HYDROGEN ABSORPTION INTO ALPHA TITANIUM ALLOYS

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Abstract: Ti-2 alloy electrodes were cathodically polarized with constant current in acidified NaCl solution to investigate the influences of current density on hydrogen uptake. It was found that the hydride formed on the surface of the electrode catalyzed the proton reduction reaction. The hydrogen evolution mechanism changed with current density and polarization time. The total absorbed hydrogen increased over the current density range of 0.01 to 3.0 mA/cm$^2$. The hydride layer thickened with increasing current density. However, the composition of the hydride didn’t change much with current density. With TiH$_x$ layer thickening, the hydride formed on the surface showed both electrical resistance and physical blocking effects, causing the absorption efficiency decreased from more than 50% at 0.05 mA/cm$^2$ to 1.96% at 3 mA/cm$^2$.

Key words: Hydrogen absorption; Ti-2 alloy; Galvanostatic polarization; Hydrogen absorption efficiency; Hydride layer

Introduction

Hydrogen absorption leading to hydrogen-induced cracking (HIC) is a well documented mode of failure for titanium alloys. Corrosion can lead to hydrogen absorption into Ti alloys by two main routes: (a) via crevice corrosion, and since there is only a very thin oxide film on the surface of the electrode, hydrogen can be absorbed relatively rapidly; (b) via passive corrosion, when hydrogen absorption will be slow because of the presence of an oxide film. Here we focus primarily on hydrogen absorption under simulated crevice corrosion conditions.

Hydrogen absorption is industrially expressed as the hydrogen uptake efficiency or hydrogen absorption efficiency. The quantity can be defined as the fraction of the hydrogen produced electrolytically that is absorbed into the metal [1]. The key factors that affect hydrogen absorption are as following: i) the alloy microstructure; ii) alloying additions (Ni, Mo, Pd) and impurities (Fe); iii) pH; iv) oxide film; v) temperature; and iv) surface preparation.

Qin and Shoesmith [2] have developed a model to predict when failures caused by HIC might occur. This model is very conservative in the assumption that absorbed hydrogen is immediately distributed throughout the alloy, but it only takes into account the hydrogen produced by general corrosion. It does not include the possibility that a period of crevice corrosion, while not challenging the integrity of the structure by wall penetration, could lead to a significant amount of hydrogen absorption. Our primary goal is to improve this model by modifying some of the over-simplified assumptions used, and by measuring improved values for the key modelling parameters.

Experimental

The experimental cell (Fig. 1) was a three-electrode cell with two side arms for the reference and counter electrodes. The reference electrode was a commercial saturated calomel electrode (SCE), and the counter electrode was a piece of Pt foil rolled up to form a cylinder in the counter electrode compartment.

The nominal dimensions of the simulated crevice corrosion electrodes were 10 mm × 5 mm × 4 mm. The electrodes were polished with wet carbide sand paper in the sequence 120,
220, 320, 500, 600 grit. The samples for the images were polished further to 50 nm with aluminum oxide powder. All the experiments were done with freshly polished surfaces.

The solution was a mixture of 0.27 mol·L\(^{-1}\) NaCl and 0.60 mol·L\(^{-1}\) HCl. Deaeration was accomplished by bubbling Ar gas through the electrolyte to exclude air from the cell during the experimental duration. All of the electrodes were from the same Ti-2 plate. The chemical composition of this Ti-2 plate is shown in Table 1:

| Composition (wt%) of Ti Grade-2 used in the experiments |
|---------------------------------|--------|--------|--------|--------|--------|--------|
| Fe  | C     | O      | N      | Ni     | Ti     |
| Ti-2 | 0.110 | 0.010  | 0.127  | 0.010  | 0.023  | Bal.   |

**Results and Discussion**

**Galvanostatic polarization**

All of the Experiments were carried out with Ti-2 alloy electrodes at 25ºC for 96 hours in the solution of 0.27 mol·L\(^{-1}\) NaCl plus 0.60 mol·L\(^{-1}\) HCl. Fig. 2 shows the potential response as a function of applied current density.

Initially, the potential was very negative, and was more negative the larger the applied current. The potential increased over the subsequent 20–30 hours. The potential increase was much more marked for the higher current density experiments. In the period 30–40 hours, the potential began to reach a plateau. At the longer times, the potential at high current densities decreased. Hackerman and Hall [3] observed the same potential trends during cathodic polarizations in 0.5 mol·L\(^{-1}\) NaCl solution. They also found the potential increased at the beginning and that the higher the current density, the faster the potential reached a plateau. Unfortunately, they didn’t perform long time polarizations for high current densities, so they didn’t see the later potential decreases.

