Hydrogen-Assisted Degradation of Titanium Based Alloys

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Titanium base alloys are among the most important advanced materials for a wide variety of aerospace, marine, industrial and commercial applications, due to their high strength/weight ratio and good corrosion behavior. Although titanium is generally considered to be reasonably resistant to chemical attack, severe problems can arise when titanium base alloys come in contact with hydrogen containing environments. Titanium base alloys can pick up large amounts of hydrogen when exposed to these environments, especially at elevated temperatures. If the hydrogen remains in the titanium lattice, it may lead to severe degradation of the mechanical and fracture behavior of these alloys upon cooling. As a consequence of the different behavior of hydrogen in α and β phases of titanium (different solubility, different diffusion kinetics, etc), the susceptibility of each of these phases to the various forms of and conditions of hydrogen degradation can vary markedly. This paper presents an overview of hydrogen interactions with titanium alloys, with specific emphasis on the role of microstructure on hydrogen-assisted degradation in these alloys.

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1. Introduction

Titanium and its alloys have been proven to be technically superior and cost-effective materials for a wide variety of aerospace, industrial, marine and commercial applications, because of their excellent specific strength, stiffness, corrosion resistance and their good behavior at elevated temperatures. However, the interaction between titanium alloys and hydrogen can be extreme¹⁾ and severe problems may arise when these alloys come in contact with hydrogen containing environments. Hydrogen effects in titanium can be divided into two main categories; the effects of internal hydrogen, already present in the material as hydride or in solid solution, and the effects of external hydrogen, produced mainly by the environment and its interaction with the titanium alloy. The precise role of internal¹⁻⁷⁾ and environmental hydrogen has been extensively investigated.⁸⁻¹⁶⁾ The current paper will address to this division of hydrogen effects; the first part will review the behavior of internal hydrogen, including the solubility of hydrogen in α and β phases of titanium and hydride formation, while the second part will summarize the detrimental effects of hydrogen in different titanium alloys, with specific emphasis on the role of microstructure on hydrogen assisted degradation.

2. Hydrogen-Titanium System

According to the binary constitution phase diagram of titanium-hydrogen system described in Fig. 1,^{17,18)} at a temperature of 300°C, the β phase dissociates into the α + hydride phases by a simple eutectoid transformation.

The strong stabilizing effect of hydrogen on the beta phase field results in a decrease of the alpha to beta transformation temperature from 882°C to an eutectoid temperature of 300°C. At this eutectoid temperature, the concentrations of hydrogen in the alpha, beta and delta (hydride) phases are 6.72 at%, 39 at% and 51.9 at%, respectively. The terminal hydrogen solubility in the beta phase (without the formation of a hydride phase) can reach as high as 50 at% at elevated temperatures above 600°C. On the other hand, in the alpha

Fig. 1 The binary phase diagram of Ti-H system (at $P = 0.1$ MPa).^{17,18)}

phase, the terminal hydrogen solubility is only approximately 7 at% at 300°C and decreases rapidly with decreasing temperature. At room temperature, the terminal hydrogen solubility in alpha titanium is quite negligible (~ 0.04 at%).^{19,20)}

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, the hexagonal closed packed (hcp) lattice of alpha titanium exhibits only 4 tetrahedral and 2 octahedral interstitial sites. In the group IV transition metals hydrogen tends to occupy tetrahedral interstitial sites.²¹⁾ The sublattice of the tetrahedral interstitial sites of the hydrogen forms a simple cubic lattice in the fcc δ -hydride phase TiH_x . All the tetrahedral interstitial sites are occupied for the maximum concentration (x) of 2.

Hydrogen content measurements (by means of a LECO RH-404 hydrogen determinator system) that the authors conducted on a Ti-6Al-4V alloy, thermo-mechanically

Table 1 Hydrogen content in fully lamellar and duplex microstructures of Ti-6Al-4V alloys hydrogenated electrochemically in a H_3PO_4 :glycerine (1:2 volume) electrolyte, for 69 hours, at different current densities.

