The Hydrogen Embrittlement of Titanium-Based Alloys

Ervin Tal-Gutelmacher and Dan Eliezer

Titanium-based alloys provide an excellent combination of a high strength/weight ratio and good corrosion behavior, which makes these alloys among the most important advanced materials for a variety of aerospace, marine, industrial, and commercial applications. Although titanium is considered to be reasonably resistant to chemical attack, severe problems can arise when titanium-based alloys come in contact with hydrogen-containing environments, where they can pick up large amounts of hydrogen, especially at elevated temperatures. The severity and the extent of the hydrogen interaction with titanium-based alloys are directly related to the microstructure and composition of the titanium alloys. This paper addresses the hydrogen embrittlement of titanium-based alloys. The hydrogen-titanium interaction is reviewed, including the solubility of hydrogen in α and β phases of titanium and hydride formation. Also, the paper summarizes the detrimental effects of hydrogen in different titanium alloys.

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, and corrosion resistance as well as their good behavior at elevated temperatures. However, the interaction between titanium alloys and hydrogen can be extreme[1] and severe problems may arise when these alloys come in contact with hydrogen-containing environments. The precise role of both internal[1–7] and environmental hydrogen has been extensively investigated.[8–16]

This article reviews the hydrogen-titanium interaction, including the solubility of hydrogen in α and β phases of titanium and hydride formation. Also discussed are the detrimental effects of

> This article reviews the hydrogen-titanium interaction, including the solubility of hydrogen in α and β phases of titanium and hydride formation.

hydrogen in different titanium alloys, with specific emphasis on the role of microstructure on hydrogen embrittlement of these alloys.

HYDROGEN-TITANIUM INTERACTION

The hydrogen interaction with titanium takes the form of a simple eutectoid transformation with the α + hydride phases forming directly from the β phase.[17,18] The strong stabilizing effect of hydrogen on the β phase field results in a decrease of the alpha-to-beta transformation temperature from 882°C to a eutectoid temperature of 300°C. The terminal hydrogen solubility in the β phase (without the formation of a hydride phase) can reach as high as 50 at.% at elevated temperatures above 600°C. In the α phase, however, the terminal hydrogen solubility is only approximately 7 at.% at 300°C and decreases rapidly with decreasing temperature. In the group IV transition metals, hydrogen tends to occupy tetrahedral interstitial sites.[19] As a result, 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-centered-cubic (bcc) structure, which consists of 12 tetrahedral and six octahedral interstices. In comparison, the hexagonal-close-packed (hcp) lattice of alpha titanium exhibits only four tetrahedral and two octahedral interstitial sites.

Hydrogen content measurements (by means of a LECO RH-404 hydrogen determinator system) were conducted on a Ti-6Al-4V alloy, thermomechanically treated in two distinguished microstructures—duplex and fully-lamellar—after electrochemical hydrogenation at varying charging conditions. Results are presented in Table I. Comparing hydrogen absorption in duplex and fully lamellar Ti-6Al-4V alloys after electrochemical hydrogenation, the hydrogen concentration 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

Table I. Hydrogen Content Measurements

	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 %)

Figure 1. Scanning-electron micrographs revealing the microstructures of Ti-6Al-4V specimens; (a) fully lamellar microstructure showing continuous β phase, (b) duplex microstructure showing equiaxed primary α and lamellar packets of transformed β (secondary α).

in the β phase than in the α phase,[8] microstructures with more continuous β phase, such as a fully lamellar microstructure (Figure 1a), will absorb more hydrogen than those with discontinuous β, such as the fine equiaxed α in the duplex microstructure (Figure 1b). 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.

Three different kinds of titanium hydrides (δ, ε, and γ) have been observed around room temperature.[17,19–21] The δ-hydrides (TiH$_x$) have a face-centered cubic lattice with the hydrogen atoms occupying the tetrahedral interstitial sites (CaF$_2$ structure). The non-stoichiometric ratio, x, of the δ-hydride exists over a wide range (1.5–1.99). At high hydrogen concentrations (x ≥ 1.99), the δ-hydride transforms from diffusionless into ε-hydride, with a face-centered tetragonal (fct) structure (c/a ≤ 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.

