

Prevention of Hydrogen Degradation in Titanium by Deposition of TiN Thin Film

S.-C. Lee, W.-Y. Ho, and T.-M. Chen

This paper describes the effects of using a TiN film as a possible protection layer for titanium in an aggressive chemical environment. The TiN film as a barrier of hydrogen permeation into the material was evaluated by electrochemical cathodic charging of the specimens in solutions with different pH values and temperatures. Results revealed that the thickness of hydride on the surface of the uncoated titanium increased with the increase of charging time. Higher charging temperature and lower pH value promoted the formation of hydride phases. For titanium coated with a TiN film, it effectively retarded the permeation of hydrogen into the titanium substrate. However, this was at the sacrifice of the TiN film itself.

Keywords

cathodic charging, hydrogen degradation, plasma nitriding, TiN thin film, titanium

1. Introduction

TITANIUM and titanium alloys are widely used in many applications, such as airframe, pressure vessel, steam turbine blades, marine components, etc. Titanium and titanium alloys are susceptible to hydrogen embrittlement. The effect of hydrogen on the mechanical properties of pure titanium is to decrease notch toughness without affecting tensile properties (Ref 1). Nelson et al. (Ref 2) demonstrated that embrittlement of Ti-6Al-4V alloy with α - β structures was caused by the segregation of hydrogen at the α - β interphase boundaries. Segregation reduces the cohesive strength of the boundaries and promotes intergranular fracture. Fracture toughness of Ti-6Al-4V is also significantly decreased with the embrittlement caused by higher hydrogen content (Ref 3). Current methods of alleviating the hydrogen embrittlement and hydrogen attack problems were evaluated by many authors (Ref 4-7). Surface modification is considered one of the methods and is becoming increasingly important for titanium alloys of technical and economic value. Murray (Ref 5) suggested that both metallic and nonmetallic solid films on the substrates can prevent or reduce hydrogen entry if the film possesses less binding energy for hydrogen than the base material, or low solubility and/or low diffusivity for hydrogen.

Titanium and titanium alloys generally exhibit poor wear resistance due to their low surface hardness. Plasma nitriding to form a hard layer such as a TiN film on the surface can resolve this problem (Ref 8-10). Because of TiN film on titanium alloy, the mechanism of hydrogen permeation may be changed. In reviewing the reports on hydrogen embrittlement of titanium alloys (Ref 2, 11-13), apart from hydrogen charged in gaseous environment with variations of hydrogen pressure and gas composition (Ref 2), cathodic charging of hydrogen in order to simulate severe environment is also frequently reported by many researchers (Ref 11-13). Thus, this research adopted

cathodic charging of hydrogen into titanium deposited with TiN thin film in order to evaluate the feasibility of preventing hydrogen embrittlement of the titanium.

2. Experimental Procedure

Pure titanium used in this study was obtained commercially in solution-treated, 3-mm-thick sheet. The chemical composition is as shown in Table 1. Specimens from the sheet metal were cut into 3 × 3 cm coupons, metallographically polished prior to the test in order to remove oxide or hydroxide layer on the surface, which might act as barriers to hydrogen uptake or cause poor adherence of TiN thin film.

A low voltage, electron beam (LV-EB) evaporation technique was used as the surface modification method for the specimens. TiN depositions were carried out in a commercial batch-type physical vapor deposition (PVD) system. The essential process parameters for the TiN deposition included sputter-etching in order to further clean the substrate and TiN coating deposition later on. The substrate temperature was kept below 450 °C, and the total gas pressure of the Ar+N₂ gas mixture was maintained at 0.2 Pa during deposition. The detailed process of TiN deposition conducted by a LV-EB technique is described elsewhere (Ref 14). X-ray diffraction (XRD) analyses with CuK α radiation at the voltage of 40 kV and scanning electron microscopy (SEM) were applied to characterize the microstructure and the morphology of the coated film. Hardness of the film was measured by a Vickers hardness tester with a 10 g load.