	Fully lamellar microstructure	Duplex microstructure
As-received	$C_H = 58$ [ppm mass]	$C_H = 44$ [ppm mass]
Hydrogenated at 50 mA/cm^2	$C_H = 0.060$ [mass%]	$C_H = 0.020$ [mass%]
Hydrogenated at 100 mA/cm^2	$C_H = 0.110$ [mass%]	$C_H = 0.024$ [mass%]

Fig. 2 SEM micrographs showing microstructures of Ti-6Al-4V (a) fully lamellar microstructure showing continuous β phase, (b) duplex microstructure showing equiaxed primary α and lamellar packets of transformed β (secondary α).

treated in two distinguished microstructures, duplex and fully-lamellar, after electrochemical hydrogenation at varying charging conditions, are presented in Table 1. Comparing between hydrogen absorption in duplex and fully lamellar Ti-6Al-4V alloys after electrochemical hydrogenation, 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,⁸⁾ microstructures with more continuous β phase, such as fully lamellar microstructure (Fig. 2a), will absorb more hydrogen than those with discontinuous β , such as the fine equiaxed α in the duplex microstructure (Fig. 2b). Increasing the applied current densities led to higher hydrogen concentrations in both materials, but the hydrogen uptake is much higher in the fully lamellar alloy.

3. Titanium Hydrides

Three different kinds of titanium hydrides (δ , ε , γ) have been observed around room temperature.^{17,21–23)} The δ -hydrides (TiH_x) have an fcc lattice with the hydrogen atoms occupying the tetrahedral interstitial sites (CaF_2 structure). The non-stoichiometric ratio, x , of the δ -hydride exist over a wide range (1.5–1.99). At high hydrogen concentrations ($x \geq 1.99$), the δ -hydride transforms diffusionless into ε -hydride, with an fct structure ($c/a \leq 1$ at temperatures below 37°C). At low hydrogen concentrations (1–3 at%) the metastable γ -hydride forms, with an fct structure of c/a

higher than 1. In the γ -hydride structure the hydrogen atoms occupy one-half of the tetrahedral interstitial sites.

Previous studies^{24,25)} have shown that the δ -hydride would precipitate in the α -phase matrix when the stoichiometric ratio is less than 1.56. The coexisting α -phase could be the solid solution of hydrogen in α -titanium. Once the hydrogen content is over a critical value, $x = 1.56$, a single δ -hydride with x ranging from 1.56 to 1.89 would be observed. The lattice constants of the δ -hydrides vary with the hydrogen concentrations.

The presence of hydrogen in solid solution in both α and β phases results in lattice expansions. The β phase is the most affected with about 5.35% volume increase near its terminal hydrogen solubility.²⁶⁾ The transformation from α -titanium to the δ -hydride phase is followed by a volume expansion of about 17.2%.²⁷⁾ Such a volume increase results in a sizable elastic and plastic constraint induced in the α lattice.²⁸⁾

Titanium hydrides can be prepared by gas-equilibrium,²³⁾ direct Ti-H reaction,²⁴⁾ electrolytic hydrogenation^{25,29–31)} and vapor deposition.³²⁾ The hydriding behavior among different hydrogenating processes is quite distinct and is a function of various parameters. Hydrides can precipitate at α/β interfaces^{33,34)} and at free surfaces. Hydride formation at these locations seems to suffer less from the constraint effects present in the formation of transgranular hydrides. When a hydride is formed on the titanium surface at the gas-metal interface, the overall hydrogen transport process is changed. The hydrogen absorption step must now be an exchange reaction with the bound hydrogen of the hydride phase. Since the δ -hydride phase has an fcc lattice with a larger lattice

constant than the hcp α lattice, hydrogen transport through this hydride is faster than through the α phase.²⁵⁾ In addition, hydride formation can also be significantly affected by material factors such as, alloy composition, microstructure and yield strength.^{35,36)}

4. Hydrogen-Assisted Degradation

Hydrogen damage of titanium and its alloys is manifested as a loss of ductility (embrittlement) and/or reduction in the stress-intensity threshold for crack propagation.³⁷⁾

4.1 Commercially pure (CP) titanium

Commercially pure titanium is very resistant to hydrogen embrittlement when tested in the form of fine-grained specimens at low-to-moderate strain rates in uniaxial tensile tests. However, it becomes susceptible to hydrogen embrittlement in the presence of a notch, at low temperatures or high strain rates, or large grain sizes. The last effect was reported to be a consequence of the enhancement of both void nucleation and void link-up at large grain sizes or biaxial stresses.^{38,39)}

