
Hydrogen and Crystal Defects Interactions: Effects on Plasticity and Fracture

9.1. Introduction

Many mechanisms have been proposed to describe the different hydrogen embrittlement processes. The materials' variability and their properties, their conditions of use and the nature of the surrounding environment make it difficult to establish a single fundamental theory or approach to describe hydrogen embrittlement (HE). Experimental validations of these mechanisms are often based on a set of conditions (metallurgy, mechanical loading, surface hydrogen activity, volume concentration, etc.) which are favorable to the emergence of a particular mechanism, making it difficult to get an overview of the various interaction modes between the adsorbed hydrogen or hydrogen in solid solution and the crystal defects. Kirchheim points out that from a thermodynamic point of view, all the approaches proposed in the literature are based on a decrease of the defect formation or emission energy (dislocations, vacancies, microcavities), of the cohesion and surface energies, or the energy associated with the displacement of defects such as dislocations, in the presence of adsorbed or absorbed hydrogen [KIR 07, KIR 15]. The brittle fracture of deformable crystal materials subjected to quasi-static monotonic loading arises from a competition between, on the one hand, the accumulation rate of elastic energy at the crack tip until a critical value intrinsic to the material is reached (the critical elastic energy release rate, related to the fracture toughness and to Young's modulus) and, on the other hand, the dynamics of crystal defect creation/multiplication that blunt the existing cracks or their nuclei, or screen the loading applied to them [ROB 02]. Understanding the hydrogen-induced damage

and fracture requires taking into account the effects of hydrogen on the crystal cohesion as well as the plasticity or the phase transformations at the crack tip. In the presence of intrinsically brittle interfaces, heterogeneities or phases, hydrogen can affect the material's cohesion through (co-)segregation effects, through the accumulation of deformation incompatibilities or induced precipitation. If, from a formal point of view, these mechanisms belong to the two preceding categories (intrinsic embrittlement or plasticity modification), from a practical point of view, their study and modeling have led to specific developments. We thus find four major classes of hydrogen-assisted damage mechanisms in the literature: brittle fracture through the reduction of the material's cohesion, damage due to the formation of vacancies and their condensation, fracture due to the local increase of plasticity ("direct", through localized shear; or "indirect", through the accumulation of internal stresses near the interfaces) and fracture through the formation of a brittle phase (hydride). The first model is based on the idea of the decrease in the interfaces' cohesion energy (lattice, grain boundaries, inter-phase, etc.) caused by the segregation of hydrogen, which promotes the formation and propagation of cracks [TRO 66, LYN 79, ORI 70]. The second model is based on the formation of new defects such as vacancies followed by microcavities in the presence of hydrogen [FUK 05, CAR 04, TAK 08]. The multiplication and localization of these defects can lead to the initiation and propagation of cracks. The third approach of HE is based on the emission of dislocations favored by the presence of hydrogen (decrease of elastic interactions and line tension) which can induce the initiation of a crack and the localization of the plastic deformation in front of the crack tip [BEA 72, BIR 89, DEL 01, SOF 01]. Finally, the fourth model is based on the formation of a brittle hydrogen-rich hydride phase. In order to better understand the different aspects of the hydrogen-material interaction as well as its harmful effects, we will describe in more detail the four HE models and the various associated mechanisms.

9.2. The role of hydrogen during interface decohesion

Hydrogen atom segregation at an interface, like for many solutes, can lead to the decrease of its cohesion energy. This mechanism is based on the accumulation of atomic hydrogen on crystal planes and/or interfaces such as grain boundaries, interphases and interfaces between inclusions/precipitates and the matrix. The decrease in inter-atomic cohesion forces is induced by the modification of the neighboring metal atoms' electronic environment, their positions and their vibration modes. From a thermodynamic point of view, in an ideally diluted system, the mechanism is based on the decrease of surface energy as a function of the surface coverage ratio by hydrogen [GRI 21, GIB 28, PET 52, CAH 79, HIR 80, KIR 07, KIR 15]. This decrease in surface energy has been evaluated under static atomic-scale conditions in many systems, thanks to the evolution of computing powers. Without going into much detail, we will highlight the studies carried out on α iron,