Cathodic charging was carried out in three types of solutions, namely, NaOH solution of pH value 12.5, 0.05M (NH₄)H₂PO₄ + 0.04M NaOH solution of pH value 7.5, and HNO₃ solution of pH value 1.5, respectively. Thiourea (1 g/L) was added as a hydrogen recombination poison. Cathodic charging was for 48, 96, or 144 hours. Current density was maintained at a constant value of 1 mA/cm². Subsequent analy-

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Table 1 Chemical composition of pure titanium

N	Composition, wt%			Ti
	H	Fe	O	
0.073	0.005	0.014	0.19	Balance

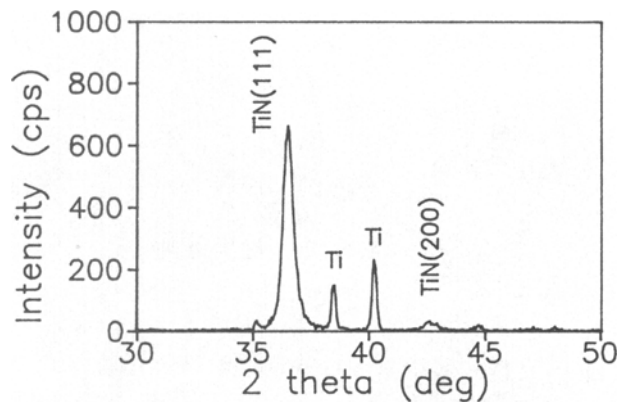


Fig. 1 XRD pattern of TiN coating on titanium substrate

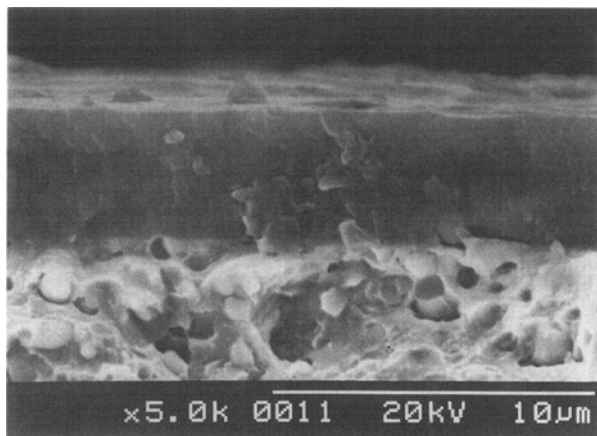


Fig. 2 SEM photograph of the cross-sectional view of TiN film on titanium substrate

sis of the specimens on the effectiveness of the TiN film as a barrier to hydrogen permeation into substrate was conducted immediately after the cathodic charging.

3. Results and Discussion

3.1 TiN Thin Film

TiN thin film deposited on the surface of pure titanium was analyzed using an x-ray diffractometer, as shown in Fig. 1. Diffraction patterns of the coated specimens clearly revealed the TiN peak with (111) preferential orientation. Diffraction peaks of pure titanium were also seen and were the peaks of the substrate. The cross-sectional view of TiN film on titanium observed by SEM is shown in Fig. 2. The thickness of the thin film was $\sim 4 \mu\text{m}$. Surface hardness of TiN-coated specimens measured by Vickers was 1000 HV, whereas the hardness of the as-received alloy was only 350 HV.