Stress-strain curves for uncharged and hydrogenated up to different hydrogen concentrations grade 2 titanium are shown in Fig. 3.⁴⁰⁾

From Fig. 3 it can be clearly seen that the strain to failure decreases with increasing hydrogen concentration, while at

Fig. 3 The stress-strain curves for uncharged and hydrogenated up to different hydrogen concentrations grade 2 titanium.⁴⁰⁾

the same time, the yield strength and the ultimate tensile strength increase. Hydrogen effect on the fracture surface is presented in Fig. 4. When increasing the hydrogen content, the fracture surface changed from large microvoids coalescence in the uncharged material (Fig. 4a) to smaller microvoids in the 600 wppm charged specimen (Fig. 4b) and finally to brittle facets in the specimen that contains 3490 wppm hydrogen (Fig. 4c).⁴⁰⁾

Testing on oxygen-strengthened titanium demonstrated no effect of hydrogen on the fracture toughness, but pronounced effect on impact resistance.^{41,42)} In testing under sustained load the room temperature rupture times were observed to decrease.⁴³⁾

4.2 Alpha and alpha + beta 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.¹⁾

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.⁹⁾ 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. High voltage electron microscope investigations of the hcp α Ti-4%Al alloy⁴⁴⁾ (Fig. 5), revealed that in 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.⁴⁴⁾

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

Fig. 4 (a) and (b) nucleation and growth of hydrides in α -Ti-3Al alloy, (c) dislocation emission from a growing hydride, (d) hydride field ahead of a crack.^{44,54)}

Fig. 5 Fracture surface of uncharged and hydrogenated grade 2 titanium, failed during tensile testing: (a) uncharged specimen (b) hydrogenated up to 600 wppm, (c) hydrogenated up to 3400 wppm.⁴⁰⁾

(a)

(b)

Fig. 6 SEM micrographs of Ti-6Al-4V alloys after electrochemical hydrogenation (1 H_3PO_4 : 2 glycerine, 50 mA/cm^2 , 69 hours) 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 .

generally be more severe with severity of degradation reflecting the hydrogen pressure dependence of hydrogen transport within the β phase.⁴⁵⁾ Hydrogen-induced cracking is related also to the environment. During cathodic charging and exposure to electrolytic solution of duplex and fully lamellar Ti-6Al-4V alloy, the authors observed that 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. 6).

In their investigation of the effect of hydrogen and strain rate upon the ductility of mill-annealed Ti-6Al-4V, Hardie and Ouyang¹³⁾ revealed that the added hydrogen produces an embrittling effect, as indicated by elongation and reduction in area at fracture (Fig. 7). This effect, although apparent at both strain rates investigated, occurs at a lower hydrogen level at the slower strain rate.¹³⁾

Fig. 7 Hydrogen effect on the ductility of mill-annealed Ti-6Al-4V strained to failure at two different strain rates: (a) reduction in area (b) elongation.¹³⁾

The substantial effect of the microstructure is also demonstrated in the Ti-8Al-1Mo-1V alloy, undergoing different heat treatments; in the near- α alloy the cleavage-like fracture occurred, and in the $\alpha+\beta$ alloys an alternating extensive α cleavage and ductile rupture of the β ligaments became active.^{12,46)}

When only internal hydrogen is present within the α -containing alloys, hydrogen-induced cracking can occur as the result of the long term presence of a locally high tensile stress, either applied or residual. This form of degradation is termed sustained load cracking (SLC). The influence of the microstructure on SLC is primarily determined by the amount and the distribution of the β phase. The presence of the β phase in a primarily α microstructure will enhance hydrogen transport and accelerate crack growth.²⁰⁾ The β phase can also serve as a sink for hydrogen requiring increased internal hydrogen concentrations for SLC.⁴⁷⁾ Lastly, the more ductile β phase can blunt a propagating crack in the α phase and reduce the rate of SLC. The fracture in the Ti-6Al-6V-2Sn alloy was characterized by extensive cleavage of the α grains separated by ductile rupture of the β

ligaments from threshold to near failure under plane strain conditions, and the material, fractured in the plane stress regions, failed in a ductile mode.⁴⁸⁾

