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Electrochimica Acta 52 (2006) 1169–1181
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Hydrogen absorption into alpha titanium in acidic solutions

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Received 4 July 2006; received in revised form 10 July 2006; accepted 10 July 2006
Available online 24 August 2006

Abstract

The absorption of hydrogen into commercially pure alpha titanium (Grade-2) has been studied on oxide-free ($pH \leq 3$) surfaces at 25 °C under both potentiostatic and galvanostatic conditions. The rate of hydrogen absorption was found to be extremely rapid on oxide-free surfaces and the formation of surface hydrides catalyzed the proton reduction process. Complete hydride coverage of the surface very significantly suppressed the rate of hydrogen absorption, which is consistent with the known decrease in diffusivity of hydrogen in the hydride phase. SIMS imaging showed that absorption occurred preferentially at iron-containing intermetallic particles located along grain boundaries, leading to the coexistence of cathodically active hydrided sites and anodically active alpha titanium sites.

Keywords: Ti alloys; Hydrogen absorption; Catalysis; SIMS; Iron-containing β-phase and intermetallics

1. Introduction

Because of their excellent corrosion resistance, alpha and near alpha alloys of titanium are commonly employed when aggressive corrosion conditions are encountered. For this reason, the Pd-containing Grade-7 alloy is a candidate material for the fabrication of sections of the engineered barriers system in the proposed high level nuclear waste repository at Yucca Mountain, NV, USA [1]. The anticipated corrosion performance in this application has been reviewed [2] and models developed to predict corrosion performance [3–5]. If failure by corrosion is to occur eventually it is likely to be due to hydrogen-induced cracking (HIC) as a consequence of hydrogen absorption.

Although crevice corrosion is not anticipated under Yucca Mountain conditions it is the most likely condition by which hydrogen absorption can occur in this application [6,7]. We have undertaken extensive studies on the crevice corrosion of alpha titanium materials, with a primary emphasis on determining the influence of environmental [8,9] and metallurgical [10,11] variables on the accumulation of corrosion damage. These studies show that ≥80% of the crevice corrosion processes sustained is driven by proton reduction within the acidified crevice area, a process that leads to considerable hydrogen absorption by the active metal surface [12]. Consequently, even if failure by crevice corrosion is avoided, the alloy may be rendered susceptible to HIC. Whether or not HIC will then occur will be determined by a combination of the rate and extent of hydrogen absorption and the distribution of stresses within the crevice corroded area.

Numakura and Koiwa [13] reported that in the α-alloys of titanium at low temperatures, i.e., 40–60 °C, titanium hydride could form three different crystal structures and morphologies depending on the different values of x in TiH_x: γ hydride (the ordered face-centered tetragonal structure) with a low hydrogen concentration ($TiH_{0-1.5}$); δ hydride (face-centered cubic structure) with an intermediate hydrogen concentration ($TiH_{1.5-1.9}$); and ε hydride (face-centered tetragonal structure) with a high hydrogen concentration ($TiH_{1.9-2.0}$). Since hydride precipitation in alpha titanium causes a 15–21% volume increase, large compressive stresses are induced in the matrix [14], providing the main contribution to hydrogen embrittlement.

The α-alloys of titanium possess a hexagonal close-packed crystal structure with a low solubility for hydrogen (20–100 $\mu g\,g^{-1}$ at room temperature [15]), and when this is exceeded, brittle titanium hydrides are readily formed. Near α-alloys contain small amounts of the body-centered cubic β-

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0013-4686/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2006.07.017

phase in which the hydrogen solubility is considerably greater (>9000 μg g^{-1} [15]). In a hydrogen gas environment at 400 °C, the solubility of hydrogen goes up to around 1800 μg g^{-1} in α-phase titanium and more than 2×10^4 μg g^{-1} in β-phase titanium [16]. As a result of this large difference, strong effects of alloy microstructure on HIC are encountered [17].

Metallurgical features, i.e., alloying content, can also be expected to influence hydrogen absorption. Alloying elements (Ni/Mo, Pd, Ru) are added to α-Ti primarily to enhance corrosion resistance in the reducing acidic conditions that prevail within actively propagating crevices [18–20]. These improvements are generally achieved by the depolarization of the cathodic reduction of protons. However, alloying additions capable of catalyzing proton reduction are likely also to catalyze hydrogen absorption. Fukuzuka et al. [21] showed that proton reduction occurred at much lower overpotentials on Pd-containing alloys than on the commercial Grade-2, and that there was a clear correlation between the alloy corrosion rate under reducing acid conditions and the rate of hydrogen absorption. This catalysis is indicated by a reduction in the Tafel slope for proton reduction (from >−120 mV^{-1} to −50 to −60 mV^{-1}). A similar effect was observed by Schutz and Xiao [22] whose measured Tafel slopes indicate that the ability to catalyze proton reduction decreases as the Pd content in the titanium decreases.