γ iron, α' martensite, nickel, aluminum and tungsten regarding crystal planes [JOH 10, JIA 04, ALV 15, GEN 18], on the iron-cementite system, iron-carbide systems and the grain boundaries [MIR 17, MAT 11, SHE 14, TIM 17, DIN 17, GEN 18]. In all the situations considered, the cohesion energy decrease is relatively moderate, which leads to the consideration of other processes such as defect formation, phase transformation or a dynamic redistribution of energy. However, this approach is the basis of the decohesion mechanism (hydrogen enhanced decohesion, HEDE) introduced by Troiano and subsequently developed by Oriani and Lynch [TRO 66, ORI 70, LYN 79, LYN 07]. More recently, DFT (density functional theory) approaches associated with cohesive models have shown their interest in predicting the role of hydrogen on crack propagation. For some examples see [JAR 01, RIM 10, CHA 12, BEN 13, MOR 14, ALV 15]. However, these models encounter scale transition problems and the recurrent question of the size of the critical defect. From an experimental point of view, as shown by some studies, it is still difficult to prove the HEDE mechanism without defect intervention. In particular, the fact that the segregation of hydrogen promotes brittle intergranular fracture has been reported in the presence or absence of precipitate without favoring the decohesion mechanism [BEC 09, BEN 11, OUD 14]. In addition, as shown by the measurements of the homogeneous emission of dislocations by nanoindentation under cathodic polarization, hydrogen's surface activity helps the homogeneous nucleation of surface defects [GAS 14a]. Whether the same type of mechanism operates at the crack tip is still a debated question [SON 10, SON 13]. Under these conditions, the effect of hydrogen on the critical elastic energy release rate through the decrease of the surface energy operates either together and/or in competition with the effects on crack tip plasticity [GER 91].

9.3. The effect of hydrogen on plastic deformation processes

9.3.1. *Basic mechanisms in face-centered cubic alloys*

Interstitial hydrogen is the most mobile impurity in solid solution. In face-centered cubic crystals at room temperature, this mobility is equal to or greater than the apparent mobility of dislocations under monotonous loading. The most direct indication of this dynamic interaction is the emergence of plastic deformation instabilities related to the strain rate sensitivity of the flow stress. In particular, Portevin-Le Chatelier instabilities (PLC) were observed, which result from a dynamic strain ageing phenomenon (DSA) by mobile solutes in monotonic traction at low temperature in pure nickel [GOO 63, COM 70] or in nickel-chromium binary alloys [GIR 04a]. More detailed information on these thermally activated jump/ageing sequences is given by [DEL 12]. For ordinary quasi-static tensile strain rates, these instabilities appear at around -150 to -100°C in nickel and nickel-based binary alloys [GIR 04a]. This has two consequences at room temperature:

- the hydrogen in solution is more mobile than the dislocations and the latter are permanently aged to saturation during their waiting time between two thermally activated jumps;

- macroscopically, we can consider that the deformation at room temperature is accompanied by a “solute drag” induced by mobile dislocations. The associated drag stress is of the order of 10 MPa per 1000 atomic ppm of hydrogen in solution in nickel and its binary alloys [GIR 04a].

