HYDROGEN EMBRITTLEMENT IN HYDRIDE- AND NON HYDRIDE-FORMING SYSTEMS – MICROSTRUCTURAL/PHASE CHANGES AND CRACKING MECHANISMS

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ABSTRACT
Hydrogen-assisted cracking (HAC) or hydrogen embrittlement (HE) are the most commonly used terms to describe a time-dependant failure process, characterized by mechanical properties degradation, mainly ductility reduction, and a change in the fracture mode. With almost no direct techniques for observing atomic-scale events at crack tips in bulk specimens, HE/HAC mechanisms are deduced mainly from fractography, microscopic investigation of microstructure changes, surface-science observations, and atomistic or continuum modeling. This paper addresses to HE/HAC mechanisms into two different systems; hydride-forming and non-hydride forming materials. As a representative example of the hydride-forming systems, the discussion focuses on the hydrogen-induced second phase formation (e.g. hydrides) phenomena in titanium based alloys. Due to the large differences in the behavior of hydrogen in α and β phases of titanium, the susceptibility of titanium-based alloys to the various forms and conditions of hydrogen embrittlement can vary markedly. The microstructural changes and hydrogen-induced second phase formation due to exposure at various charging conditions, as well as the difference in hydrogen absorption/desorption behavior as a function of the prior microstructure of titanium alloys, are highlighted. In non-hydride forming materials, where as representative examples stainless steels are chosen, the paper concentrates on the qualitatively same phenomena of hydrogen-induced second phase embrittlement,. The phase transitions related to hydrogen-induced cracking, the hydrogen related failure sequences and fracture modes in austenitic and supermartensitic stainless steels and a potential modeling of hydrogen-assisted cracking in these structural metallic materials are discussed.

1 INTRODUCTION

Hydrogen-assisted cracking (HAC) can be regarded microscopically as the local interaction between the microstructure and the local mechanical load and hydrogen concentration [1]. Establishing the mechanisms of HAC has proved difficult because there are no direct techniques for observing atomic-scale events at the crack tips in bulk specimens. Mechanisms therefore have to be deduced mainly from fractography, microscopic investigation of microstructure changes, surface-science observations, and atomistic or continuum modeling [2]. It is suggested to divide any discussion on HAC mechanisms into two different systems; hydride-forming and non-hydride forming materials, where as representative examples of these systems, titanium based alloys and stainless steels are respectively chosen. The discussion starts with hydrogen-induced second phase formation (e.g. hydrides) phenomena in titanium based alloys. Although titanium is generally considered to be reasonably resistant to chemical attack, severe problems may arise when titanium based alloys come in contact with hydrogen-containing environment. If hydrogen is allowed to remain in the titanium lattice, upon cooling, severe degradation in the mechanical and fracture behaviors of the titanium base alloy will occur [3]. Due to the differences in the behavior of hydrogen in α and β phases of titanium, their susceptibility to the various forms and conditions of hydrogen degradation can vary markedly [4]. Therefore, during the discussion, specific emphasis is given to the microstructural changes and second phase formation induced from hydrogen exposure at various charging conditions and the difference in hydrogen absorption/desorption behavior as a function of the prior microstructure of titanium alloys. Afterwards, the paper addresses to the qualitatively same phenomena of hydrogen-induced second phase embrittlement in non-hydride forming materials. The phase changes related to hydrogen-induced cracking and hydrogen related failure sequences and fracture modes in austenitic and supermartensitic stainless steels are described in detail. Some first links to consistent and quantitative modeling of hydrogen-assisted cracking in these structural metallic materials are also presented.

2 HYDRIDE-FORMING SYSTEMS

A number of metallic systems have demonstrated hydrogen embrittlement due to stress induced formation of brittle hydride phases and their subsequent "cleavage" fracture. The typical system which exhibits failure by this mechanism is required to form stable hydrides in the absence of stress. Among systems which tend to form stable hydrides and have been clearly shown to exhibit hydride embrittlement, are the groups IV and V transition metals (Ti, Zr, Nb, Vand Ta) and their alloys. This part of the paper will focus on titanium and its alloys, as a representative example of these hydride-forming systems.