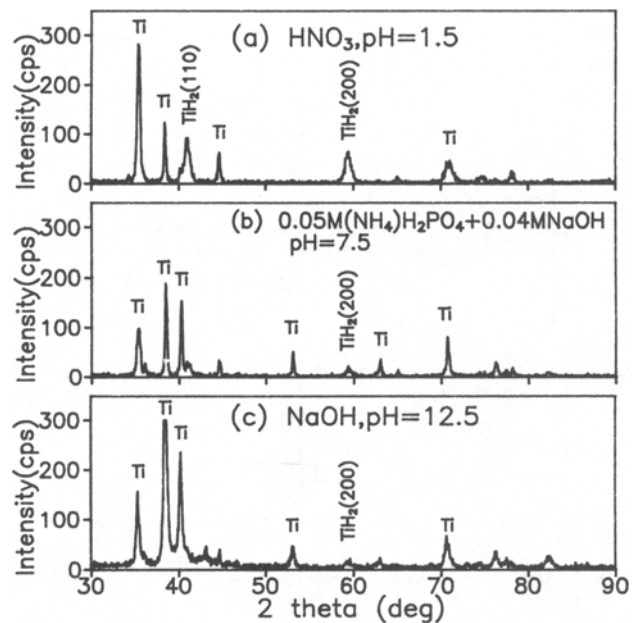


Fig. 3 XRD pattern of pure titanium charged in different solutions of pH values at 25 °C for 48 hours. (a) 0.1M HNO₃, 1.5 pH. (b) 0.05M (NH₄)₂H₂PO₄+0.04M NaOH, 7.5 pH. (c) 0.1M NaOH, 12.5 pH

3.2 Cathodic Charging of Uncoated Titanium

3.2.1 Effect of pH

Cathodic charging of the as-received titanium specimens was conducted in three different kinds of solutions with pH values of 1.5, 7.5, and 12.5, respectively, at 25 °C for 48 hours. Figure 3 shows the diffraction peaks of specimens after such treatments. Diffraction peaks of TiH₂ hydride phase in the preferred (200) orientation were seen for all of the solutions. However, a comparison of the peak intensity of the hydride phases in the figure shows that the solution with the pH value of 1.5 (charged in HNO₃ solution) resulted in highest peak intensity of hydrides. Therefore, the rate of hydrogen absorption increased as the pH decreased. Similar results (Ref 14) also have reported that the effects of solutions on the hydrogen permeation depended on the cation compositions and the pH values of solutions. Increasing the pH values of solutions would decrease specimen surface coverage with adsorbed hydrogen atom and subsequently decrease hydrogen absorption. In addition, for NaOH solution with high pH value, formation of hydride layers was retarded by the cation of Na⁺, which accumulated on the oxide film to decrease the hydrogen permeation rate in the substrate.

3.2.2 Effect of Temperature

The influence of temperature on hydrogen charging of uncoated titanium specimens was investigated in NaOH solution at 25 and 57 °C, respectively. Figure 4 shows the XRD analysis results of specimens after cathodic charging at both temperatures. The diffraction peaks of the hydrides TiH₂(200) formed on the substrates at 57 °C were higher than those at 25 °C. Ob-

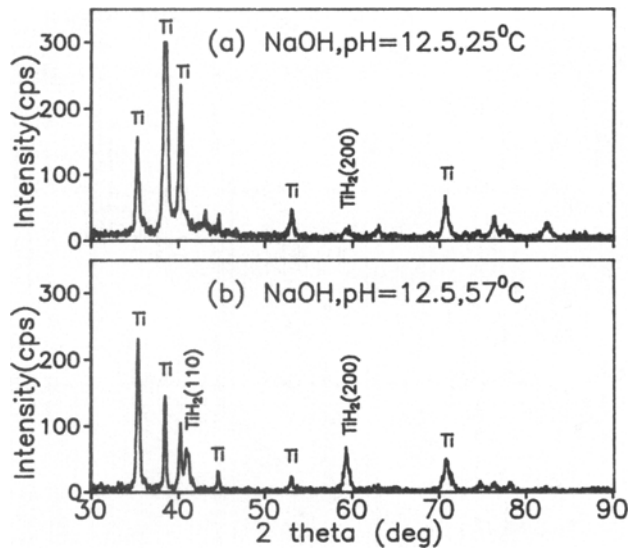


Fig. 4 XRD pattern of pure titanium cathodic charged in NaOH solution of pH value 12.5 for 48 hours