The aging of the sessile or mobile dislocations during their waiting time between two jumps corresponds to solute diffusion in the local hydrostatic stress gradients, particularly those generated by the dislocation core structures. Saturation corresponds to an equilibrium distribution with these local gradients from a locally uniform distribution [CAH 79, SOF 95]. Starting from a uniform local concentration, the solutes migrate from hydrostatically compressed zones to tensile zones to relax the volume distortions of the host lattice. The redistribution of solutes offsets local hydrostatic stress gradients and associated stress concentrations, irrespective of their sign. In practice, this results in a decrease in pair interactions between the dislocations with a Burger vector with non-zero edge component and a decrease of their line energy. This screening effect of pair interactions between dislocations has led several authors to develop models based on hydrogen-induced local softening [BIR 94]. These models are widely adopted because they are based on a coherent theoretical framework, but above all because they are used to explain the many and consistent observations of deformation localization in the presence of hydrogen in solution. As discussed in section 9.3.4, in FCC crystals, pair interactions between dislocations make a minor and largely indirect contribution to flow stress, which is mainly governed by the thermally activated crossing of forest dislocations. Localization effects result from hydrogen’s indirect effects, which affects deformation microstructures and the distribution of obstacles through a strong effect on the cross-slip probability, as well as on the line tension of screw dislocations.

The hypothesis of a hydrogen distribution in equilibrium with the local stress gradients, confirmed by the static and dynamic aging tests presented above, makes it possible to avoid calculating the distribution of hydrogen around the dislocation configurations and introduces a dimensionless “screening coefficient” of the pair interactions between edge Burgers vectors, which contains all the first-order lattice dilatation effects by hydrogen. It is therefore possible to introduce this screening effect into the classical results obtained with the elastic theory of dislocations (see section 18.2.2.1). We thus predict [CHA 02, GIR 04b, DEL 12]:

- a decrease in the line tension of the screw component of the dislocation segments (effect on the sweeping of forest dislocations);

- a decrease in the critical stress for the activation of a Franck-Read source (effect on dislocation multiplication);
- a screening of the attractive interactions between the edge components of the Schockley partials of a dissociated dislocation, an effect which, along with stacking-fault energy decrease, contributes to the decrease of the cross-slip probability;
- a decrease in dislocation junction strength. The extent of this decrease depends on the type of junctions involved and is most pronounced for collinear junctions, which are formed during the stage I deformation of single crystals oriented for simple slip.

These effects on the basic mechanisms of FCC metal plasticity are confirmed by deformation tests and TEM observations on nickel and nickel-chromium single crystals oriented for simple slip in the presence of hydrogen concentrations of between 1500 and 2000 atomic ppm [GIR 04b, GIR 15]. For more complex polycrystalline metals, the effects on cross-slip probability are the ones with the most important practical consequences.

9.3.2. Elementary mechanisms in body-centered cubic alloys

Carrying out a comparable experimental approach (deformation tests on pure metals or binary solid solutions pre-charged with hydrogen) on body-centered cubic (BCC) materials is possible but entails particular experimental difficulties related to the hydrogen's greater mobility and lower solubility. The effects are reproducible but small and it is, for example, difficult to study the effects of a change in the hydrogen concentration independently of other parameters in a single material [GAS 14b, GAS 14c]. The plasticity of BCC metals is characterized by the transition between a "high temperature" regime with low lattice friction and where the flow stress is controlled by the sweeping of the forest by mobile dislocations as in FCC structures, and a "low temperature" regime in which perfect dislocations spontaneously decompose into sessile configurations and progress through local recombination, nucleation and a sideways progression of double-kinks along the screw dislocation lines. This highly thermally activated mechanism generates a strong lattice friction, which is the major contribution to the flow stress, along with dislocation multiplication through homogeneous or heterogeneous nucleation. The transition temperature, T_a , between these two regimes, is an important property of the plasticity of BCC materials. It directly affects their brittle to ductile transition temperature. Deformation tests on Fe-15%Cr polycrystals charged with hydrogen show that in the presence of a hydrogen solution of between 2 and 4 wt. ppm [GAS 14b]:

- the transition temperature, T_a (close to room temperature), increases by about 10 K per atom percent of solute hydrogen;

- the dislocation structures formed by a 2% deformation at liquid nitrogen temperature and observed in TEM correspond to a more pronounced “low temperature” behavior (screw dislocation mobility);
- the effective stress at 0 K [SMI 69, BRA 78] decreases;
- the double-kink nucleation enthalpy decreases by approximately 10%, which results in a reduction of the Peierls stress at low temperature;
- in this concentration range, no significant effect is observed on the activation volume.