HYDROGEN EMBRITTLEMENT OF TITANIUM ALLOYS

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.[22]

Commercially Pure 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.[23,24]

Alpha and Near-Alpha 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]
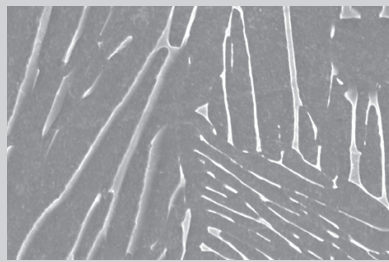
The titanium alloys whose microstructures contain mostly the α phase, when exposed to an external hydrogen environment at around room temperature, will degrade primarily through the repeated formation and rupture of the brittle hydride phase at, or very near, the gas-metal interface.[9] When only the 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.

Birnbaum et al.[25] 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 forma-
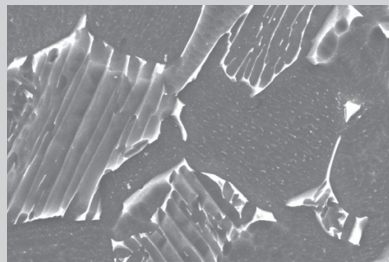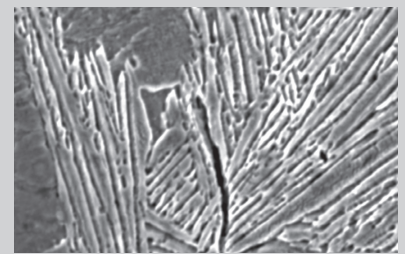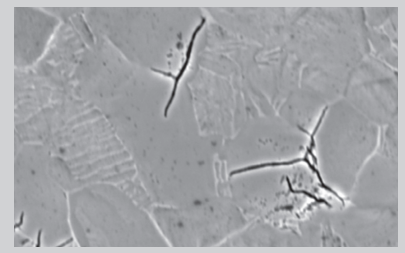
tion and cleavage fracture of hydrides. At high stress intensities, the fracture mode transition occurred when the crack propagation rate exceeded the rate at which the hydride could form in front of the crack, and the hydrogen-enhanced localized plasticity was the responsible cracking mechanism.

Alpha + Beta Alloys

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.[26] 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 alloys, x-ray diffraction microstructure observations of both alloys before and after hydrogenation revealed that the

Figure 2. Scanning-electron micrographs of Ti-6Al-4V alloys after electrochemical hydrogenation (1 H$_3$PO$_4$: 2 glycerine, 50 mA/cm², 69 h) 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.

presence of hydrogen in solid solution in both α and β phases resulted in lattice expansions. The result is similar to the observations after gas-phase hydrogenation, reported elsewhere.[27] In both specimens, increasing the applied current density resulted in a further expansion of the cell volume of the α phase, as well as in the precipitation of cubic δ-TiH$_x$ (with a cell parameter of 4.34 ± 0.19 Å in the fully lamellar specimen and 4.54 ± 0.17 Å in the duplex specimen). However, in duplex material, the δ-TiH$_x$ formed even at lower current densities, but the lattice parameter of the hydride was lower than that formed at higher current densities (4.23 ± 0.17 Å instead of 4.54 ± 0.17 Å). Scanning-electron microscopy investigations revealed that hydrogen-induced cracking will usually take place in the α phase or along the α/β interface, depending on the prior microstructure of the alloy (Figure 2).

Applying higher current densities resulted in severe pitting and microcracking, as well as oxygen contamination of the hydrogen-attacked areas in both Ti-6Al-4V alloys. However, in comparison to the random distribution of the microcracks in the fully lamellar alloy, the pitting and the microcracks in the duplex alloy were located mainly in the equiaxed grains of primary α, rather than in the β-transformed lamellar grains (Figure 3).