Another crucial parameter whose influence is very significant on the hydrogen degradation process is the temperature. A rapid decrease in the crack growth rate is usually seen as the temperature is increased above room temperature, and is usually attributed to the increased difficulty for the δ -hydride to nucleate and grow in the α phase.²⁸⁾ However, the most significant effect of raising the temperature, is the resulting rapid increase in the rate of hydrogen transport. At temperatures above the titanium-hydrogen eutectic temperature, absorbed hydrogen can force the transformation of the α phase to the more stable β phase. Most of the hydrogen picked up during an elevated temperature exposure will be retained when the alloy is cooled, and will transform to the δ -hydride phase. If sufficient hydrogen is picked up at the elevated temperature, it is not unusual for the α phase in α and $\alpha+\beta$ titanium alloys to completely disintegrate upon cooling as the result of the formation of massive amounts of titanium hydride.²⁰⁾

4.3 Beta alloys

Since beta titanium alloys exhibit very high terminal hydrogen solubility and does not readily form hydrides, until lately they were considered to be fairly resistant to hydrogen, except possibly at very high hydrogen pressures.⁴⁹⁾ However, recent investigations have demonstrated that these alloys can be severely degraded exposure to hydrogen in different ways. For example, hydrogen embrittlement was observed to occur in Ti-Mo-Nb-Al alloy,⁵⁰⁾ Ti-V-Cr-Al-Sn alloy⁵¹⁾ and Ti-V-Fe-Al (Fig. 8)⁵²⁾ well below hydrogen concentration required

Fig. 8 (a) ultimate tensile strength and (b) reduction in area as a function of hydrogen concentration in Ti-10V-2Fe-3Al alloy.⁵²⁾

Fig. 9 Fracture surfaces of β -Ti6Al4V alloy. At hydrogen concentrations higher than $H/M = 0.2$ (17.7 at% H), the ductility is reduced to zero and the fracture mode changes from (a) ductile micro-void coalescence to (b) transgranular cleavage failure.^{53,54)}

to hydride the β phase. The most evident way of degradation is by the formation of the δ -hydride phase, which is brittle at low temperatures. This form of degradation is similar to that in the primarily α alloys, except that it requires higher hydrogen pressures.²²⁾

In addition, since hydrogen is a strong β stabilizer, the α phase present in these β alloys can be transformed to the β phase with hydrogen exposures at elevated temperatures. Therefore, since the presence of a finely precipitated, acicular α phase is the primary strengthening mechanism in most β alloys, their strength will decrease with hydrogen absorption at elevated temperatures.⁵³⁾

Finally, 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 transition of the bcc β alloys. Hydrogen can raise the transition temperature from below about -130°C in a hydrogen-free material to 100°C , 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.^{20,53)} Investigations of β -21S titanium alloy^{54,55)} revealed that the hydrogen-induced ductile-to-brittle transition occurred abruptly at a critical hydrogen concentration (Fig. 9), that decreased with decreasing tensile test temperature.

Also the yield strength of ductile specimens and the fracture stress of brittle specimens were reduced by the solute hydrogen. In this case no hydrides were associated with the fracture process, eliminating the stress-induced hydride formation and cleavage mechanism. The hydrogen-enhanced localized plasticity mechanism was excluded, since hydrogen enhanced the dislocation mobility and no fracture due to localized ductile processes was observed. Therefore, the mechanism responsible for the sharp ductile-to-brittle transition and the decrease in the fracture load of the brittle specimens with increasing hydrogen concentration, is the decohesion mechanism of hydrogen embrittlement.^{54,55)}

5. Summary

Titanium alloys are among the most important structural materials for a wide variety of technological applications, particularly in the aerospace industry, because of their high strength-to-weight ratio and superior corrosion resistance.

However, problems may arise when hydrogen comes in contact with titanium base alloys. These alloys can pick large amounts of hydrogen, especially at elevated temperatures, when hydrogen diffusion and its solubility increase. At a critical hydrogen concentration, titanium hydrides will precipitate. Since hydrogen behaves differently in the hcp α phase and bcc β phase, the susceptibility of titanium alloys to hydrogen degradation varies markedly. 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. If hydrogen is present within the bulk of these alloys, they can be highly susceptible to sustained-load cracking, as the result of repeated formation and rupture of strain-induced hydrides. Beta titanium alloys are less susceptible to hydrogen degradation at room temperature. However, lately 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 stabilization of the β phase, the sharp ductile-to-brittle transition and the change in the fracture mode.