Finally, nanoindentation tests in the presence of a cathodically polarized electrolyte show that the critical shear stress for dislocation homogenous nucleation decreases when hydrogen activity at the surface is high. This is consistently observed in vanadium [TAL 10], iron-3%Si [BAR 10] and nickel [BAR 06]. The decrease of the theoretical critical shear stress is estimated between 10 and 20% in cathodically polarized Fe-15Cr [GAS 14a]. To conclude, if the influence of hydrogen on the plasticity of BCC metals is clearly established, the elementary mechanisms involved remain to be explained. An important issue is the possible effect of solutes and their interactions with hydrogen on the mobility of screw dislocations.

9.3.3. Elementary mechanisms in hexagonal close packed alloys (Zr, Ti)

Given its low solubility and high mobility at room temperature, the effects of hydrogen in solid solution on the mechanical behavior of titanium and zirconium alloys have been less studied than on BCC and FCC alloys. Furthermore, accommodating plastic deformation in these alloys requires the activation of multiple $\langle a \rangle$ and $\langle c+a \rangle$ Burgers vector slip systems where the solute sensitivities may be very different. Finally, the plastic deformation mechanisms in Ti and Zr alloys are strongly affected by the solute content, particularly oxygen. Therefore, to understand the impact of hydrogen in solid solution on plastic behavior, it is necessary to take into account its interaction with oxygen. Despite these difficulties, certain aspects are now well-established, based on studies carried out at temperatures of 250 to 400°C. Tensile tests carried out on zirconium alloys highlight, in particular, the fact that the hydrogen content leads to a softening of the stress which strongly depends on the oxygen content [CON 17]. In addition, an increase in creep rates has also been observed, reflected in an easier viscoplastic flow [FEA 09a, RUP 00, BAR 15, CON 17]. Using relaxation tests for the same alloys, it has been found that for a moderate oxygen content (0.31% equivalent oxygen content O_{eq}), hydrogen increases the activation volume. On the other hand, no significant effect has been observed for a higher oxygen content [CON 17]. This last point seems to be confirmed by the results obtained with zircaloy-4 (O_{eq} 0.8 at %), where the

hydrogen content has a negligible effect on the activation volume [CON 17]. All these results are not affected by different stress orientations despite the crystallographic texture [BAI 94]. Thus, the role of hydrogen is similar on slip systems involving $\langle a \rangle$ and $\langle c + a \rangle$ dislocations. All the characteristics discussed seem to be directly related to the presence of oxygen and its effect on the mobility of screw dislocations. Therefore, the common explanation given for the effect of hydrogen in terms of elastic screening cannot be used in the case of Ti- α and Zr- α alloys [SOF 95, CHA 02]. Despite this, the TEM observations under hydrogen pressure in Ti- α show an increase in the mobility of screw dislocations with the hydrogen content [SHI 88]. On the other hand, based on *ab initio* calculations, Domain *et al.* showed that hydrogen seems to decrease the stacking fault energies of $\langle a \rangle$ type dislocations, which favors the spreading of the dislocation core in the prismatic plane and thus hinders cross-slip in the Zr-H system [DOM 04]. In fact, there are no experimental results to confirm or invalidate these observations and the interactions between hydrogen and oxygen are not taken into account in these calculations. On the other hand, atomic-scale simulations show a repulsive interaction between oxygen and hydrogen at a very short distance in the Zr- α atomic lattice [DOM 04]. Hydrogen located on the tetrahedral sites near a screw dislocation is therefore likely to reduce the number of octahedral sites available for oxygen through a simple repulsive effect. This analysis is in agreement with the increase of the activation volume as a function of the hydrogen content observed at 300°C in Zr- α [CON 17]. At this temperature, the activation volume evolution is associated with an increase in the jump distance between two sessile configurations of a screw dislocation. Therefore, the decrease in the number of octahedral sites available for oxygen in the presence of hydrogen seems to lead to an increase in the jump distance and consequently to a decrease in the sensitivity to the deformation rate. This last point needs to be confirmed by *in situ* tensile tests in TEM carried out under controlled hydrogen partial pressure. Even though all these works are very promising, we must not forget that oxygen and hydrogen are mobile in the temperature regime under consideration (250–400°C). As a result, the jump distance can only be considered as an average value at a given moment.