Here, the main reaction steps involved in this system, and the Tafel slopes [4] expected if they are the rate determining steps (RDS), should be introduced before the explanations of those observations are proposed. The mechanism requires two steps:

\[
H^+ + e^- + Ti \rightarrow TiH_{ads} \quad (A) \quad -120 \text{ mV/decade}
\]
followed by hydrogen desorption

$$2\text{TiH}_{\text{ads}} \rightarrow 2\text{Ti} + \text{H}_2$$ \hspace{1cm} (B) \hspace{1cm} -30 \text{ mV/decade}

or

$$\text{TiH}_{\text{ads}} + \text{H}^+ + \text{e}^- \rightarrow \text{Ti} + \text{H}_2$$ \hspace{1cm} (C) \hspace{1cm} -40 \text{ or } -120 \text{ mV/decade}

or hydrogen absorption

$$\text{TiH}_{\text{ads}} \rightarrow \text{TiH}_{\text{abs}}$$ \hspace{1cm} (D) \hspace{1cm} -60 \text{ mV/decade}

Since the reactions B, C and D proceed in parallel with each other, and in series with reaction (A), the rate determining step will be the slower of reaction A and the fastest of the second mechanistic step reactions (B, C, or D).

At the beginning of the polarization, the surface of the metal was fresh and the surface coverage by hydride was low. Since the Ti-H bond is strong [4], reaction A happened faster than all the other three reactions. Reaction B was the slowest. The hydrogen absorption efficiency was relatively high at this moment. From the hydrogen analysis results (Fig. 5 (a)) we noticed that for low current densities ($I < 0.18 \text{ mA/cm}^2$), the hydrogen absorption efficiency could be larger than 50%, but for the high current densities, it was still lower than 50%. That means the rate of reaction C was higher than that of reaction D at high current densities. So the rate determining step should be reaction C at high overpotential, Fig. 4 (a). The plot of Log($I$) vs potential also confirmed this statement. It had a slope of -129 mV/decade ($I$) which was close to the Tafel slope of the one-electron reduction, Fig. 3 (a), which was in good agreement with Thomas and Kobe’s explanation to the determining step for HER within the Tafel region [5].

At 35 hours, Fig. 4 (b), reaction A could be catalyzed by hydride formation and the potential was relaxed to a lower overpotential. The rate of reaction A was still high. With the surface coverage of hydride becoming higher and higher, the surface became saturated with hydride. Reaction D became slower and slower. At this time the Ti-H bond was not as strong as on the fresh surface. Reactions B and C became easier compared to their behaviours at the beginning of the period. As Fig. 3 (b) showed, the slope switched from about $-120 \text{ mV}^{-1}$ at the beginning to a higher value. At the high current densities, the transition in RDS was achieved and the polarization curves reached the slope of $-40$ or $-30 \text{ mV/decade}(I)$. At the low current densities, the switch in RDS was unfinished. The $-40$ or $-30 \text{ mV/decade}(I)$ slope means the rate determining step was reaction C at low overpotentials or reaction B.

For the longer times, the thickening hydride layer produced two conflicting effects on hydrogen evolution: catalysis of the proton reduction reaction, but also action as a resistive barrier on the electrode surface. Whether or not polarization of the hydrogen evolution reaction increased (i.e., the measured potential decreased with time) depended on which of these effects predominated. For lower current densities, the potential remained at a steady state, suggesting that these two conflicting effects canceled each other. The potential at high current densities decreased, indicating an increased polarization of the H$^+$ reduction reaction. This was presumably attributable to an increase in the thickness of the surface TiH$_x$ layer, leading to an increased resistance to electron or H atoms transport through the surface. Reaction A was slowed by the resistive hydride layer and gradually became the rate determining step, Fig. 3 (c) and Fig. 4 (c).

**Results of Hydrogen analysis**

The electrodes charged from the galvanostatic polarization were analyzed by the hydrogen analyzer to determine the hydrogen content. The hydrogen content in the metal was measured using a RH-404 hydrogen determinator (LECO Corporation). The accuracy of this technique is ±0.05 ppm
or ±2% of a reading, and the precision is ±0.01 ppm or 0.1% of a reading (whichever is greater). The relationships between hydrogen absorption, absorption efficiency and the current density at 25°C are shown on Fig.5.

Fig. 5 (a) and (b) show that the hydrogen content increased with current density. The absorbed hydrogen thickened the hydride layer. However, the absorption efficiency decreased dramatically with increasing current density. The absorption rate and absorption efficiency were high as the current densities were low (i.e. 0.01 mA/cm², 0.05 mA/cm²). The absorption efficiency dropped from more than 50% at 0.01 and 0.05 mA/cm² to 1.94% at 3 mA/cm². This was consistent with Phillips et al.’s [6] results. They observed that both absorbed hydrogen and the thickness of hydride layer increased parabolically with charging time. However it disagreed with Noël’s [1] results. Noël obtained that the hydrogen absorption efficiency was only related to the total charge passed, while it was almost independent on the applied current densities over the current range of 0.19 mA/cm² to 1.9 mA/cm².