The substantial effect of the microstructure is also demonstrated in the Ti-8Al-1Mo-1V alloy under 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.[12,28]

Beta Alloys

Since beta titanium alloys exhibit very high terminal hydrogen solubility and do not readily form hydrides, until lately they were considered to be fairly resistant to hydrogen, except possibly at very high hydrogen pressures.[29] However, recent investigations have demonstrated that these alloys can be severely degraded by exposure to hydrogen. For example, hydrogen embrittlement was observed to occur in the Ti-Mo-Nb-Al,[30] Ti-V-Cr-Al-Sn,[31] and Ti-V-Fe-Al[32] alloys, well below the hydrogen concentration required to hydride the β phase. The most evident degradation is the formation of the δ-hydride phase, which is brittle at low temperatures, similar to that in the primarily α alloys except that it requires higher hydrogen pressures.[20] 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.[33]

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 fraction 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.[33]

Investigations of the β-21S titanium alloy[34,35] revealed that the hydrogen-
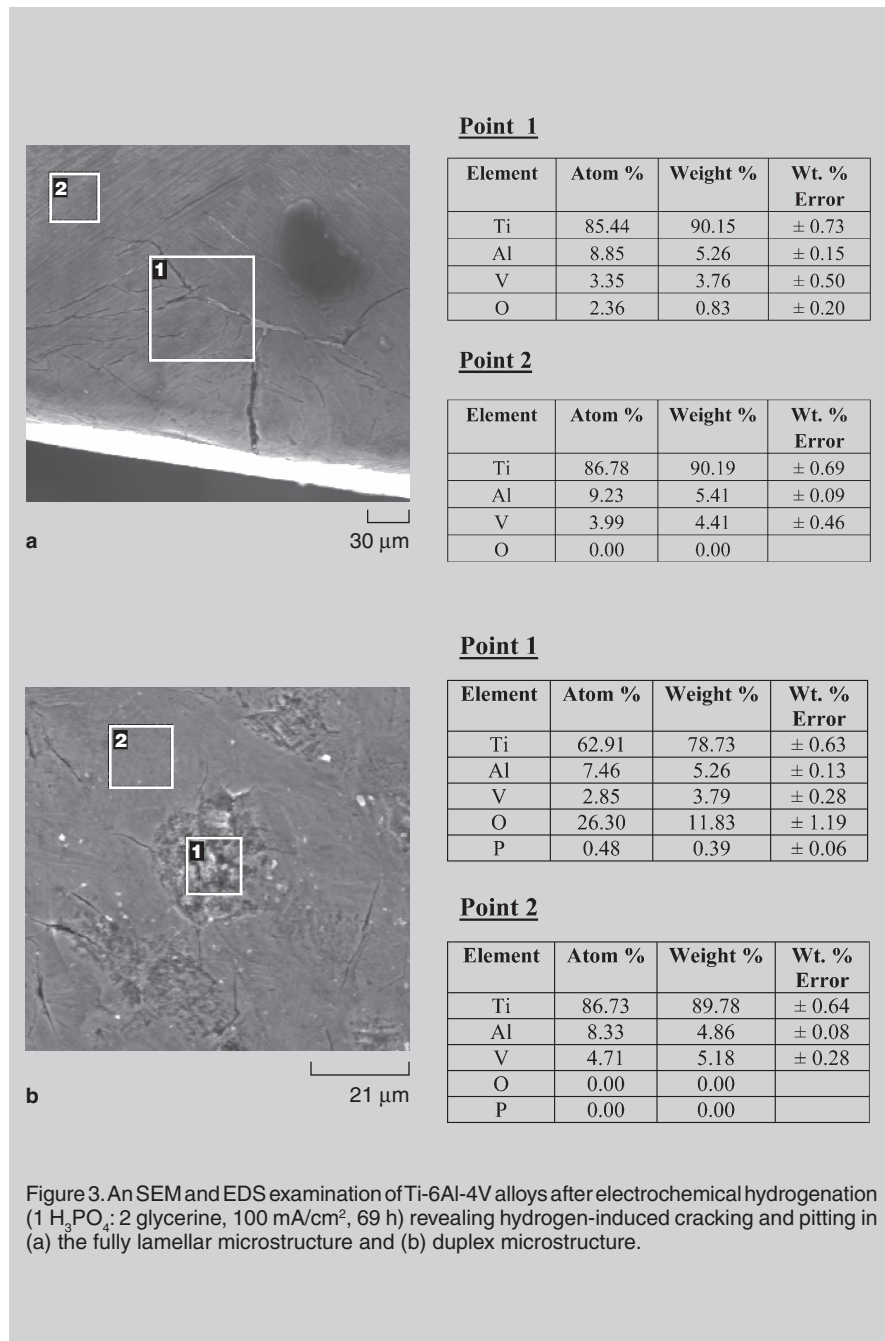
Point 1