9.3.4. Influence of hydrogen on collective dislocation mechanisms

The effects of hydrogen in solid solution on the collective mechanisms associated with plasticity remain a highly controversial topic. The basic mechanisms presented in section 9.3.1 do not make use of any particular hypothesis on the crystallography of the solid solution, except for the nature of the interstitial sites. On the other hand, studied configurations with one or two dislocations are the ones that control the collective behavior and the flow stress in the different crystallographies. At this stage, it is useful to distinguish the situations in which the lattice friction is the main contribution (HCP and BCC alloys at “low temperature”)

from those in which the lattice friction is weak compared to the shear stress for the thermally-activated sweeping of forest dislocations (BCC and HCP crystals at medium and high temperature and FCC crystals at all temperatures for all multiple slip configurations – predominant in practice). If “one-dislocation models” can effectively predict the effects on the macroscopic flow stress, in the second case, the line tension and thermally-activated sweeping of the forest determine the bulk of the mechanical response. In this case, it is a risk to predict the effects of hydrogen in solution on the macroscopic response solely based on the effects on the basic properties without considering the consequences of these effects on the development of the deformation microstructures.

The net effect of hydrogen on the macroscopic flow stress can either be to harden [TOB 77, ASA 78, CAS 81, YAG 03, GIR 04b] or to soften [GIR 04b, BUC 97, KIM 83, KIM 87] whilst, in general, establishing little relationship with the dislocation density and distribution (cell size and dislocation density) [ROB 09, ROB 12]. Based on numerous experimental observations of slip traces on the surface of a sample deformed in the presence of hydrogen, there is quite a consensus relating to the fact that hydrogen in solid solution promotes planar slip and slip localization [AUB 08, AUB 10, AUB 12, YAG 10, BAR 11]. “Planar slip”, “planar glide” and “slip planarity” are commonly used terms based on observations of dislocation distributions in FCC metals and alloys. They refer to the same phenomenon: planar dislocation configurations in relation to the fact that cross-slipping is relatively difficult in the presence of solute [FEA 99, HON 90].

In order to obtain additional information on the different work hardening mechanisms, some authors have proposed to use the observations of slip lines and/or the evolution of slip bands on the crystal surface [NEU 83, TAK 87, COU 04, KAW 79, ZAI 04, KRA 05]. According to the classification proposed by Neuhauser, several slip lines spaced from 1 to 10 nm are grouped together to form a slip band [NEU 83]. Experimental results in copper and aluminum suggest that the hardening stages are correlated with the formation and evolution of slip band characteristics [NEU 83, TAK 87, KRA 05]. The effect of hydrogen on the localization of plastic deformations on the surface, that is, the formation of these deformation bands, has been reported under various conditions (single and multiple slip, low and high stacking-fault energy, etc.) [LOU 83, KRA 84, XIA 94, ULM 91, ABR 95]. The increase in the slip band emergence heights in the presence of hydrogen reported in these works is seen as the expression of slip localization.