REFERENCES

- 1) H. G. Nelson: *Hydrogen Embrittlement — Treatise on Materials Science and Technology*, Vol. 25, Embrittlement of Engineering Alloys, (Eds.: C. L. Briant, S. K. Banejri), (Academic Press, New-York, NY, 1983), pp. 275–359.
- 2) D. N. Williams and R. I. Jaffee: *J. Less-Common Met.* **2** (1960) 42–48.
- 3) D. N. Williams: *J. Inst. Metals* **91** (1962–63) 147–152.
- 4) G. F. Pittinato and S. F. Frederick: *Metall. Trans.* **1** (1970) 3241–3243.
- 5) D. A. Meyn: *Met. Trans.* **5** (1974) 2405–2414.
- 6) A. Vassel: *J. Less-Common Met.* **69** (1980) 293–299.
- 7) H. Hoeg, B. Hollund and I. W. Hall: *Metall. Sci.* **14** (1980) 50–56.
- 8) H. G. Nelson, D. P. Williams and J. E. Stein: *Metall. Trans.* **3** (1972) 469–475.
- 9) D. P. Williams and H. G. Nelson: *Metall. Trans.* **3** (1972) 2107–2113.
- 10) D. A. Meyn: *Metall. Trans.* **3** (1972) 2302–2305.
- 11) G. H. Koch, A. J. Bursle, R. Liu and N. Pugh: *Metall. Trans.* **12A** (1981) 1833–1843.
- 12) N. R. Moody and W. W. Gerberich: *Metall. Trans.* **13A** (1982) 1055–1061.
- 13) D. Hardie and S. Ouyang: *Corros. Sci.* **41** (1999) 155–177.
- 14) D. Eliezer: *Metallurgy and New Materials Researches*, Vol. II (1994) 4, 1.
- 15) G. Solovioff, D. Eliezer, P. B. Desch and R. B. Schwartz: *Scr. Metall. Mater.* **33** (8) (1995) 1315–1320.
- 16) F. H. Froes, D. Eliezer and H. G. Nelson: *5th Inter. Conf. on the Effect*

