Analysis of microstructural characteristics of hydrogen charged Zr-2.5wt%Nb pressure tube

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Abstract - *We analyzed the microstructural characteristic of δ hydrides in Zr-2.5wt%Nb pressure tube. The hydrogen was charged cathodically and the hydride-contained sample was evaluated using the advanced analysis methodologies. We performed a DCS (Differential Scanning Calorimeter) analysis to more quantitatively understand the thermodynamics of the hydride formation/growth process. We characterized the micrograph of hydride-contained Zr samples to estimate the microstructural characteristics of the hydrides. We investigated effects of hydrogen concentration and homogenization heat temperature on average hydride density, average length and their distributions. Those microstructural measures were quantitatively analyzed and the mechanism of the Zr-hydrides growth was discussed.*

1 Introduction

Zr alloys have been used for structural materials of the nuclear system due to their excellent corrosion resistance and extremely small neutron absorption cross-section. The CANDU (CANada Deuterium Uranium) type reactor contains 380 pressure tube channels (in the case of CANDU-6 reactor) and chemical composition of the tube is Zr-2.5wt%Nb. A main concern about the Zr-alloys in the nuclear systems is that Zr-based materials are susceptible to the hydrogen-assisted degradation mechanism, such as hydrogen embrittlement and delayed hydrogen cracking [1]. Since integrity of the pressure tube is a key factor of the CANDU reactor safety, behavior of the Zr hydrides in a pressure tube have been extensively investigated for past decades [2, 3]. First of all, we measured the hydrogen concentration in the sample and compare the compositions with the existing models proposed by Kearns [4] and Khatamian [5]. Secondly, We assessed the Nb concentrations on the α and β phases, respectively, to confirm that the microstructure reached equilibrium. The 4-step mechanism of how metastable Zr-rich β phase transforms to the stable Nb-rich β phase was already proposed, we measured the Nb concentration on the β phase and evaluated the degree of approach to the equilibrium of the pressure tube according to the heat treatment temperature. In addition, we assessed the microstructural characteristics of the δ hydrides in the hydrogen charged Zr-2.5wt%Nb pressure tube depending on the temperature. We altered homogenizing heat treatment temperature, as a result, containing hydrogen concentration varies accordingly. Since δ hydride is most commonly seen in Zr-2.5wt%Nb pressure tube [2, 3], we evaluated the microstructural characteristics of the δ hydride depending on the heat treatment temperatures. Since the microstructural characteristics of the δ hydride heavily affect the mechanical properties of the pressure tube, it is quite important to systematically evaluate the microstructural characteristics of the hydrogen charged pressure tube. According to our best knowledge, the hydride microstructural characteristics in Zr-2.5wt%Nb alloy have not been quantitatively estimated. In this study, we investigated the microstructrual characteristics evolution of δ hydride depending on the heat treatment temperature.

2 Hydrogen Charging

A test piece was cut from the hoop-radial plane of a commercial Zr-2.5wt%Nb alloy. We cathodically charged the hydrogen into the sample as below:

- Produce 0.5M sulfuric acid solution (100cc 98 % + 0.5g As + H_2O 2L) and heat it up to 85 Âś 5 °C.
- Install Pb bar as an anode material and Zr-2.5wt%Nb piece ($3cm \times 10cm \times 0.43cm$) as a cathode material.
- Apply 8A current.
- Stay 24 hours to form hydride on Zr-2.5wt%Nb tube surface.
- Heat treatment at given temperature for the homogenization. More details about this procedure describes in references [4].

We have eight types of hydrogen charged Zr-2.5wt%Nb samples and heat treatment conditions. The amount of hydrogen in the specimen is measured by a LECO RH-404 hydrogen determinator.

We estimated the hydrogen solubility using the equation of Zircalloy-2 or Zircalloy-4 proposed by J. Kearns [4] in Eq. 1 and model of Zr-2.5wt%Nb proposed by D. Khatamian in Eq. 2 [5].

$$1.2 \times 10^5 \times \exp \frac{-8950}{RT} \tag{1}$$

In this relation, they used the gas constant $R = 1.987$ $cal/K \cdot mol$ [4].

$$C_H = C_0 exp(-Q/RT) \tag{2}$$

when $C_0 = 45072 \times exp(0.0173 \times [Nb])$ and $Q = 29653 + 98.01 \times [Nb]$ [5]. In this relation, they used the gas constant $R = 8.314$ $J/K \cdot mol$ [5].