Fig. 3 The plots of Log (I) vs E for different polarization times derived from Fig. 2, k is the slope value of the best fit line in plots (a) and (c). In plot (b), the data are plotted beside three lines drawn illustrate the slopes expected from theory if reaction A, B, or C were rate determining; (a) log(I) vs E at 5 hours; (b) log(I) vs E at 35 hours; (c) log(I) vs E at 90 hours

Fig. 4 Mechanisms of hydrogen evolution at different polarization times at 25°C in the solution of 0.27 mol·L⁻¹ NaCl plus 0.60 mol·L⁻¹ HCl: (a) the mechanism at the beginning of the polarization; (b) the mechanism at about 35 hours; (c) the mechanism at the end of the polarization

The hydride that was formed showed both electrical resistance (increased overpotential for
proton reduction at high current densities for polarization times longer than 50 hours) and physical blocking effects (low hydrogen absorption efficiency). The images from the optical microscope show that the hydride layer formed at 25°C was smooth, compact and composed of a single layer (Fig. 6). At very low current densities, i.e., 0.01 mA/cm², a discontinuous thin layer was formed on the surface of the metal, which showed a weak blocking effect (i.e., high hydrogen absorption efficiency and a plateau of potential for long time polarization). The hydride layer became thicker with increasing current density, reaching almost 25 µm at 3 mA/cm². The thickening layer showed more and more evident blocking effects on hydrogen absorption (i.e., low hydrogen absorption efficiency and increased overpotential for long time).

Fig. 5 hydrogen analysis results for the galvanostatic polarization experiments at 25°C in the solution of 0.27 mol·L⁻¹ NaCl plus 0.60 mol·L⁻¹ HCl: (a) relationship of hydrogen content and absorption efficiency to current density; (b) relationship of thickness of the hydride layer and absorption efficiency to current density; (c) relationship between hydrogen content and thickness of the hydride layer; (d) relationship between hydride composition and current density.

The curve of hydrogen content vs thickness of hydride layer was plotted out (Fig. 5 (c)). The linear relationship between hydrogen content and the thickness of the hydride layer at 25°C means the average composition of the hydride (x value of TiHₓ) did not change much (Fig. 5 (d)). The chemical properties of the hydride layer should not change a lot, but with the hydride layer thickening, the resistance of the layer was physically enhanced. A plot of the hydrogen content vs the hydride layer thickness is given in Fig. 5 (c). This helped to explain the increase of polarization for longer times. The error bars of Fig. 5 (c) and (d) show that the measurement of the hydride layer thickness was not as accurate as that of the hydrogen content. The thickness measurement error could be as high as 57.6% (at 0.18 mA/cm²), so the values of the thickness of the hydride layer were only used as reference values. However, Philips et al. [7] found that the composition of the hydride layer significantly increased with current density. It was unrelated to the charging duration. Their values for the average composition of hydride are shown in table 2. Our data show that the thickness of the hydride layer was not very uniform across the hydrogenated surface. The measurement error could cause much bigger differences
than the increase of composition with current density reported by Philips et al. Because they did not show the measurement error, their conclusion that the average composition of hydride increased with current density is debatable.

Table 2 Effect of current density on the average composition of the hydride [7]

<table>
<thead>
<tr>
<th>Current density (mA/cm²)</th>
<th>Average composition of hydride (H/Ti atom ratio)</th>
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</thead>
<tbody>
<tr>
<td>3.0</td>
<td>1.48</td>
</tr>
<tr>
<td>1.0</td>
<td>1.39</td>
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<tr>
<td>0.3</td>
<td>1.31</td>
</tr>
<tr>
<td>0.1</td>
<td>1.21</td>
</tr>
</tbody>
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Conclusions

From the experimental results, the following conclusions are drawn:
1. The hydride layer that formed on the Ti-2 electrode surface catalyzed the proton reduction reaction, but also acted as a barrier for hydrogen absorption.
2. At 25°C, the total absorbed hydrogen amount increased with current density, while the absorption rate and efficiency decreased rapidly.
3. The composition of the hydride layer didn’t change much with current density. However, the resistance of the hydride layer increased with hydride layer thickening.

Reference

2. Z. Qin and D.W. Shoesmith, "Lifetime Model for Ti-7 Drip Shields within the Yucca Mountain Repository", Proc. of NACE Northern Area Eastern Conf., Ottawa, ON,, 2003, NACE International, Houston, TX

Fig. 6 Optical microscopy of hydride layers (the cross sections of the galvanostatic polarization electrodes) at different current densities: (a) 0.01 mA/cm²; (b) 0.25 mA/cm²; (c) 3 mA/cm²