**MODELING HYDROGEN-INDUCED CRACKING OF TITANIUM ALLOYS
IN NUCLEAR WASTE REPOSITORY ENVIRONMENTS**

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Fred Hua*, Kevin Mon†, Pasu Pasupathi* and Gerald Gordon†

*Bechtel SAIC Company, LLC/†Framatome ANP

1180 Town Center Dr.
Las Vegas, NV 89144, USA

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David Shoesmith
Department of Chemistry
University of Western Ontario
London, ON, N6A 5B7, Canada

ABSTRACT

This paper reviews the current understanding of hydrogen-induced cracking (HIC) of Ti Grade 7 and other relevant titanium alloys within the context of the current waste package design for the repository environmental conditions anticipated within the Yucca Mountain repository. The review concentrates on corrosion processes possible in the aqueous environments expected within this site. A brief background discussion of the relevant properties of titanium alloys, the hydrogen absorption process, and the properties of passive film on titanium alloys is presented as the basis for the subsequent discussion of model developments. The key corrosion processes that could occur are addressed individually. Subsequently, the expected corrosion performance of these alloys under the specific environmental conditions anticipated at Yucca Mountain is considered. It can be concluded that, based on the conservative modeling approaches adopted, hydrogen-induced cracking of titanium alloys will not occur under nuclear waste repository conditions since there will not be sufficient hydrogen in the alloy after 10,000 years of emplacement.

Keywords: Titanium Alloys, Nuclear Waste, Palladium, Hydrogen-Induced Cracking

INTRODUCTION

The Nuclear Waste Policy Act of 1982 (as amended in 1987) designated Yucca Mountain in Nevada as the site to be characterized for potential disposal of high-level nuclear waste (HLW).^[1] Long-term isolation of waste and subsequent slow release of radionuclides into the geosphere will rely on a system of natural and engineered barriers including a robust waste isolation design, comprising an Alloy 22 waste package (WP) covered by a mailbox-shaped drip shield (DS) composed predominantly of Ti Grade 7 with Ti Grade 24 structural support members.^[2] Over the years, numerous studies have been performed to evaluate the susceptibility to stress corrosion cracking, general, localized, galvanic and microbially influenced corrosion for Alloy 22^[3, 4, 5, 6, 7, 8, 9, 10, 11] and Ti Grade 7.^[4, 5, 12, 13, 14]

Figure 1. Schematic of the relationship between the relevant titanium alloys. Alloys grouped by the dotted lines have the same mechanical properties regardless of chemical composition (note that the total Pd content of Ti Grade 7 is 0.12 – 0.25 wt%).

The titanium alloys proposed for use in the nuclear waste repository are Ti Grade 7 and Ti Grade 24, and the relationships between these and other relevant titanium alloys are shown in Figure 1. ASTM B 265-02^[15] specifies the chemical compositions and mechanical properties of these alloys. A key point to note is that the mechanical properties of the relevant titanium alloys

are not changed as the alloying palladium content increases to the desired level as shown in Figure 1.

The purpose of this paper is to review the processes leading to, and the process of, hydrogen-induced cracking (HIC) of Ti Grade 7 and other relevant titanium alloys, and to consider the expected corrosion performance of these alloys under the specific environmental conditions at Yucca Mountain.

HYDROGEN UPTAKE BY TITANIUM ALLOYS

Alloying elements, and Pd in particular, are added to α -titanium alloys primarily to enhance their corrosion resistance in reducing acid conditions, partially because they accelerate proton reduction kinetics in acid solutions compared to most other metals, thereby re-enforcing passivity.^[16, 17] On the other hand, alloying elements capable of catalyzing proton reduction may also catalyze hydrogen absorption into the alloys.