Element	Atom %	Weight %	Wt. % Error
Ti	85.44	90.15	± 0.73
Al	8.85	5.26	± 0.15
V	3.35	3.76	± 0.50
O	2.36	0.83	± 0.20

Point 2

Element	Atom %	Weight %	Wt. % Error
Ti	86.78	90.19	± 0.69
Al	9.23	5.41	± 0.09
V	3.99	4.41	± 0.46
O	0.00	0.00	

Point 1

Element	Atom %	Weight %	Wt. % Error
Ti	62.91	78.73	± 0.63
Al	7.46	5.26	± 0.13
V	2.85	3.79	± 0.28
O	26.30	11.83	± 1.19
P	0.48	0.39	± 0.06

Point 2

Element	Atom %	Weight %	Wt. % Error
Ti	86.73	89.78	± 0.64
Al	8.33	4.86	± 0.08
V	4.71	5.18	± 0.28
O	0.00	0.00	
P	0.00	0.00	

Figure 3. An SEM and EDS examination of Ti-6Al-4V alloys after electrochemical hydrogenation (1 H$_3$PO$_4$: 2 glycerine, 100 mA/cm², 69 h) revealing hydrogen-induced cracking and pitting in (a) the fully lamellar microstructure and (b) duplex microstructure.

induced ductile-to-brittle transition occurred abruptly at a critical hydrogen concentration 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, and the mechanism responsible was decided to be the decohesion mechanism of hydrogen embrittlement.