2.1 *Titanium Based Alloys*

In near-alpha and alpha + beta titanium alloys the main mechanism of hydrogen embrittlement was often suggested to result from the precipitation and decomposition of brittle hydride phases. At lower temperatures, the titanium hydride becomes brittle and severe degradation of the mechanical and fracture behaviors of these alloys can occur [3]. The titanium alloys whose microstructures contain mostly the α phase, when exposed to an external hydrogen environment at around room temperature, will degrade primarily through the repeated formation and rupture of the brittle hydride phase at, or very near, the gas-metal interface [5]. When only the α phase is present, degradation is insensitive to external hydrogen pressure, since hydride formation in the α phase can occur at virtually any reasonable hydrogen partial pressure. Birnbaum *et. al.* [6] revealed that in the hcp α Ti-4%Al alloy, exposed to a gaseous hydrogen environment at room temperature, two fracture mechanisms could operate, depending on the stress intensity. At low stress intensity, the cracks propagated by repeated formation and cleavage fracture of hydrides. At high stress intensities, the fracture mode transition occurred when the crack propagation rate exceeded the rate at which the hydride could form in front of the crack, and the hydrogen-enhanced localized plasticity was the responsible cracking mechanism.

In the alpha + beta alloys, when a significant amount of β phase is present, hydrogen can be preferentially transported within the β lattice and will react with the α phase along the α/β boundaries. Under these conditions, degradation will generally be more severe with severity of degradation reflecting the hydrogen pressure dependence of hydrogen transport within the β phase [7]. In a Ti-6Al-4V alloy, thermo-mechanically treated in two distinguished microstructures, duplex and fully-lamellar, as described extensively elsewhere [8], hydrogen content measurements after high [4] and low fugacity hydrogen charging [8], revealed that the hydrogen concentrations absorbed in the fully lamellar alloy is always higher than in the duplex microstructure, irrespective of the charging conditions. Since the rate of hydrogen diffusion is higher by several orders of magnitude in the β phase than in the α phase [9], microstructures with more continuous β phase, such as fully lamellar microstructure, will absorb more hydrogen than those with discontinuous β, such as the fine equiaxed α in the duplex microstructure. In the group IV transition metals hydrogen tends to occupy tetrahedral interstitial sites [10]. The higher solubility, as well as the rapid diffusion (especially at elevated temperatures) of hydrogen in the beta titanium results from the relatively open body center cubic (bcc) structure, which consists of 12 tetrahedral and 6 octahedral interstices in comparison to 4 tetrahedral and 2 octahedral interstitial sites in the hexagonal closed packed (hcp) lattice of alpha titanium. The presence of hydrogen in solid solution in both α and β phases resulted in lattice expansions. In the electrochemically hydrogenated Ti-6Al-4V specimens, precipitation of the tetragonal γ-TiH occurred initially at relatively low hydrogen concentrations, which was followed by the formation of the tetragonal δ-TiH$_x$ with the increase in the hydrogen concentration (Fig. 1). Due to the lower solubility of hydrogen in the α phase [11], the hydrides precipitation in the duplex microstructure occurred at lower hydrogen concentrations in comparison to the alloy with a fully lamellar microstructure and a more continuous β-phase.
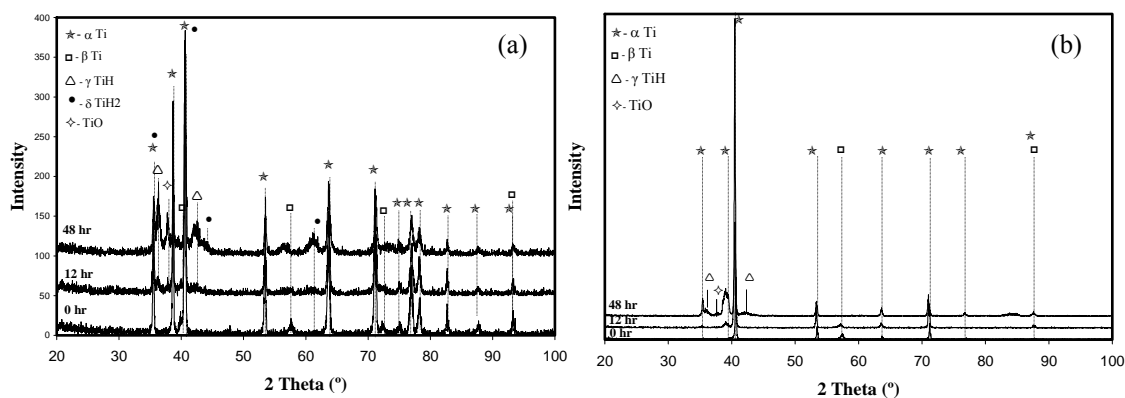

Fig. 1:   X-Ray diffraction patterns of uncharged and electrochemically hydrogenated (at RT, in a 1:2 (vol.) H$_3$PO$_4$: Glycerine solution, at 50 mA/cm^2) (a) duplex and (b) fully lamellar Ti-6Al-4V specimens.