Corrosion processes occurring on titanium are often accompanied by hydrogen production introducing the possibility of the absorption of hydrogen into the material. Crevice corrosion, once initiated, is supported by both the reduction of oxygen on passive surfaces external to the crevice and the reduction of protons ($\text{Ti} + 4\text{H}^+ \rightarrow \text{Ti}^{4+} + 2\text{H}_2$) inside the crevice, leading to the absorption of atomic hydrogen in sufficient quantities to produce extensive hydride formation.^[18] For passive non-creviced or inert crevice condition, corrosion could be sustained by reaction with water under neutral conditions ($\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 2\text{H}_2$) and should proceed at an extremely slow rate. In the first step to possible failure by HIC, the hydrogen generated must pass through the TiO_2 film before absorption into the underlying Ti alloy. For absorption to proceed, redox transformation ($\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$) in the oxide film are necessary.^[18] This requires significant cathodic polarization of the metal, generally only achievable by galvanic coupling to active materials, such as carbon steel, or the application of a cathodic protection potential. This permeability is only significant at potentials $< -0.7 \text{ V}_{(\text{SEC})}$,^[19] as demonstrated by Murai et al.^[20] in long-term hydrogen absorption measurements, Figure 2(a). These measurements suggest a threshold potential of $-0.6 \text{ V}_{(\text{SCE})}$ above which no hydrogen

absorption occurs.^[18] Redox transformations in the oxide occur once the potential is sufficiently negative of the flatband potential for surface degeneracy to be established, and is illustrated schematically in Figure 2(b).^[18] When the potential is sufficiently negative for these transformations to occur titanium hydrides are thermodynamically stable with respect to the metal,^[21, 22] and the passive film can only be considered as a transport barrier to hydrogen. Beyond this threshold potential, the rate of absorption of hydrogen into the metal is effectively independent of potential down to ~ -1.0 V_(SCE), Figure 2(a),^[20] and there is ample evidence to claim that hydrogen is not transported through the oxide film at any significant rate until a potential of ≤ -1.0 V_(SCE) is reached.^[23, 24, 25]

Figure 2. The hydrogen absorption rate as a function of applied potential measured on Ti Grade 2 electrodes in flowing artificial seawater with a flow velocity of 2.0 ms^{-1} at 30°C (a)^[20] and a schematic illustrating the cathodic transformations occurring in TiO_2 films, which lead to the absorption of hydrogen (b).^[18]

For the Pd-containing titanium alloys (Ti-1Pd and Ti-0.15Pd (i.e., Ti Grade 7)), proton reduction in acidic solutions occurs at much lower potentials and with much smaller Tafel slopes ($50 - 65 \text{ mV}^{-1}$) than generally observed on Ti. A slope of this value is consistent with the catalytic behavior observed on noble metals such as Pd.^[26] Schutz and Xiao^[27] compared the kinetics of proton reduction on Ti Grade 2 7 and Ti Grade 16, although no attempt was made to identify any threshold value. The Tafel slope for Ti Grade 16 (100 mV^{-1}) was larger than that

obtained for Ti Grade 7 (80 mV^{-1}) indicating that catalysis of proton reduction decreases as the Pd content decreases. Fukuzuka et al.^[28] found a similar comparative behavior. These results suggest that proton reduction on Ti-Pd alloys need not be tied to redox transformation in the oxide. A possible explanation is that proton reduction occurs on intermetallic precipitates rich in noble metal content, which function as "hydrogen windows" in the oxide.^[18]

While concerns exist that alloying with Pd could promote hydrogen absorption into titanium,^[29] there is evidence to show that Ti-Pd alloys are not necessarily sensitive to hydrogen absorption,^[28, 30] especially in aerated solutions. For instance, Fukuzuka et al. demonstrated that, while the hydrogen absorption efficiency of Ti-Pd alloys increased with an increase in Pd content in deaerated HCl, both the corrosion rate and hydrogen absorption efficiency were decreased in aerated HCl.^[28] This influence of aeration was attributed to the ennoblement of the corrosion potential on addition, or increase in content, of Pd, and to the low over-voltage of Pd for oxygen reduction which competes with and suppresses the production of absorbable hydrogen by water reduction.^[17]

