mechanism. For example, crack-arrest markings could be produced by intermittent bursts of dislocation egress around cracks associated with a dislocation substructure ahead of cracks.

2.3.4 Slip-band fractures

Hydrogen-assisted cracking along slip bands, while less common than other fracture modes, is sometimes observed in materials where there is an inherent tendency for planar slip, e.g. in stainless steels and nickel-based superalloys

[82–84]. 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 hydrogen-free specimens in some materials, and the HELP mechanism is probably significant in promoting more planar slip as a result of a greater effect of hydrogen on edge-dislocation activity than screw-dislocation activity, so that the tendency for cross-slip is reduced [43]. 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.

Void-initiation appears to occur at slip-band intersections and at precipitates, and contributions from HEDE (at precipitate–matrix interfaces) could be involved. 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.

2.4 General comments

The conclusion that IHE and HEE involving localised plasticity predominately occur by AIDE (for cleavage-like and some intergranular fractures) is at odds with the more general popularity of HELP. The widespread acceptance of HELP seems to stem from (i) the diverse and convincing evidence that the phenomenon does occur, and (ii) the fact that hydrogen can diffuse rapidly in many materials so that solute hydrogen is present ahead of cracks in most circumstances. However, whether the magnitude of the HELP effect in bulk material* is sufficiently large to promote sub-critical cracking, and whether HELP is consistent with other observations is not usually critically considered.

Mechanisms of HE must be able to account, in particular, for (i) the detailed fracture characteristics and crystallography, and (ii) the effects of temperature,

*Hydrogen effects on dislocations in thin foils observed by TEM do appear to be large, but these effects may only be partly due to HELP, with contributions to increased dislocation activity on introducing hydrogen arising from non-uniform hydrogen concentrations that induce stresses, and from surface effects, e.g. hydrogen-induced reductions of oxide films.

crack-tip strain rate, hydrogen-pressure and other variables. A mechanism based predominantly on HELP cannot account for these observations for many 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 major 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 [15, 54, 55].

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 ~25 nm diameter, with the cusps only ~4 nm 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 apparent. Thus, HEDE could be 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 in the past 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 the 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 growth of 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 [85], 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 is often the case when changing from a hydrogen 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 adsorbate–adsorbate bonds plus weak metal–adsorbate bonds, and thereby facilitate dislocation emission, as mentioned previously. However, a good understanding of why only some weakly adsorbing metal species produce embrittlement is lacking, and further quantum-mechanical modelling of the effects of various adsorbates on bonding would be worthwhile.

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 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. Further quantum-mechanical-based atomistic and multi-scale modelling of HE (and LME) to get a better understanding of these aspects, and HE in general, are clearly merited.

2.5 Conclusions

Several mechanisms of hydrogen-assisted cracking have significant experimental and theoretical support, namely those based on: (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) in the plastic zone ahead of cracks, and (iv) hydrogen-enhanced decohesion (HEDE) (involving hydrogen at crack tips or hydrogen segregated at grain boundaries and at particle–matrix interfaces ahead of cracks). There is also emerging evidence that hydrogen-vacancy complexes and vacancy clusters may play some role. In other words, as suggested by Oriani some time ago [86], hydrogen can be considered as a ‘versatile embrittler’.

The mechanisms of cracking mentioned above may occur conjointly in some circumstances, and the dominant mechanism probably depends on the fracture-path and fracture-mode which, in turn, depend on the material, microstructure, environment, temperature, stress-intensity factor, and other variables. In the absence of hydrides, the AIDE mechanism probably predominates for cleavage-like fractures and for dimpled intergranular/transgranular fractures in steels. The HEDE mechanism probably predominates for brittle intergranular fractures (where SEM shows essentially flat facets) when high hydrogen concentrations, in conjunction with segregated embrittling impurities, are present at grain boundaries. The HELP mechanism contributes to the initiation of slip-band fractures by localising slip in some materials, e.g. Ni-base superalloys and stainless steels, but probably plays only a minor role for other fracture modes.

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