The hydride formation and cracking will usually take place in the α phase or along α/β interface, depending on the prior microstructure of the alloy (Fig. 2).
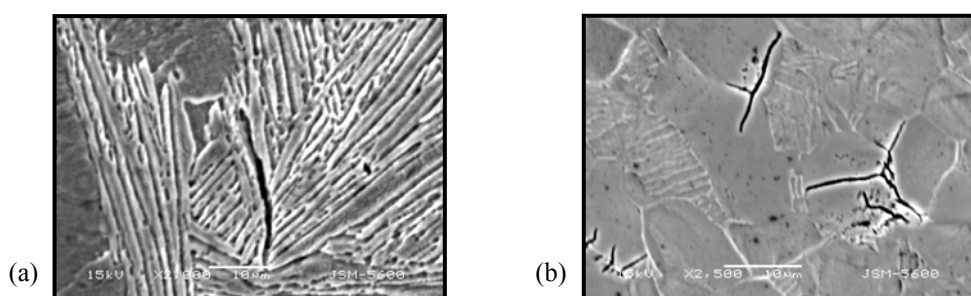

Fig. 2: SEM micrographs of Ti-6Al-4V alloys after electrochemical hydrogenation revealing hydrogen-induced cracking in: (a) the fully lamellar microstructure, between the α and β lamellas, (b) duplex microstructure, in the boundaries and inside the equiaxed grains of primary α.

Beta titanium alloys do not tend to form hydrides due to their high hydrogen solubility and usually, especially at room temperature and low hydrogen pressures, they are considered to be fairly resistant to hydrogen embrittlement. For example, after exposure to electrochemical hydrogen environment of as-received mill-annealed and peak-aged β-21S alloy, except of strain induced in the lattice parameters (0.6% maximum lattice expansion of the of mill-annealed in comparison to 0.4% in the peak-aged alloy), no hydrides precipitation was observed in XRD patterns and SEM investigations did not reveal hydrogen-induced cracking in both specimens.
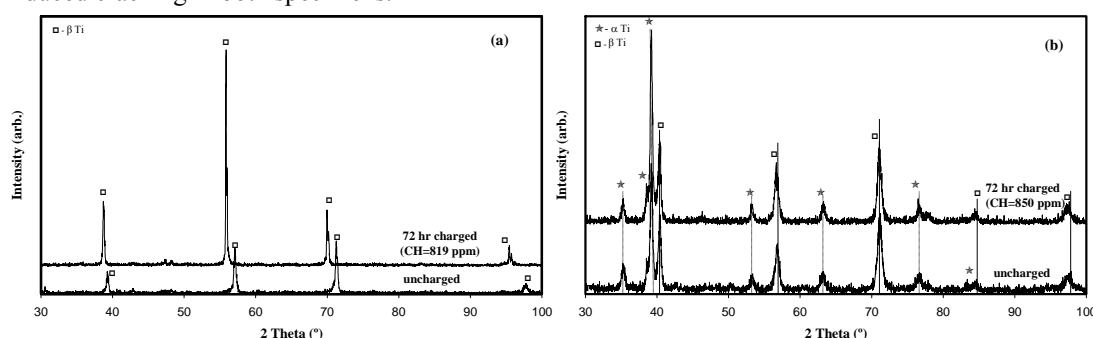

Fig. 3: X-ray diffraction patterns of uncharged and 72 hours hydrogenated (a) as-received and (b) peak-aged β-21S alloy.

However, recent investigations have demonstrated that beta titanium alloys can be severely degraded on exposure to hydrogen in different ways. The most evident way of degradation is by the formation of brittle hydride phases, similar to the degradation of primarily α alloys, except that it requires higher hydrogen pressures [12]. In addition, it has been observed that hydrogen in solid solution in the β lattice, well below the expected terminal solubility limit for the formation of a hydride, can have a significant effect on the ductile-to-brittle fraction transition of the bcc β alloys. Hydrogen can raise the transition temperature from below about -130ºC in a hydrogen-free material to 100ºC, following a high temperature, low pressure hydrogen exposure. Associated with this ductile-to-brittle transition is a change in the fracture mode from ductile, micro-void coalescence to brittle, cleavage [13]. Investigations of β-21S titanium alloy [14, 15] revealed that the hydrogen-induced ductile-to-brittle transition occurred abruptly at a critical hydrogen concentration, that decreased with decreasing tensile test temperature, without any hydrides associated with the fracture process.