Studies on the influence of other alloying elements and/or impurities such as nickel^[31,32] and iron^[33, 34, 35, 36, 37] have produced conflicting results, probably attributable to variations in their concentration and distribution within the metal matrix. Thus, while the intermetallic Ti_xFe has been shown to be a hydrogen absorber, it is claimed that it is difficult to activate for hydrogen absorption.^[38] Hence, the presence of Fe could impede hydrogen absorption because the hydride formed on this intermetallic possesses less lattice distortion than that formed on $\alpha\text{-Ti}$, a feature claimed to retard the diffusion of hydrogen as suggested by Wu^[38] and by Schutz et al..^[39]

If a coherent layer of TiO_2 does exist not over intermetallic precipitates, then they could act as "hydrogen windows" and redox transformations in the oxide would not be a prerequisite for hydrogen absorption, which could then occur at $E > -0.6V_{(\text{SCE})}$. However, in the absence of inter-connected β phase in the bulk of the alloy, this hydrogen would remain stored in surface hydrides^[40] and would not affect the material's bulk mechanical properties. Impedance studies^[41, 42] suggest the intermetallics in Ti Grade 16 are inert, while those in Ti Grade 12

(Ti₂Ni) can corrode and potentially act as hydrogen windows. Also, the presence of Ni-containing β phase as ligaments along α grain boundaries would allow transport of H into the bulk of the alloy. Such a susceptibility to corrosion has been demonstrated for β -phase in Ti Grade 12 when its Ni content is high.^[43]

The results of Okada^[32] clearly show that any tendency for the Pd content in titanium alloys to accelerate hydrogen absorption is suppressed when a passive oxide is present (*i.e.* for $\text{pH} \geq 4$), and Tomari et al. found that the rate of hydrogen absorption decreased parabolically with time, even under cathodically polarized conditions when hydrogen absorption would be expected to be accelerated through a reduced oxide film.^[44] Kim and Oriani^[45, 46] found a similar parabolic dependence for Ti Grade 12 as well as an absorption rate almost independent of temperature in saturated brine. Such a time dependence suggests surface absorption sites are becoming saturated and that the rate of absorption will eventually become controlled by the rate of diffusive transport into the alloy. Further evidence that oxide films severely limit hydrogen absorption comes from observations made on alloys covered by thermally grown oxides. Hydrogen absorption is severely suppressed in aggressive brine environments (6% NaCl) up to 120°C,^[47] and in deaerated HCl ($2 \leq \text{pH} \leq 4$; 50°C to 250°C) was completely stopped by aerated conditions.^[48]

CORROSION AND HYDROGEN ABSORPTION

The choice of Ti Grade 7 effectively eliminates the possibility of crevice corrosion. A number of studies^[18, 49] (and references therein) have shown that susceptibility to crevice corrosion is eliminated through the alloy series Ti Grade 2 $\rightarrow$ Ti Grade 12 $\rightarrow$ Ti Grade 16. This immunity has been confirmed by extensive measurements of critical potentials (E_{crit}) in a range of environments relevant to anticipated repository conditions.^[50] In all environments tested E_{crit} , when compared to E_{corr} , shows a safety margin against crevice corrosion between 995 and 1652 mV. Thus, the primary potential failure mechanism becomes HIC, and the primary concern is that a combination of enhanced passive corrosion accompanied by hydrogen absorption at the sites exposed to seepage drips within the repository will eventually lead to susceptibility to failure by this mechanism.

General Passive Corrosion

There are two processes by which hydrogen could be produced, and possibly absorbed, under passive conditions: direct absorption of hydrogen produced by water radiolysis, and absorption of atomic hydrogen produced by the corrosion process to produce oxide.^[18] The direct absorption of radiolytically produced hydrogen does not appear to be significant except at high dose rates ($> 10^2$ Gy/h) and high temperatures ($> 150^\circ\text{C}$)^[18] well beyond those anticipated in the repository.

Under anoxic conditions, when passive corrosion should prevail, the corrosion potential for passive titanium must reside at a value at which water reduction can couple to titanium oxidation,

and, hence, must be at, or more negative than, the thermodynamic stability line for water. Since titanium hydrides are thermodynamically stable at these potentials, the passive film can only be considered as a transport barrier and not an absolute barrier. The rate of hydrogen absorption will be controlled by the rate of the corrosion reaction, which dictates the rate of production of absorbable hydrogen. Since TiO_2 is extremely insoluble, the corrosion reaction will be effectively limited to an oxide film growth reaction.