On the other hand, the effect of hydrogen on the spacing of slip bands has been little discussed. Recent advances in topographic measurements have been obtained using atomic force microscopy (AFM) [RIS 08, COU 04, ZAI 04, KRA 05, NIB 06, MEN 08, AUB 08, AUB 10, AUB 12, HUV 09, DEL 08, BAR 11, YAG 10]. In polycrystalline austenitic stainless steel AISI 316L, hydrogen led to an increase in

the average slip band height for macroscopic plastic deformation levels of 3% and 10% [AUB 10, AUB 16]. On the other hand, the slip band average width appears to increase at a low deformation, but remains almost constant at a larger plastic deformation [AUB 12, AUB 16]. More recently, the association of AFM surface observations with those conducted in TEM has demonstrated a direct link between the spacing between polarized dislocation boundaries (or geometrically necessary boundaries, GNBs) and the thickness of the deformation bands in the case of nickel alloy single crystals with simple slip orientation [HUV 09, GIR 15].

In other words, dislocation boundaries confine plasticity and reduce the mobile dislocations' mean free path whereas equiaxed cells only hinder the dislocation movement in their role as obstacles. The effect of atoms in solid solution on the spacing between boundaries is clearly established for chromium and hydrogen, which decrease this characteristic quantity. The decrease of the mean free path leads to hardening in stages II and III. The origin of GNBs observed at the end of hardening stage II is the progressive transformation of the pile-ups into grids and then boundaries of polarized dislocations [FEA 99, FEA 09B, FUJ 83]. Thus, the GNB's spacing decrease with the planar character of the deformation can be considered to arise from an increase in the number of dislocation sources when the cross-slip is reduced. This has been widely reported in the past in various alloys with a substitutional solid solution such as Ni-Co [MAD 63], Cu-Al [SWA 63] and Al-Zn [SWA 63] in relation with the decrease of the stacking-fault energy. The feature that has been reported by all is the decrease in the size of equiaxed cells with the decrease in stacking-fault energy, which favors planar slip.

Following Miyata [MIY 03], Girardin *et al.* [GIR 15] have shown that the addition of chromium promotes the localization of plastic deformation at "high" plastic deformation levels in relation to a decrease in stacking-fault energy. It should be noted that the planar nature of the slip does not necessarily arise from a decrease in the stacking-fault energy. The effect of chromium on planar slip and, therefore, on the localization of deformation, can result from factors such as an increase of the shear modulus, the lattice friction, and the short-range ordering of solutes [HON 90]. Regarding hydrogen, the fact that this solute affects the plasticity mechanisms is supported by *in situ* TEM observations [ROB 86, BON 88, FER 99], the activation energies and the activation volumes resulting from the relaxation tests [SIR 92] as well as the models based on hydrogen elastic screening [SOF 95, CHA 02].

All these approaches highlight the fact that hydrogen increases dislocation emission and mobility, decreases the elastic energy of dislocation junctions and favors planar slip (decreased probability of cross-slip) through the decrease of the stacking-fault energy, the elastic screening of interactions between partial dislocations and the decrease of the dislocation constriction per unit length [DEL 12]. Therefore, such as with chromium, the hydrogen content reduces the probability of

cross-slip and consequently decreases the GNB spacing which leads to hardening (decrease of the dislocation mean free path).

The localization effects on deformation, by reducing the cross-slip probability and by local softening, are the cause of micro-ductile fractures by localized shear, predicted by the HELP model [BIR 94, LIA 03]. They are observed in austenitic stainless steels when the concentration of hydrogen in solution and/or its surface activity is high [ABR 95, ULM 91, BRA 06]. In nickel and its alloys, tensile fracture is usually brittle intergranular [BON 36, GIR 04a]. When the concentration is low, it requires hydrogen "transport" by mobile dislocations [GIR 04a]. Regarding the flow stress, elementary mechanisms that in the early stages of deformation can lead to a softening mechanism (stage I), may subsequently lead to hardening in the work-hardening stages associated with larger deformations (stages II and III). Depending on the experimental conditions, this can explain many observations which at first may seem contradictory.