Hydrogen embrittlement by hydride formation is observed under conditions where hydrides can form at a rate sufficient to preclude other forms of failure. The extent of hydride embrittlement is dependant on the diffusivity controlled hydride growth rate. For example, XRD and TEM investigation of Ti-6Al-4V after deuterium gas-phase charging [8] didn't reveal any hydrides formation. However, an increased density of dislocations was observed mainly inside the β-lamellas (Fig. 4.a), and slightly less in the α-equiaxed (tangled dislocations in Fig. 4b), generated by the strain induced due to hydrogenation. The high number of dislocations, located at the boundary between the β-lamellae and the α-phase, and their assumed enhanced movement, resulted into a segmented lamellae (Fig. 4.c). Hydrogen role on reduction of the stress for dislocation motion and consequently for dislocation generation has been extensively studied by Birnbaum and his group [16, 17]; enhanced dislocation velocities were observed for different kinds of dislocations (edge, screw, mixed etc.) and materials (fcc, bcc and hcp), indicating the generality of the mechanism

causing hydrogen enhanced dislocation motion, which is not restricted to a particular type of material or dislocation type.
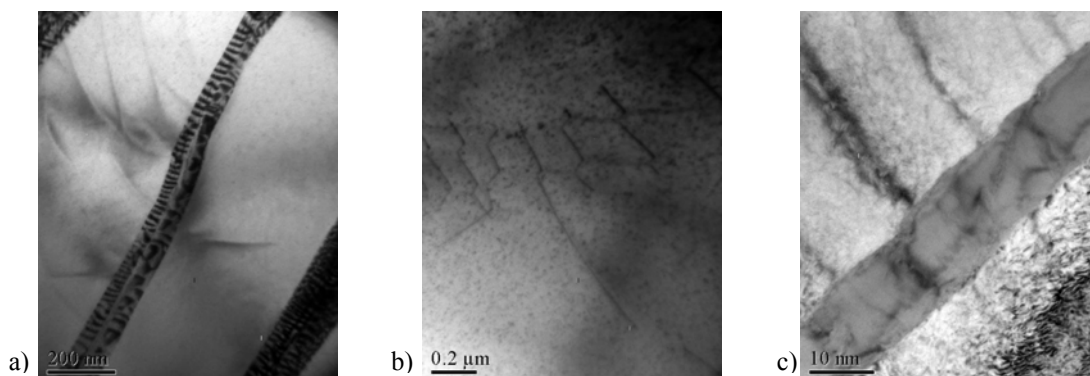

Fig. 4:   TEM bright field images of deuterium gas-phase charged (350ºC, 5 atm., 5h) Ti-6Al-4V alloy.