While the rate of hydrogen production and, hence, absorption may be assumed directly proportional to the rate of film growth, the fraction of hydrogen absorption, f_h , needs to be determined. Based on experimental measurements on Ti Grade 2 by Okada,^[32] a value in the range of 0.005 to 0.015 may be adopted for f_h . These values represent the minimum and maximum values measured in the pH range 4 to 5 and are conservative since they were measured at an applied current density of 0.5 mA/cm^2 at 25°C in sodium sulfate solutions at $\text{pH} = 4$. The electrode potential achieved during these experiments was $-1.14 \text{ V}_{(\text{SCE})}$, more than 500 mV more negative than the threshold value of $-0.6 \text{ V}_{(\text{SCE})}$ for hydrogen absorption. The applied current density used was $500 \text{ } \mu\text{A/cm}^2$ compared to a value of 1.45 nA/cm^2 calculated as the current that

would flow at a general corrosion rate of 50 nm/year, the 70th percentile value of general corrosion rates measured for Ti Grade 16 in the LTCTF at LLNL.^[50] Similar measurements on Pt and Ni-coated Ti Grade 2 specimens gave a value of i_h only marginally higher under these conditions,^[32] a clear indication that the Pd-content of Ti Grade 7 would not be expected to increase the efficiency of hydrogen absorption.

Galvanic Coupling of Ti Alloys to Less Noble Metals

A potential hydrogen-generating mechanism is the galvanic coupling of Ti to other metals such as zinc, magnesium,^[19] Cu-Ni alloys,^[51] aluminum^[52] and carbon and stainless steels.^[19] Galvanic couples with other passive metals, such as the Alloy 22 waste package are unlikely to be active, and the accumulation of significant damage by either material is extremely remote. However, H generation on the surface of the drip shield due to galvanic coupling with stainless steel or carbon steel ground support materials (such as rock bolts, wire mesh, and steel liners used in drifts) which fall onto the shield, while unlikely, cannot be ruled out.

In the case of nuclear waste repository, the ability of Fe-Ti galvanic couples to cause hydrogen-induced cracking of the titanium drip shield will be limited. The corrosion potentials for such materials, especially stainless steels, are generally close to that of titanium as shown in Figure 3. While temperatures are high ($> 80^\circ\text{C}$), the duration of aqueous conditions able to sustain an active galvanic couple (due to intermittent seepage drips) will be short, thereby limiting hydrogen absorption while temperatures are high enough to drive hydrogen transport into the metal. For temperatures below 80°C , even galvanic polarization below the potential threshold of $-0.6 V_{(\text{SCE})}$ produces only innocuous surface hydride films.^[19] In addition, dissolved O_2 in the solutions will suppress polarization of the galvanic potential to below $-0.6 V_{(\text{SCE})}$, and the ready formation of calcareous and mineral deposits, known to dramatically suppress galvanic currents, will stifle hydrogen absorption.^[53] Experimental evidence exists to show that galvanic currents^[54], and the rate of hydrogen absorption,^[53] will decrease with time as deposits (calcite from available CO_2 and silicates from groundwaters) accumulate. Moreover, any tendency for acidification or the development of alkaline conditions will increase the ferric ion solubility. Under evaporative conditions, this could lead to quite high dissolved ferric ion concentrations

and the establishment of a galvanic potential sufficiently positive to avoid hydrogen absorption into the titanium. It is well documented that only parts per million concentrations of multivalent transition metal cations such as Fe(III) are required to polarize titanium to passive conditions^[19, 35,] and ferric oxide deposits are passivating to Ti.^[35] Based on this discussion-, the high critical hydrogen concentration required for susceptibility to HIC (see below) and the large volume of available titanium in the drip shield to act as a hydrogen sink, hydrogen embrittlement of the titanium drip shield is highly unlikely.

Figure 3. Galvanic series of metals in ambient seawater.^[56] The arrows indicate the potential galvanic driving forces for Ti coupled to active carbon steel or active stainless steel Type 316.