9.4. Embrittlement through vacancy formation

In recent years, among the various hydrogen-induced damage models, the hydrogen-induced vacancy formation is an approach that has attracted much interest with the ability to calculate the vacancy formation energy in DFT for many materials and alloys [NAZ 10, TAN 14, MET 16]. The model is based on the ability of absorbed hydrogen to form new vacancies known as super abundant vacancies (SAV) and to stabilize them [FUK 95, ZAN 99]. Thermodynamically, hydrogen reduces the vacancy formation energy leading to much higher concentrations than those of thermal origin. This mechanism can be superimposed on that with a mechanical origin and lead to the formation of nanocavities near or far from structural defects (dislocations, grain boundaries). Experimental measurements of vacancy concentrations in the presence of hydrogen confirm the SAV mechanism [FUK 03, FUK 05, CAR 04, CAR 06, OUD 12, LI 17a, HAC 18].

Moreover, nanocavities have been observed by TEM in nickel following a hydrogen charging of single crystals [LI 17a, HAC 18] and bi-crystals [LI 17b]. In the case of single crystals, the presence of these nanocavities leads to a much larger decrease of the elasticity moduli than hydrogen in solution alone [HAC 18] and consequently a much more coherent screening of the elastic interactions. In the case of polycrystalline alloys, the formation of vacancies is predominant in grain boundaries [VAM 09, BAI 12, TSC 12, HAL 16] and this process is all the more favorable in the presence of hydrogen. Chandler *et al.*, through their calculations at the atomic scale, showed that the formation of microcavities on the nickel grain boundaries is a function of the type of boundary and the hydrogen concentration [CHA 08]. It has therefore been suggested through experimental observations that

intergranular fracture in the presence of hydrogen is not directly associated with the solute but with the formation of nanocavities [OUD 14].

More generally, the work by Takai and Nagumo also point in this direction. Indeed, these authors have developed an experimental approach based on mechanical tests which demonstrates that the loss of ductility in α iron is associated with the formation of hydrogen-induced defects and not with the presence of hydrogen in the crystal [DOS 13, HAT 14, NAG 16, TAK 08]. Finally, the observation of defect characteristics suggests, in some cases, that the formation of nanocavities is responsible for inter-crystalline fracture [NEE 12].

9.5. Embrittlement through hydride formation

Under very strong global or very local hydrogenation conditions (defects, mechanically loaded crack tip, etc.) palladium, nickel, iron or titanium and zirconium-based alloys may lead to the formation of a thermodynamically stable or unstable hydride [HIR 80, NAR 82, ROZ 84, MYE 92, HUE 98, PUL 05, CON 07, FUK 07, FEA 09a, CON 17]. The precipitation of a hydride more stable than the solid solution of the same stoichiometry, or made more stable by applying stress, comes with a very large increase in volume. This increase, depending on the nature and the epitaxial relations of the phase with the matrix, leads to a highly localized elastic deformation [PUL 05, CON 17], whether or not partially accommodated by dislocation emission [CON 17]. This process can occur at an edge dislocation core level [VON 11, CUI 18], near a grain boundary [CHA 08] or at a crack tip [SHI 88, KIM 07]. Experimental measurements [ROD 83, HEU 08] suggest the possibility of hydride formation near the stress field singularity of an edge dislocation following hydrogen segregation.

This result is supported by atomistic calculations in nickel and iron which show that it is not necessary to have a significant hydrogen concentration for it to be locally sufficient to form a hydride following a segregation process in the hydrostatic field of the edge dislocation [VON 11]. This process leads to the screening of elastic interactions between dislocations, which is more important than the one predicted by linear elasticity for the solid solution [VON 11]. The lattice elastic distortions near the grain boundaries with or without stress applied also promote hydrogen segregation and can lead to local hydrogen levels which are enough to form hydrides and thus weaken the grain boundaries [CHA 08].