- of *Hydrogen on the Behavior of Materials*, (TMS, Moran, WY, USA, 11-15 September 1994) pp. 719–733.
- 17) H. Numakura and M. Coiwa: *Acta Metall.* **32** (1984) 1799–1807.
 - 18) G. C. Woo, C. E. Weatherly, C. E. Coleman and R. W. Gillbert: *Acta Metall.* **33** (1985) 1897–1906.
 - 19) N. E. Paton and J. C. Williams: *Effect of Hydrogen on Behavior of Materials*, (Eds.: A. W. Thompson, I. M. Bernstein), (AIME, New York, NY, 1976) pp. 409–432.
 - 20) H. G. Nelson: *Hydrogen Effects in Metals*, (Eds.: A. W. Thompson, N. R. Moody), (TMS, Warrendale, PA, 1996) pp. 699–715.
 - 21) H. Wipf, B. Kappesser and R. Werner: *J. Alloys Comp.* **310** (2000) 190–195.
 - 22) D. S. Shih and H. K. Birnbaum: *Scr. Metall.* **20** (1986) 1261–1264.
 - 23) M. M. Tsai and J. M. Howe: *Metall. Trans. A* **26** (1995) 2219–2226.
 - 24) P. E. Irving and C. J. Beevers: *Metall. Trans.* **2** (1971) 613–615.
 - 25) P. Millenbach and M. Givon: *J. Less-Common Met.* **87** (1982) 179–184.
 - 26) W. W. Gerberich, N. R. Moody, C. L. Jensen, C. Hayman and K. Jatavallabhula: *Hydrogen Effects in Metals*, (Eds.: A. W. Thompson, I. M. Bernstein), (TMS-AIME, Warrendale, PA, 1981), pp. 731–744.
 - 27) J. C. Williams: *Effect of Hydrogen on Behavior of Materials*, (Eds.: A. W. Thompson, I. M. Bernstein), (AIME, New York, NY, 1976) pp. 367–380.
 - 28) W. R. Pardee and N. E. Paton: *Metall. Trans. A* **11** (1980) 1391–1400.
 - 29) I. I. Phillips, P. Poole and L. L. Shreir: *Corros. Sci.* **12** (1972) 855–866.
 - 30) T. I. Wu and J. K. Wu: *Mat. Chem. Phys.* **74** (2002) 5–12.
 - 31) E. Tal-Gutelmacher, D. Eylon and D. Eliezer: *Ti-2003 Science and Technology*, (Ed. G. Luetjering), (Wiley-VCH, Weinheim, March 2004), in print.
 - 32) S. R. Peddada, I. M. Robertson and H. K. Birnbaum: *J. Mater. Res.* **8** (1993) 291–296.
 - 33) C. G. Rhodes, J. C. Williams: *Metall. Trans. A* **6** (1975) 1670–1671.
 - 34) C. G. Rhodes and N. E. Paton: *Metall. Trans. A* **10** (1979) 209–216.
 - 35) N. E. Paton and R. A. Spurling: *Metall. Trans. A* **7** (1976) 1769–1774.
 - 36) I. W. Hall: *Metall. Trans. A* **9** (1978) 815–820.
 - 37) N. R. Moody and J. E. Costa: *Microstructure/Property Relationship in Titanium Alloys and Titanium Aluminides*, (Eds.: Y. W. Kim, R. R. Boyer), (TMS-AIME, Warrendale, PA, 1991) pp. 587–604.
 - 38) D. A. Gerard and D. A. Koss: *Scr. Met.* **19** (1985) 1521–1524.
 - 39) C. W. Lentz, D. A. Koss, M. G. Stout and S. S. Hecker: *Met. Trans.* **14A** (1983) 2527–2533.
 - 40) C. L. Briant, Z. F. Wang and N. Chollocoop: *Corros. Sci.* **44** (2002) 1875–1888.
 - 41) M. L. Wasz, C. C. Ko, F. R. Brotzen and R. B. McLellan: *Scr. Metall.* **23** (1989) 2039–2042.
 - 42) M. L. Wasz, C. C. Ko, F. R. Brotzen and R. B. McLellan: *Scr. Metall.* **24** (1990) 2043–2046.
 - 43) M. L. Wasz, F. R. Brotzen and R. B. McLellan: *Scr. Metall.* **28** (1993) 483–487.
 - 44) D. S. Shih, I. M. Robertson and H. K. Birnbaum: *Acta Metall.* **36** (1988) 111–124.
 - 45) H. G. Nelson: *Metall. Trans.* **4** (1973) 364–367.
 - 46) N. R. Moody, F. A. Greulich and S. L. Robinson: *Metall. Trans.* **15A** (1984) 1955–1958.
 - 47) G. F. Pittinato and W. D. Hanna: *Metall. Trans.* **3** (1972) 2905–2909.
 - 48) J. E. Hack and G. R. Leverant: *Metall. Trans. A* **13** (1982) 1729–1738.
 - 49) N. E. Paton, R. A. Spurling and C. G. Rhodes: *Hydrogen Effects in Metals*, (Eds.: A. W. Thompson, I. M. Bernstein), (TMS-AIME, Warrendale, PA, 1981) pp. 269–279.
 - 50) G. A. Young Jr. and J. R. Scully: *Scr. Metall. Mater.* **28** (1993) 507–512.
 - 51) D. G. Kolman and J. R. Scully: *Effects of the Environment on the Initiation of Crack Growth*, (ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 1997) pp. 61–73.
 - 52) J. E. Costa, J. C. Williams and A. W. Thompson: *Metall. Trans. A* **23** (1987) 1421–1430.
 - 53) D. A. Hardwick and D. G. Ulmer: *Hydrogen Effects in Metals*, (Eds.: A. W. Thompson, N. R. Moody), (TMS, Warrendale, PA, 1996) pp. 735–744.
 - 54) D. F. Teter, I. M. Robertson and H. K. Birnbaum: *Acta Mater.* **49** (2001) 4313–4323.
 - 55) P. Sofronis, I. M. Robertson, Y. Liang, D. F. Teter and N. Aravas: *Hydrogen Effects on Material Behavior and Corrosion Deformation Interactions*, (Eds.: N. R. Moody, A. W. Thompson, R. E. Ricker, G. S. Was, R. H. Jones), (TMS-AIME, Warrendale, PA, 2003) pp. 537–548.