CRITICAL HYDROGEN CONCENTRATION FOR HIC

The critical hydrogen concentration (H_C) is the threshold value above which slow crack growth is no longer observed and only fast crack growth occurs. Failure by fast crack growth is not inevitable at this hydrogen content, but the possibility of fast failure increases once this critical value is achieved or exceeded. Consequently, H_C can be viewed as a property that defines a material's susceptibility to failure by HIC. To then assume failure occurs rapidly is to ignore crack growth kinetics.

Values of H_C have been measured for Ti Grade 2 and Ti Grade 12,^[56, 57, 58] and Figure 4 shows an example of the plot of stress intensity factor as a function of hydrogen concentration. A generalized form of such plots, illustrating how they can be used to identify H_C , is shown in Figure 4(b).^[59] Based on such measurements, Ikeda and Quinn^[40, 60] showed that H_C for Ti Grade 16 is at least $1000 \mu\text{g}\cdot\text{g}^{-1}$ and may be much greater. In addition, Clarke et al.^[56, 58] have shown that H_C rises markedly with temperature, achieving a value of $\sim 1000 \mu\text{g}/\text{g}$ for Ti Grades 2 and 12 in the temperature range 92°C to 100°C .

Figure 4. Variation of the critical stress intensity factor with hydrogen content for Ti Grade 2 (transverse-longitudinal [T-L] orientation): o – slow crack growth (K_{ISCC}); • – fast fracture (K_{IH}) (a)^[56] and schematic showing the combinations of stress intensity factor and hydrogen concentration leading either to fast crack growth (brittle failures, K_{IH}), slow crack growth (K_{ISCC}) due to either sustained load cracking or ductile rupture, or no failure (b).^[59]

Based on the similarity between Ti Grade 7 and Ti Grade 16 and the role of Pd, it has been rationalized that the H_C for Ti Grade 7 is at least 1,000 $\mu\text{g/g}$.^[61] H_C is a function of the stress intensity factor^[59] and, therefore, is determined by both the hydrogen solubility and the response to material stress. Ti Grades 7 and 16 are α -alloys containing minimal amounts of β -phase. It is reasonable to expect that both alloys will exhibit very similar responses to applied stresses in an acidic environment. Thus, the controlling factor in determining the H_C will be the solubility of the hydrogen in the alloy, which increases with palladium-content. Ti Grade 7 contains more intermetallic particles that can absorb more hydrogen. It is agreed that the titanium-palladium alloys should exhibit a higher H_C than titanium alloys without Pd.^[62] This is due predominantly to the prevention of hydride formation in the matrix as a result of the higher solubility of hydrogen in the palladium-containing intermetallic particles.^[18, 63]

In the absence of experimental data, an approximate H_C value for Ti Grade 24 can be inferred from that of Ti Grade 5 based on a similar comparison to that used to infer the behavior of Ti Grade 7 from that measured on Ti Grades 2 and 16. As illustrated in Figure 1, Ti Grade 5 and Ti Grade 24 have the same mechanical properties (tensile and yield strengths) despite the addition of Pd to the latter, and testing of these two materials in boiling HCl showed that the addition of Pd to Ti Grade 5 improves the alloy's corrosion resistance in an analogous manner to that observed when Pd is added to the Ti Grade 2 alloy to produce Ti Grade 16.^[27, 49, 64] The mechanism by which Pd improves the corrosion resistance of Ti Grade 24 as compared to Ti Grade 5 is expected to be similar to that for Ti Grade 7 as compared to Ti Grade 16, *i.e.*, the accumulation of Pd in the corroding surface ennobles the corrosion potential of the alloys and increases the hydrogen solubility in the alloy.