An important question though, is what happens when relatively small amounts of hydrogen, not able to form hydrides, are present or trapped inside different microstructural defects or morphological features? Thermal desorption analyses (TDA) is a unique and very accurate technique which allows to evaluate hydrogen desoprtion and trapping characteristics. Thermal desorption analyses of deuterium gas-phase charged fully lamellar and duplex Ti-6Al-4V alloys (Fig. 5) revealed one distinctive trapping state at elevated temperatures (above 550ºC). The mutual desorption peak in the TDA plots of both alloys might be related to the α/β interfaces, which might provide trap sites, as noted by Young and Scully [18]. The amount of deuterium evolved from the fully lamellar alloy was significantly larger and the calculated desorption energy was higher in comparison to the specimen with a duplex microstructure [8]. The high desorption energy values, calculated for both alloys, indicate that this trapping site is probably irreversible. It is known that irreversible traps are beneficial to hydrogen embrittlement [19], which might explain the fact that no cracking was observed in these alloys. The different desorption response of the alloys results from the difference in their microstructures morphology. The enhanced dsorption and the higher energy values in the fully lamellar microstructure are probably related to the initially higher amount of deuterium absorbed in the fully lamellar microstructure than in the duplex microstructure, as well as to the more continuous beta phase in the fully lamellar alloy.
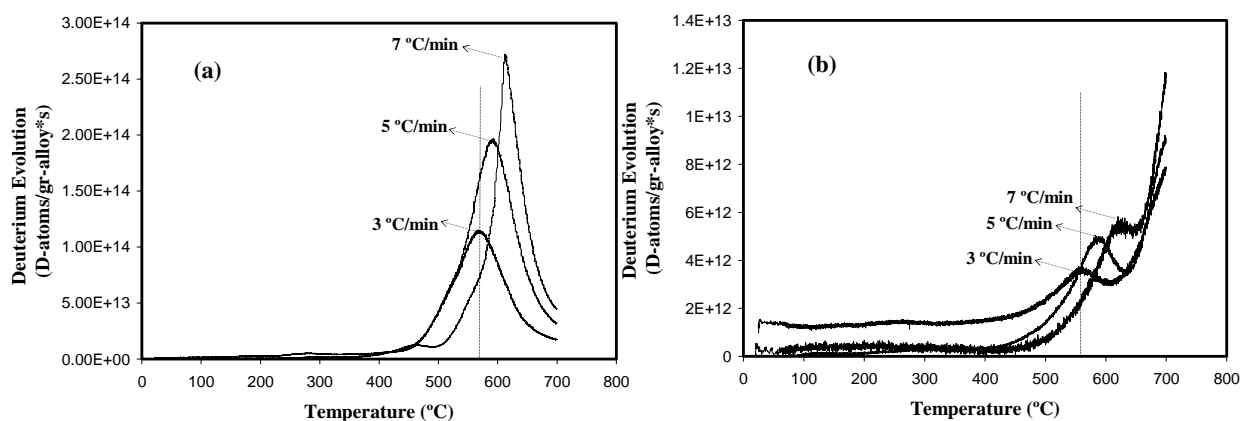

Fig. 5:   Temperature ramp dependence of deuterium evolution from (a) fully lamellar and (b) duplex
           Ti-6Al-4V alloys, after deuterium gas-phase charging.

3 NON HYDRIDE-FORMING SYSTEMS

Based on Birnbaum's qualitative description of hydride embrittlement [16, 20], under the applied stress, the chemical potential of the solute hydrogen and the hydride is reduced at the crack tip, allowing hydrogen diffusion to these elastic singularities and then, precipitation of hydrides occurs. The phase change to the hydride is accompanied (a) by a decrease in the critical stress intensity for crack propagation; from $K_{1C}^{solid\ solution}$ to $K_{1C}^{hydride}$ and (b) by a high compressive local stress field due to the very large $\Delta V_{formation}$. This reduces the local stress intensity, K_1, caused by the externally applied stress. Thus, there are two countervailing effects; a reduction in the stress intensity and a reduction in the fracture toughness, K_{1C}. In general, the latter effect dominates and the decreased K_{1C} allows rapid crack propagation with a moderately increased applied stress. The crack propagates by cleavage until the hydride-solid solution boundary is reached. At that point the crack enters a ductile phase having a high $K_{1C}^{solid\ solution}$ and the crack stops until

more hydride is formed by a diffusion controlled process. The process repeats itself resulting in a discontinuous crack growth through the stress induced hydride phase.

In a qualitative sense the phenomena described above for hydride embrittlement can apply to hydrogen-induced formation of other brittle phases, stabilized by the crack tip stress field. In all cases the important factors, such as the stress effects on the stability of the precipitated second phases, the kinetics of phase transitions and the mechanical properties of the new second phases, are the same [16]. One significant difference between hydride embrittlement and other second phase embrittlement is that the hydrogen diffusivity is much higher than that of other solutes at low temperatures, indicating that the embrittlement phenomena can be observed where the stress influence on precipitation is the highest [21].