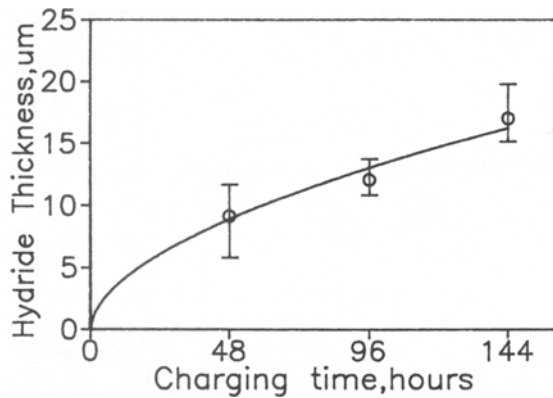


Fig. 5 Effect of cathodic charging time on hydride layer thickness of pure titanium in HNO₃ solution of pH value 1.5 at 25 °C

viously, the rate of hydrogen absorption for titanium increased with increasing charging temperature.

3.2.3 Effect of Charging Time

The effects of cathodic charging time on the hydrogen permeation of as-received titanium were studied by electrochemical charging specimens in HNO₃ solution at 25 °C. Increasing cathodic charging time from 48 to 144 hours increased the thickness of hydrides, but the rate of hydrogen absorption decreased parabolically with charging time (see Fig. 5). Figure 6 shows the cross-sectional view of hydride thickness of specimens after prolonged periods of charging in HNO₃ solution at 25 °C. Obviously, the thickness of hydrides increased with the increase of cathodic charging time. The accumulated hydride thickness of specimens increased as the charging time increased from 48 to 144 hours. On the contrary, the rate of growth of the hydride decreased with increasing charging time.

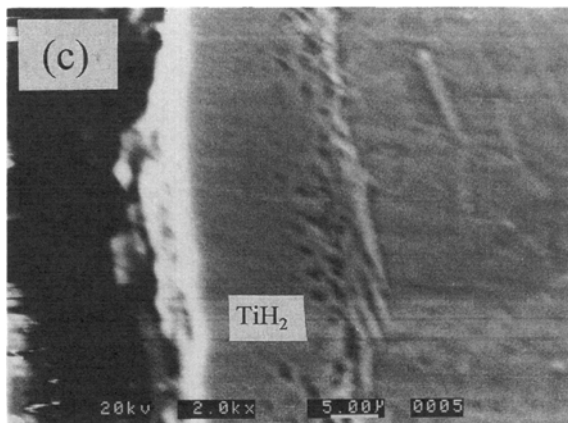
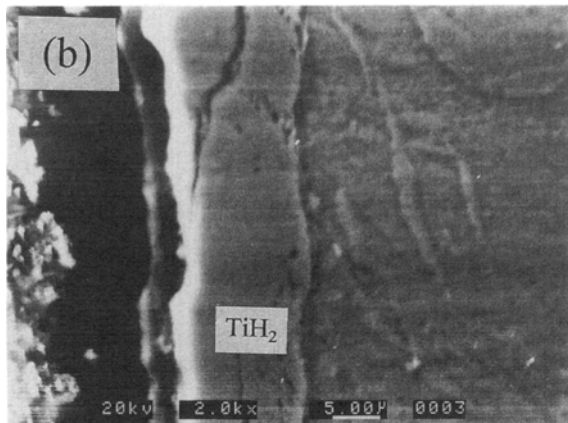
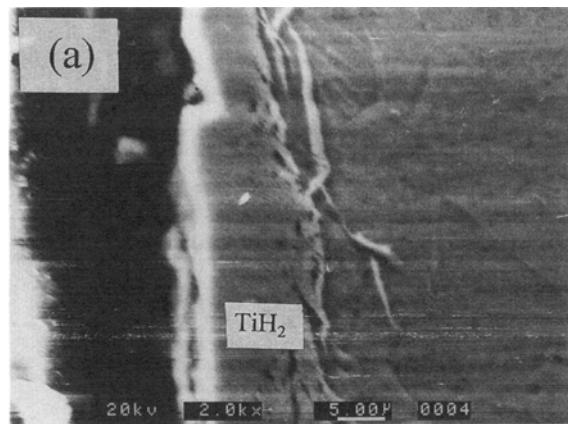