For pre-cracked compact tension specimens pre-charged with known amounts of hydrogen, the fracture toughness of Ti Grade 5 was shown not to alter until the hydrogen level in the alloy exceeded 200 $\mu\text{g/g}$.^[65] For smooth tensile specimens, the reduction in area and elongation of Ti Grade 5 did not decrease until the hydrogen concentration reached about 1,500 ppm.^[65] Based on these values and the analogy above for Ti Grade 16 and Ti Grade 7, it can be conservatively estimated that H_C for Ti Grade 24 should be in the range of 400 - 600 $\mu\text{g/g}$, if not higher. This estimated value of H_C is conservative. For instance, Kitayama et al.^[64] evaluated

the effect of Pd addition to Ti-6Al-4V (Ti Grade 5) and Ti-3Al-2.5V (Ti Grade 9) on their hydrogen-induced cracking behavior. By cathodically charging hydrogen into Pd-containing Ti-6Al-4V (an equivalent to Ti Grade 24) to approximately 1,000 and 1,100 ppm, the 0.2 percent proof stress was found to be 175 and 145 ksi, respectively,^[64] suggesting that no degradation in mechanical properties at this level of hydrogen content.

MODELING HIC OF TITANIUM ALLOYS

Attempts have been made to evaluate the hydrogen content in Ti Grade 7 for passive general corrosion and galvanic corrosion under repository conditions and thus to determine whether the drip shield could fail by HIC within 10,000 years of emplacement.^[18, 61]

Shoesmith et al.^[18] derived that the concentration of hydrogen in titanium (H_A , in g/mm^3) can be calculated as a function of corrosion rate and time of emplacement (t in years) according to Eq. 1:

$$H_A = 4 \times 10^6 f_h R_{uc} t [M_{Ti} (d_o - R_{uc} t)]^{-1} \quad (\text{Eq. 1})$$

where H_A is the hydrogen content (g/mm^3), ρ_{Ti} is the density of Ti (4.50 g/cm^3),^[66] f_h is the fractional efficiency for hydrogen absorption, R_{uc} is the rate of general passive corrosion (mm/yr), t is the time of emplacement (years), M_{Ti} is the atomic mass of Ti (47.9 g/mol)^[66] and d_o is the half thickness of the metal.

The measured general corrosion rates for Ti Grade 16 and Ti Grade 7 in repository relevant environments (from weight change measurements) are shown in Table 1.^[50] Table 1 These corrosion rates measured on planar and creviced specimens, are used to calculate the corrosion rates of the inner and outer surfaces of the drip shield, respectively. The average of the maximum values in Table 1 are used to estimate the hydrogen content in the metal according to Eq 1. It should be pointed out that the upper boundary of the fractional efficiency of hydrogen absorption, f_h , for titanium alloys, in the range of 0.005 to 0.015 as reported by Okada,^[32] is used for modeling HIC. As discussed earlier, the test conditions under which the f_h values were obtained by Okada are unachievable in the repository. Furthermore, f_h decreases with time.^[25, 44]

Using a constant value of 0.015 as the fractional hydrogen absorption efficiency is exceedingly conservative in comparison with the f_h value of 0.00014 reported by Tomari et al. ^[44] on the basis of experiments conducted for 1,440 hours under electrochemically polarized conditions.

Table 1. Summary of 1-year, 2.5-year and 5-year corrosion rate data^[50] and hydrogen contents in Ti Grade 7 10,000 years after emplacement^[61]

	Corrosion Rate, nm/yr					
	1 -Year, Ti Grade 16		2.5-Year, Ti Grade 7		5-Year, Ti Grade 16	
Specimen Type	Weight-Loss	Crevice	Weight-Loss	Crevice	Weight-Loss	Crevice
Median	0	0	6	3	5	10
Maximum	113	319	50	38	58	77
Hydrogen Concentration in Metal 10,000 Years after Emplacement, $\mu\text{g/g}$						
	510		78		124	

Thus, using $f_h = 0.015$, $d_o = 7.5 \text{ mm}$, $t = 10,000 \text{ years}$ and the average values of the maximum corrosion rates in Table 1, Eq. 1 yields $H_A = 510, 78$ and $124 \mu\text{g/g}$, respectively, based on the 1-year, 2.5-year and 5-year corrosion rate data of LLNL also shown in Table 1. Under all circumstances, the hydrogen content in Ti Grade 7 and Ti Grade 16 is well below the critical hydrogen concentration, H_C of $1,000 \mu\text{g/g}$.^[61]