To our knowledge, this last process has not been clearly established experimentally in BCC or FCC metals, however, it has been observed in HCP alloys such as titanium and zirconium [PUL 05, CON 17]. At the mesoscopic and macroscopic scales, stress concentrations favor hydride precipitation in areas of high

hydrostatic tension and lead to the partial relaxation of the stresses [CON 17]. The decomposition and/or damage of these hydrides can lead to cracking [WES 69]. The hydride precipitation at the crack tip, where the stresses are greatest, has been demonstrated experimentally and numerically [SHI 88, KIM 07, FLA 81, LUF 96]. The hydride formed is, in general, more brittle than the solid solution due in part to the elastoplastic properties which differ from those of the matrix and in part to the epitaxial phase relations that sometimes favor strain incompatibilities. The hydride precipitation embrittling role is commonly characterized by a loss of ductility, a significant decrease in the fracture load and in the fracture toughness [CHA 95, PUL 05, FEA 09a]. Since the embrittlement process is highly temperature dependent, it is possible to define a ductile-to-brittle transition when the apparent hydride habitat plane is close to a plane perpendicular to the stress axis [FEA 09a]. For the other orientations, classical ductile mechanisms intervene, where the preferred initiation site is the hydride [HUE 98]. In this last case, local fracture approach-type tools have shown their relevance in titanium and zirconium alloys [GRA 00, HUE 98].

9.6. Conclusion and unanswered questions

The diversity of the basic mechanisms and the time and space scales involved in the various mechanisms and models described in this chapter makes it difficult to summarize the effects of hydrogen in metallic materials. Beyond the specificities of certain material-environment-mechanical loading systems, the number and age of the experimental observations and the convergences between models at different scales make it possible to underline some general principles.

By only considering the effects on the cohesion energy, it is not possible to predict large enough effects to explain hydrogen embrittlement through a single intrinsic embrittlement effect. The plasticity and the interactions between the formation increase or evolution dynamics of point defects (vacancies and nanocavities), linear defects (mobile dislocations and sessile configurations) and plane defects (grain boundaries, phase boundaries, interface segregations) must be considered.

As mentioned in the introduction, hydrogen in solution lowers the energy barrier for the homogeneous formation of crystal defects. Its effects on the evolution dynamics of their populations are varied and sometimes contradictory. The debates held between 1990 and 2000 on the "softening" or "hardening" effect of hydrogen are an illustration of this. A systematic analysis of the contributions to the basic mechanisms makes it possible to rationalize these effects and to show that. From a practical point of view, hydrogen's effect on the slip's localization has more impact on the deformation and damage mechanisms than its effect on the flow stress. As for intrinsic embrittlement, this induced deformation heterogeneity is likely

to contribute to a more complex damage sequence, but is only a direct cause of micro-ductile shear fracture in particular cases [LIA 03]. On the one hand, the basic requirements for modeling hydrogen-dislocation interaction do require assumption on the crystallography of the host material. On the other hand, plasticity mechanisms and how they are affected by hydrogen are closely related to metallurgy.

The same is true for interface damaging mechanisms. Vacancy co-segregation, stabilization and condensation effects in microcavities or the damaging effects along specific crystallographic planes due to precipitation or allotropic transformations: these effects cannot be understood without a thorough knowledge of the alloy's metallurgy along with experimental studies that combine materials and model environments on the one hand and conditions that represent the service conditions on the other.

Regarding material selection and the mechanical design of structures for operating in the presence of hydrogen, mass reduction by using high-strength grades increases the number of defect types likely to interact with hydrogen and increases their densities. (Semi-)quantitative models are required to identify the limiting factors and to eliminate the constraints when implementing high-strength grades. The spatial scale-change methods developed in solid mechanics must also take into account chemo-elastic interactions and timescale changes via specific models. The identification of the relevant parameters and their experimental validation will benefit from the development of *in situ* and local probe observation methods.

9.7. References

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