

Hydrogen Pick-up and Corrosion Behavior of Ti-alloy (PT-7M) in Ammonia Water Chemistry

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1. Introduction

Ti-based alloys have been considered as candidate materials for steam generator tubes of SMART (System-integrated Modular Advanced Reactor), due to the excellent corrosion resistance, good mechanical properties, attractive density, high neutron stability and suitable durability characteristics [1-9]. When the Ti-alloys are exposed to the primary coolant water under high temperature and high pressure in PWRs, some of hydrogen resulting from the reaction of the alloy with water is absorbed into metal, and usually forms hydrides [3]. The hydrides in Ti-alloys are well known to contribute to the loss of ductility in tensile, impact strength, toughness and creep resistance [11]. In this study, long term corrosion and hydrogen pick-up behaviors of PT-7M(Ti-Al-Zr alloy) at 360°C in ammonia water chemistry were investigated. The corrosion rate constants and hydrogen pick-up were evaluated.

2. Experimental Procedure

Ti-Al-Zr alloy tubes (10 mm OD X 7 mm ID) were prepared in extruded and mill-annealed conditions. Corrosion behavior was evaluated in ammoniated water adjusted to pH 10 at 360°C under a pressure of 18.5 MPa for 105 days using a circulating loop system. The water chemistries in the inlet of heating zone (autoclave) were constantly controlled to be about 20 µg/l of dissolved oxygen, 0.2 µg/l of dissolved hydrogen, and 105 µS/cm of conductivity. The corrosion kinetics was determined by the gravimetric method. Hydrogen content of Ti-alloy was analyzed with inert gas fusion thermal conductivity determination method using RH 404 hydrogen determinator (LECO Ltd.).

3. Results and discussion

3.1 Corrosion Behaviors

Fig. 1 shows the effect of oxygen on the corrosion behavior of the Ti-Al-Zr alloy at 360°C in a pH 9.98 ammonia aqueous solution. In high oxygen concentration ($[O_2]=8$ ppm), the weight gain increased very quickly before 100 days, but after this it shows plateau to 350 days. After exposure from 350 to 450 days the weight gain was 25 mg/dm² and it was not increased to 600 days.

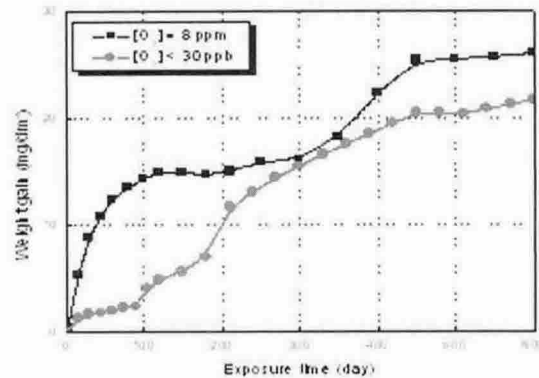


Figure 1. Effect of O₂ content on the corrosion behavior of PT-7M in pH 9.98 ammonia aqueous solution at 360°C.

In low oxygen concentration ($[O_2]<30$ ppb), Ti-alloy has very low corrosion rate before 100 days, and it has 1st and 2nd transition of corrosion rate in 100 and 200 days respectively. After exposure for 450 days the weight gain was revealed about 20 mg/dm² and has plateau. In the early corrosion period, the corrosion rate of PT-7M depends on the oxygen concentration of the environment, but in the late period, it depends on the protective oxide layer. It seems that more protective oxide layer forms in the low oxygen conditions. So after exposure 450 days, the weight gain for low oxygen content was 20% lower than that for higher oxygen content. These results imply that a layer of protective titanium oxide formed on the surface of the sample during corrosion would disturb the diffusion of oxygen through the oxide layer, giving a decrease of corrosion rate as corrosion reaction proceeded. Then, the corrosion rate constant in the low oxygen content could be represented as following equations for each step: Before transition of corrosion rate (~ 100 days)

$$\log \Delta W = -0.236 + 0.310t \quad (1)$$

After 1st transition (100 ~ 200 days)

$$\log \Delta W = -1.273 + 0.938t \quad (2)$$

After 2nd transition (200 ~ 600 days)

$$\log \Delta W = -0.090 + 0.516t \quad (3)$$

where ΔW and t are corrosion rate (in mg/dm²) and exposure time (in days), respectively.

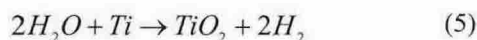
The relationship of weight gain and exposure time could then be derived from equation from (1) to (3), as follows:

$$\Delta W = K \times t^n \quad (4)$$

where K and n are empirical corrosion rate constant ($\text{mg}/\text{dm}^2/\text{day}^n$) and constant, respectively. The corrosion reaction rates showed the cubic, linear and parabolic rate law for before transition, after 1st and 2nd transition, respectively.

3.2 Hydrogen Pick-up

During the corrosion, Ti-alloys have a reaction with water as follows:



Some of hydrogen resulting from the reaction of the alloy with water to form TiO_2 is absorbed into metal. And this hydrogen pick-up fraction into the metal could be calculated by equation (6)[11]:

$$HPUF(\%) = \frac{\left(\frac{m_o}{M_n} - \frac{\Delta m}{2M_o}\right)M_n \frac{(C_H - C_{Hini})}{10^6}}{2M_H \left[\Delta m - \left(\frac{m_o}{M_n} - \frac{\Delta m}{2M_o}\right)M_n \frac{(C_H - C_{Hini})}{10^6}\right] / M_o} \times 100 \quad (6)$$

where m_o , C_{Hini} , C_H , Δm , M_O , M_H and M_{Ti} are sample mass(g), initial and final hydrogen content(ppm), weight gain(g), molecular mass of oxygen, hydrogen and Ti.

Figure 2. shows the hydrogen pick-up content and pick-up fraction with exposure time for PT-7M corroded in low oxygen environment. The hydrogen content for the as-received specimen was 48.2 ppm, and it was increased only 12 ppm during 600 day corrosion.

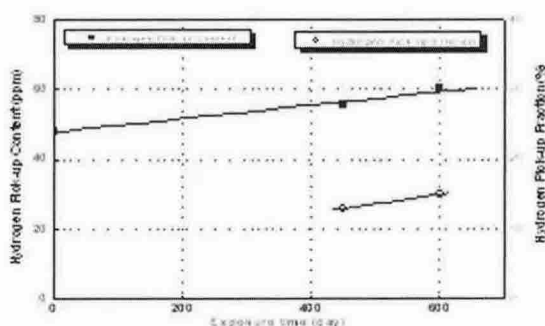


Figure 2. Hydrogen contents and hydrogen pick-up fraction values of the PT-7M with exposure time.

It was observed that hydrogen content slightly increased with exposure time, but hydrogen pick-up rate maintained at an almost constant level of about 13%, regardless of the exposure time. These data can be used to estimate the corrosion rate and hydrogen content at the life time in ammonia water chemistry.

3. Conclusion

In this study, the corrosion behavior of the PT-7M for steam generator heat exchange tubes at 360°C in a pH 9.98 aqueous ammonia solution were evaluated. The corrosion rates in the early corrosion period depend on oxygen content of the environment, but in the later period, it depend on the protective oxide layer rather than oxygen content. The corrosion rate constants for each step were estimated and hydrogen pick-up fraction was calculated.

ACKNOWLEDGMENTS

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