3.1 *Hydrogen Assisted Degradation of Stainless Steels*

Austenitic stainless steels, although generally thought less susceptible to hydrogen than ferritic or martensitic steels, can however suffer embrittlement effects under severe hydrogen environmental conditions, especially when the austenite is unstable. It is extensively reported that austenitic stainless steels undergo cathodic charging-induced surface cracking, and moreover, that ε- and α'-martensites are formed under such conditions [22-30]. For example, XRD and TEM studies carried out on electrochemically hydrogenated AISI 316 austenitic stainless steel of different grain sizes, revealed clearly the hydrogen-induced cracking related to the phase transformation of the fcc-γ phase to the hcp-ε and bcc-α' martensite phases and the kinetics of this transition [30]. The calculated hydrogen-induced stresses were of the order of 5×10^{-9} Pa, a value well above the ultimate tensile stress of 316 stainless steel [31]. These stresses induce two well known phenomenas: (a) formation of inter-granular and transgranular cracks, providing evidence of the stress relaxation that occurs following the increase in the internal stresses with the charging time, and (b) stress-induced transition of austenite to α' and ε martensites. Internal stresses or strains, which accompany the absorption of supersaturated hydrogen, may provide a significant driving force for austenite decomposition. In the 316 stainless steel the α'-phase was formed in the early stage of aging. Unique quantitative X-ray method, which employs various radiations [32], revealed that the weight fraction of the α'-martensite increased from 7% in the coarse-grained specimen to 28% in a fine-grained type 316 steel. Splitting of the $\gamma : \gamma^*$ (γ^*-expanded fcc austenitic lattice) and $\varepsilon : \varepsilon^*$ (ε^*-expanded martensite hcp-phase) diffraction peaks was observed, however there was no evidence of an α'-phase shift during aging, indicating that it absorbs less hydrogen than the γ and ε phases. Due to the large diffusivity in the bcc phase, α'-martensite may act as a suitable medium for entry into and transport of hydrogen within the γ phase. It is not known whether the α'-phase forms from the γ-phase or from the ε-phase during the charging process. A reversible ε-to-α' transition could result from the motion of partial dislocations [33] in response to a change of hydrogen concentration caused by cathodic charging or aging. The ε-phase on the other hand, forms from the matrix by a process of overlapping stacking faults on each alternate {111} γ-plane [26]. This phenomenon is believed to result from hydrogen effect that increases the stacking fault probability of stainless steel [34]. Hydrogen-induced cracks propagated mainly along the {111} γ-planes. Fracture along this plane may correspond to fracture through the ε-phase, since it exhibits a {111} habit plane in the 316 alloy. TEM observations of surface cracking revealed that crack propagation occurred along the regions with a mixed structure consisted of α'- and ε-martensite phases [30]. Numerical simulation analyses of crack propagation in supermartensitic stainless steels, based on finite elements calculations [1], support the fact that the alteration of the fracture mode depends significantly on the hydrogen levels and on the presence of other phases in the microstructure of the steel. For example, carbide precipitations behave as reversible traps and attract hydrogen particularly in medium alloyed and annealed steels, and are assumed to support intergranular cracking by mechanistic effects [35]. If the material-dependent stress-strain behavior, hydrogen transport data, and hydrogen-dependant material properties are determined experimentally as input parameters, the numerical model is transferable to any other specimen, crack geometry, and, in particular, to any other material [1, 36].

While the presence of martensitic phases at the surface of hydrogen embrittled metastable stainless steels has been established, it has not been shown whether these phases are a necessary condition for fracture or whether they are a consequence of the enhanced deformation caused by hydrogen [16, 37]. A numerical model for hydrogen assisted cracking may represent a very helpful tool to explain different failure sequences and fracture modes, not only in supermartensitic stainless steels, but also in austenitic and other metastable stainless steels, as well as in titanium based alloys.

4 SUMMARY AND CONCLUSIONS

The paper discussed the hydrogen embrittlement of two significantly different systems; hydride-forming and non-hydride forming materials. The hydrogen degradation of titanium based alloys, with specific emphasis on the role of microstructure on hydrogen-induced hydride formation mechanism, is described in detail. Alpha and alpha + beta titanium alloys, when exposed to an external hydrogen environment at room temperature, will degrade primarily through the repeated formation and rupture of the brittle hydride phase.

On the other hand, beta titanium alloys are less susceptible to hydrogen degradation at room temperature. However, they were observed to severely degrade by the exposure to hydrogen in different ways. The hydrogen embrittlement phenomena in beta titanium alloys include the brittle hydride formation (at very high hydrogen pressures), the sharp ductile-to-brittle transition and the change in the fracture mode. Afterwards, the paper addressed to the second-phase embrittling mechanisms in non-hydride forming ferrous systems. The phase transitions and the mechanisms related to hydrogen cracking in austenitic stainless steels were explained in detail, followed by the demonstration of hydrogen-induced failure sequences and fracture modes in supermartensitic stainless steels, using some first links to consistent and quantitative modeling of hydrogen-assisted cracking in these materials. The presented model is transferable to any other specimen, crack geometry, and, in particular, any other material, if the material-dependent stress-strain behavior, hydrogen transport data, and hydrogen-dependant material properties are determined experimentally as input parameters. This model can be verified experimentally and applied to other structural metallic materials.

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