References

1. H.G. Nelson, *Hydrogen Embrittlement—Treatise on Materials Science and Technology: Vol. 25, Embrittlement of Engineering Alloys,* ed. C.L. Briant and S.K. Banerji (New York: Academic Press, 1983), pp. 275–359.
2. D.N. Williams and R.I. Jaffee, *J. Less Common Metals*, 2 (1960), pp. 42–48.
3. D.N. Williams, *J. Inst. Metals*, 91 (1962–63), pp. 147–152.
4. G.F. Pittinato and S.F. Frederick, *Met. Trans.*, 1 (1970), pp. 3241–3243.
5. D.A. Meyn, *Met. Trans.*, 5 (1974), pp. 2405–2414.
6. A. Vassel, *J. Less Common Metals*, 69 (1980), pp. 293–299.
7. H. Hoeg, B. Hollund, and I.W. Hall, *Met. Sci.,* 14 (1980), pp. 50–56.
8. H.G. Nelson, D.P. Williams, and J.E. Stein, *Met. Trans.*, 3 (1972), pp. 469–475.
9. D.P. Williams and H.G. Nelson, *Met. Trans.*, 3 (1972), pp. 2107–2113.
10. D.A. Meyn, *Met. Trans.*, 3 (1972), pp. 2302–2305.
11. G.H. Koch et al., *Met. Trans.*, 12A (1981), pp. 1833–1843.
12. N.R. Moody and W.W. Gerberich, *Met. Trans.*, 13A (1982), pp. 1055–1061.
13. D. Hardie and S. Ouyang, *Corr. Sci.*, 41 (1999), pp. 155–177.
14. D. Eliezer, *Metallurgy and New Materials Researches II* (4) (1994) p. 1.
15. G. Solovioff et al., *Scripta Metall. Mater.*, 33 (8) (1995), pp. 1315–1320.
16. F.H. Froes, D. Eliezer, and H.G. Nelson, *Hydrogen Effects in Materials*, ed. A.W. Thompson and N.R. Moody (Warrendale, PA: TMS, 1994), pp. 719–733.
17. H. Numakura and M. Coiwa, *Acta Metall.*, 32 (1984), pp. 1799–1807.
18. G.C. Woo et al., *Acta Metall.*, 33 (1985), pp. 1897–1906.
19. H. Wipf, B. Kappesser, and R. Werner, *J. Alloys and Comp.*, 310 (2000), pp. 190–195.
20. D.S. Shih and H.K. Birnbaum, *Scripta Metall.*, 20 (1986), pp. 1261–1264.
21. M.M. Tsai and J.M. Howe, *Met.. Trans. A*, 26 (1995), pp. 2219–2226.
22. N.R. Moody and J.E. Costa, *Microstructure/Property Relationship in Titanium Alloys and Titanium Aluminides*, ed. Y.W. Kim and R.R. Boyer (Warrendale, PA: TMS, 1991), pp. 587–604.
23. D.A. Gerard and D.A. Koss, *Scripta Met.*, 19 (1985), pp. 1521–1524.
24. C.W. Lentz et al., *Met. Trans.,* 14A (1983), pp. 2527–2533.
25. D.S. Shih, I.M. Robertson, and H.K. Birnbaum, *Acta Met.*, 36 (1988), pp. 111–124.
26. H.G. Nelson, *Met. Trans.*, 4 (1973), pp. 364–367.
27. E. Tal-Gutelmacher, D. Eliezer, and D. Eylon, *Mat. Sci. Eng. A*, 381 (2004), pp. 230–236.
28. N.R. Moody, F.A. Greulich, and S.L. Robinson, *Met. Trans.,* 15A (1984), pp. 1955–1958.
29. N.E. Paton, R.A. Spurling, and C.G. Rhodes, *Hydrogen Effects in Metals,* ed. A.W. Thompson and I.M. Bernstein (Warrendale, PA: TMS, 1981), pp. 269–279.
30. G.A. Young, Jr. and J.R. Scully, *Scripta Met. Mater.*, 28 (1993), pp. 507–512.
31. D.G. Kolman and J.R. Scully, *Effects of the Environment on the Initiation of Crack Growth* (West Conshohocken, PA: ASTM, 1997), pp. 61–73.
32. J.E. Costa, J.C. Williams, and A.W. Thompson, *Met. Trans. A*, 23 (1987), pp. 1421–1430.
33. D.A. Hardwick and D.G. Ulmer, *Hydrogen Effects in Metals,* ed. A.W. Thompson and N.R. Moody (Warrendale, PA: TMS, 1996), pp. 735–744.
34. D.F. Teter, I.M. Robertson, and H.K. Birnbaum, *Acta Mater.*, 49 (2001), pp. 4313–4323.
35. P. Sofronis et al., *Hydrogen Effects on Material Behavior and Corrosion Deformation Interactions*, ed. N.R. Moody et al. (Warrendale, PA: TMS, 2003), pp. 537–548.

Ervin Tal-Gutelmacher and Dan Eliezer are with the Department of Materials Engineering at Ben-Gurion University of the Negev in Beer-Sheva, Israel.

For more information, contact Dan Eliezer, Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel; +972-7-646-1467; fax +972-7-646-1475; e-mail deliezer@bgumail.bgu.ac.il.