Fig. 6 SEM photomicrographs of the cross-sectional view of thickness of hydride on the pure titanium cathodic charged in HNO₃ solution of pH value 1.5 at 25 °C, for (a) 48 hours, (b) 96 hours, and (c) 144 hours

3.3 Effect of TiN Thin Film on Hydrogen Permeation

The effect of a TiN coating on hydrogen permeation was evaluated by cathodic charging in HNO₃ solution at 25 °C. The results are shown in Fig. 7. Hydride phases were not detected in

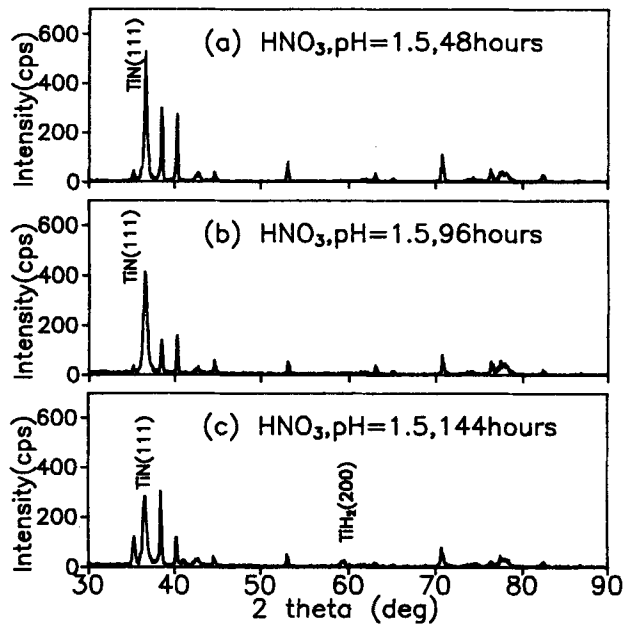


Fig. 7 Effect of TiN film protection on the cathodic charging of pure titanium in HNO_3 solution at 25°C for different periods of time

XRD patterns of samples charged for 96 hours. Even in the specimens charged for 144 hours, only a very small hydride peak was seen. However, the TiN film was attacked and eroded by the charging solution as the charging time increased. Thus, hydride phase formed after charging for 144 hours was the result of the disappearance of TiN film causing hydrogen to penetrate through TiN film and react with titanium substrate.

Therefore, TiN coating can retard the permeation of hydrogen by cathodic charging into the substrate of pure titanium up to 144 hours, with the TiN film thickness of $4\ \mu\text{m}$. Murray (Ref 5) reported that the entry of hydrogen into the substrate retarded by metallic thin film was by virtue of its low solubility for hydrogen, low diffusivity for hydrogen, surface effects involving adsorption, or by combination of these mechanisms. While embrittlement of titanium is associated with the formation of the respective hydride phases, the deposition of TiN film, which possessed chemical stability and good corrosion resistance, apparently served as a barrier to hydrogen permeation into Ti substrate.

4. Conclusions

- The accumulated hydride phases onto titanium materials increased as the charging time, and/or the temperature increased or the pH value decreased.
- The deposition of a TiN film onto titanium apparently served as a barrier to hydrogen permeation into titanium substrate. However, for the experimental conditions that

were used, this was at the sacrifice of the TiN film itself. For a TiN film of $4\ \mu\text{m}$, it took about 144 hours for a titanium hydride to form on titanium substrate by the cathodic charging ($\text{pH}=1.5$) method in this experiment.

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