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Hydrogen Charging Kinetics in Zr-Nb Alloy Cladding Tube

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1. Introduction

Hydride-related embrittlement of fuel cladding and structural component made of zirconium based alloys is one of the most important issues in LWRs [1]. It is well known that hydrogen, when present in zirconium based alloys manifests into problems like hydride blistering, hydrogen embrittlement and propagation of flaw during service [2]. Therefore, it becomes very important to understand hydrogen charging kinetics for zirconium based alloys in related to the material properties. The present work has been undertaken to study hydrogen charging kinetics in order to quantify hydrogen content in fuel cladding by hydrogen charging apparatus.

2. Experimental Procedure

All specimens for the hydrogen-charging test, OD9.5 x ID8.375 x L30 mm in size, were cut from the Zr-Nb alloy tubes and were polished by SiC paper to remove surface contaminant and then pickled in a solution of 50 vol% H_2O, 45 vol% HNO_3 and 5 vol% HF. The hydrogen charging apparatus was designed to flow mixed gases of 95%Ar and 5%H_2 into reaction chamber and to create a high vacuum atmosphere (10^{-6} torr). Hydrogen charging time ranging from 0.5 to 14 hour is dependent on the test temperature ranging from 370 to 430°C.

3. Results and Discussion

3.1. Analysis of Microstructure by Optical Microscope

The microstructure of hydrogen charged specimen was analyzed using Optical Microscope. The specimens were mounted and then polished using SiC paper up to 2400 grit. The specimens were then etched in acid solution of 50% H_2O, 45%HNO_3 and 10% HF. Fig. 1 shows the micrographs of hydrogen charged specimens. As reaction time of Zr and H_2 is increased, the circumferential hydride in zirconium matrix has formed a lot more.

Moreover, as shown in Fig. 1(c), the circumferential hydride was distributed much more throughout the cladding surface compared to Fig 1. (a) and (b). It is considered that this difference was caused by a lack of diffusion time of hydrogen in the zirconium matrix.

3.2. Derivation of Equation for Estimating Hydrogen Concentration

The hydrogen contents of specimens were analyzed by inert gas fusion-thermal conductivity detection. The results of hydrogen-charging tests have been shown in Fig. 2 in terms of Arrhenius plot. As shown in Fig. 2, the activation energy for hydrogen charging was higher than that of other results [3]. It is considered that high activation energy in this work was caused by difference of hydrogen charging time at the same temperature. The estimated hydrogen contents in this study get an equation as below;

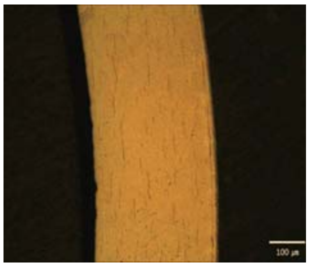
$$C_H = 1.9\times10^9 \exp\left(-\frac{115,000}{RT}\right)\times t$$

where,

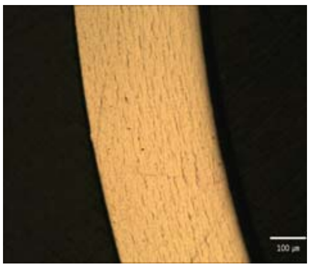
C_H; Estimated hydrogen contents (ppm),

R; Gas constant (8.314 J/mol・K),

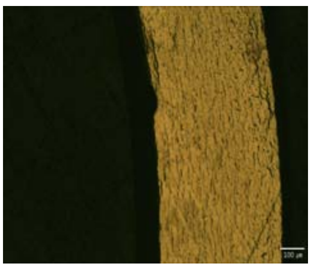
t; Reaction time of zirconium and hydrogen (min).



(a) 1hr charging, C_H = 94 ppm



(b) 5hr charging, C_H = 810ppm



(c) 10hr charging, C_H = 1630ppm

Fig. 1 Optical microstructures of circumferential hydride for hydrogen charged samples at 400°C

Using this test result, the empirical equation for estimating hydrogen contents has R-squared value of 0.93 and 7% standard deviation. This equation can be basically used to charge the hydrogen in Zr-Nb alloy by gaseous charging apparatus.

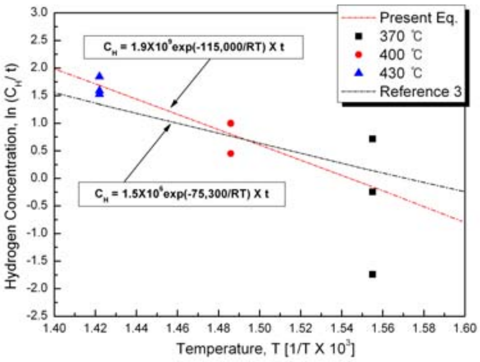


Fig. 2 Arrhenius plot of hydrogen charging test results by least squares method

4. Conclusion

In the present study, the hydrogen charging was carried out on the Zr-Nb alloy tubes. The empirical hydrogen charging equation with R-squared value of 0.93 and 7% standard deviation is below;

$$C_H = 1.9 \times 10^9 \exp\left(-\frac{115{,}000}{RT}\right) \times t$$

Acknowledgements

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