The presence of intermetallics (e.g., Ti_2Ni in the Ni/Mo-containing Grade-12 alloy) and the ubiquitous impurity, Fe, can also influence hydrogen absorption. Glass [23] demonstrated that the galvanic coupling of α-Ti to Ti_2Ni in boiling HCl (a situation which simulates active crevice conditions on the Grade-12 alloy) led to embrittlement of the intermetallic. However, the results on the influence of Fe which can also form intermetallics [24], on hydrogen absorption are inconclusive and often contradictory. Cotton [25] showed that the extent of hydrogen absorption increased with alloy Fe content (0.05–0.12 wt%) whereas, under cathodic charging conditions, Covington and Schutz [26] measured a decrease in hydrogen absorption efficiency over the same Fe content range. These inconsistencies may reflect uncertainty over the presence and performance of Ti_xFe intermetallics, which have been shown to absorb hydrogen but to possess unpredictable absorption kinetics [27,28].

For sufficiently aggressive crevice corrosion conditions, a surface hydride (TiH_x) layer is formed on the corroding surface [6,29], and numerous investigators have looked at the characteristics of such layers under cathodic charging conditions [30–37]. These studies show that while the rate of hydrogen absorption could initially be linear, suggesting rapid absorption, it eventually became parabolic as diffusion of hydrogen through the surface hydride layer to the metal/TiH_x interface became rate-controlling. Phillips et al. [30] calculated that the H/Ti ratio in the hydride increased from 1.2 to 1.5 as the applied current density was increased over the range 0.05–3.0 mA cm^{-2} (in 0.05 mol L^{-1} H_2SO_4). These claims are consistent with the higher, current-dependent ratios (1.62–1.78) obtained at higher current densities (5–20 mA cm^{-2}) and measured by X-ray diffraction [38]. Phillips et al. found that the hydrogen absorption rate remained parabolic but increased with temperature (25–100 °C).

Table 1
Composition (wt%) of Ti materials used in the experiments

	Fe	C	O	N	Ni	Ti
Ti-2a	0.122	0.010	0.127	0.010	0.017	Balance
Ti-2b	0.107	0.010	0.127	0.010	0.019	Balance
Pure Ti	Total impurities < 0.01					99.99

Here, we present a more detailed study on the kinetics of proton reduction and hydrogen absorption by Grade-2 (commercially pure) titanium. This is an essential step towards our primary goal of determining the kinetics of absorption and transport of hydrogen in a range of alpha and near-alpha alloys, in order to predict and model the process of HIC. We are particularly interested in the long-term performance of the alloys in corrosive industrial environments with a special emphasis on their use in nuclear waste disposal applications [2–5,39,40].

2. Experimental

2.1. Material compositions

Three different materials were used; the compositions of these materials are shown in Table 1. Both Ti-2a and Ti-2b are commercially pure Grade 2 Ti alloys from the same company (RMI Titanium Company, Niles, OH, USA), but with different heat numbers. Their compositions are slightly different from each other. Ti-2a was used for cathodic potentiostatic and galvanostatic polarizations; Ti-2b was used for anodic potentiostatic polarizations and SIMS analyses. Pure Ti was mainly used for comparison experiments.

2.2. Experimental cell and solution

A three-electrode cell with separate compartments for the reference and counter electrodes was used. The counter electrode was a piece of Pt foil rolled up to form a cylinder and the reference electrode was a commercial saturated calomel electrode (SCE). All potentials were quoted against this reference scale.

A 0.27 mol L^{-1} NaCl solution containing various amounts of HCl was used in cathodic potentiostatic polarization experiments to investigate the effect of pH and temperature. In galvanostatic and anodic potentiostatic experiments designed to investigate hydride formation and its effect on H^+ reduction and H absorption, a 0.27 mol L^{-1} NaCl plus 0.60 mol L^{-1} HCl solution was used. All the solutions were prepared with ultrapure water (produced by a Millipore system to yield a resistivity of 18.2 MΩ cm). The electrolyte solution was deaerated in the electrochemical cell with Ar for 20 min prior to each experiment, and continuously for the duration of the experiment.

2.3. Working electrode preparation

Two different types of working electrode were used. Disk electrodes were used in electrochemical experiments not involving hydrogen absorption measurements. Each disk electrode had