A mathematical model has been proposed to predict the hydrogen concentration in the drip shield due to galvanic coupling between the drip shield and a carbon steel segment assuming (1) The drip shield, with a thickness of h , is treated as an infinite plate, (2) the area of galvanically coupled wetted surface is considered circular in shape with a radius r_o , (3) hydrogen is absorbed into the drip shield through the contact plane and immediately reaches the other surface and (4) as hydrogen starts to diffuse in the drip shield, the radius of the circular region will expand at a constant speed v . The hydrogen content at location r at time t is shown to be^[61]

$$H_A(r) = \lambda \left(t_{\max} - \frac{r - r_o}{v} \right) \quad \text{for} \quad r_o \leq r \leq r(t_{\max}) \quad (\text{Eq. 2})$$

where λ is the hydrogen absorption rate in ppm (or $\mu\text{g/g}$) /day and $t_{\max}$ is the time at which the absorbed hydrogen concentration is maximized. The corrosion potential of carbon steel is

estimated to be about $-0.6 V_{(SCE)}$, the potential to which a galvanic couple would be expected to polarize Ti. Murai et al. showed that the maximum value of λ measured in the potential range $-0.6 V$ to $-1.0 V_{(SCE)}$ is $\sim 0.7 \mu\text{g/g/day}$.^[20] Therefore, this value is adopted as the maximum λ value in this sensitivity study. No data are available for the hydrogen diffusion rate, v , of Ti Grade 7. For the base case of the numerical example, the values used for λ and v are, respectively, $0.5 \mu\text{g/g/day}$ and 1 mm/day . For the parametric study, $\lambda = 0.5, 0.7 \mu\text{g/g/day}$, and $v = 1, 2, 3 \text{ mm/day}$ are also considered. The parametric study showed that in all cases, the hydrogen concentration does not exceed the critical hydrogen concentration of $1000 \mu\text{g/g}$ for Ti Grade 7 by a rather comfortable margin.^[61]

CONCLUDING REMARKS

Addition of $0.12 - 0.25 \text{ wt\%}$ palladium to pure titanium does not alter its microstructure (and, therefore, the mechanical properties) but significantly improves its corrosion resistance. Although alloying elements including palladium lower the threshold potential for hydrogen uptake, experimental evidence indicates that enhancement of hydrogen absorption due to Pd addition is minor. Other alloying elements can influence hydrogen absorption into titanium alloys through the formation of intermetallics which act both as "hydrogen windows" and hydrogen storage sites. The influence of a surface oxide on the absorption efficiency is remarkable, and the presence of passive oxides has been shown to almost completely suppress hydrogen absorption even in hot aggressive brine environments.

The H_C value for Ti Grade 16 is between 1000 and $2000 \mu\text{g/g}$. By analogy, it has been rationalized that the H_C for Ti Grade 7 is at least $1,000 \mu\text{g/g}$. Considering the higher strength of Ti Grade 24 compared to Ti Grade 16 and Ti Grade 7 and the H_C value of the similar, but non Pd-containing Ti Grade 5, it can be estimated conservatively, that the H_C of Ti Grade 24 should be in the range of $400 - 600 \mu\text{g/g}$, if not higher.

By using the average value of the maximum corrosion rates measured in 1-year (Ti Grade 16), 2.5-year (Ti Grade 7) and 5-year (Ti Grade 16) immersion tests, , and the conservative upper boundary of the fractional efficiency of hydrogen absorption, f_h (0.005 to 0.015) for titanium

alloys, the hydrogen concentrations in the alloy 10,000 years after the emplacement are estimated to be 510, 78 and 124 $\mu\text{g/g}$, respectively. These values are all well below the estimated critical hydrogen concentration (H_C).

Based on the models developed, which use conservative values for all parameters used, it can be conservatively concluded that the hydrogen absorbed due to passive general corrosion and galvanic coupling to carbon and stainless steels will not be sufficient for hydrogen-induced cracking to occur in Ti Grade 7 10,000 years after the emplacement.

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