We assumed that MST (Maximum Slope Temperature) determined by DSC (Differential Scanning Calorimeter) analysis is the homogenization temperature. DSC experiments

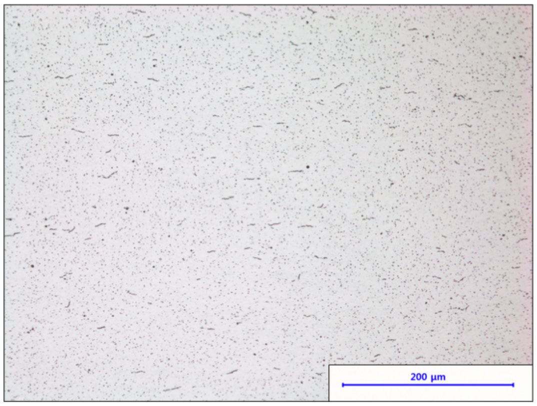

Fig. 1. Micrograph of as received (Case I) Zr-2.5wt%Nb alloy obtained by the optical microscope(×200). The hydrogen concentration is 12 ppm.

show whether the phenomena inside material is endothermic or exothermic by heating the specimen with hydrogen. The process of decomposition or precipitation of hydrides is a kind of phase transformation, in which an endothermic reaction or an exothermic reaction occurs. In the DSC, the process of dissolving the hydride as the specimen is heated is essentially an endothermic reaction since the bond between Zr and H must be broken and diffusion of these atoms must occur. On the contrary, when the hydrogen-containing material is cooled, the hydride reaction occurs when the hydride is precipitated. The reason why the hydride is precipitated is because the concentration of hydrogen dissolved in the material exceeds the solubility limit. When the hydrated material is heated to a high temperature, Terminal Solid Solubility for Dissolution (TSSD) of the material is increased. At this point, the hydride is decomposed and hydrogen is dissolved into the material. This is why the hydrides are decomposed as the temperature rises.As described above, the decomposition process of the hydride precipitated in the material is an endothermic reaction. When the reaction is completed, the endothermic reaction ends. This change is due to the change in the DSC curve, and at the end of the endothermic reaction, the slope becomes maximum. The slope change of the DSC curve is called the derivative DSC (DDSC), which is defined as the maximum slope temperature (MST).

3 Results and Conclusions - Microstructural analysis

We characterized the microstructures of one as-received (Case I) and three hydrogen charged (Case II, III, IV) Zr alloys by the Optical Microscope. To perform the rigorous statistical analysis, we evaluated 19 images for each case. A typical micrograph of hydrogen-charged pressure tube is shown in Fig. 1. We prepared the sample

From the micrographs, we found that short hydrides disappears around a long hydride. It is a evidence that Ostwald ripening takes place during hydride growth. Since the shape is highly deviates from the spherical shape, it means that elastoplastic effect strongly affects the microstructural evolution process of the Zr-2.5wt%Nb alloy. We characterized the microstructural characteristic of δ hydride in a pressure tube and

TABLE I. Microstructural characteristics measured by image analysis. We characterized 19 images for each case and average the values. 'Ave' is an abbreviation of Average.

Case	Density ($/mm^2$)	Ave length (μm)
I	366.67	5.34
II	1546.67	8.93
III	1406.06	17.94
IV	1493.94	13.50

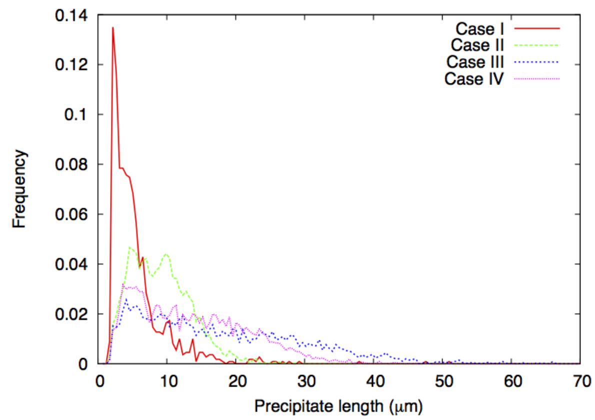

Fig. 2. Distribution of the precipitate lengths for four cases.

the results are written in table I. In the table I, it is clear that the average widths of the hydrides are mostly consistent regardless of the heat treatment temperature or hydrogen concentration. It means that hydride undergoes 1-D (needle-like) growth during the microstructural evolution.

We plotted the distribution of the precipitate lengths and normalized lengths with respect to the average length. Since there is 17% volume expansion occurs during α to δ phase transformation, plastic deformation usually accompany during the process. There have been extensive investigation to predict the behavior of diffusion driven growth process, so called Ostwald ripening, this phenomena is relatively well understood. However, the hydride growth in a Zr alloy is induced by not only diffusion but mainly also elastoplastic effect. Hillert proposed the methodology to derive the size distribution of particle based on the mean field assumption with consideration of diffusion only. So far, comprehensive framework is not well established to predict the microstructural characteristics of microstructural evolution driven by the elastoplastic effect, it is quite challenging to fully explain the results shown in Figs. 2 and 3. Before the heat treatment, the distribution is quite narrow and 88.8 % of the needle-shaped hydrides are shorter than 10μm in Fig. 2. One intriguing point of the distribution in Fig. 2, 32.5% and 40.1% of hydrides are shorter than 10 μm in Case III and Case IV, respectively. On the other hand, the average hydride length of Case III is shorter than the value of Case IV. We quantitatively evaluate the length distribution in table II and we found that the sample skewness and the sample excess kurtosis is way higher than other cases in Case I (As received). After the heat treatment, both kurtosis and skewness decreases. Once we compare the standard deviations of the distributions in Table II, we found that the distribution be-

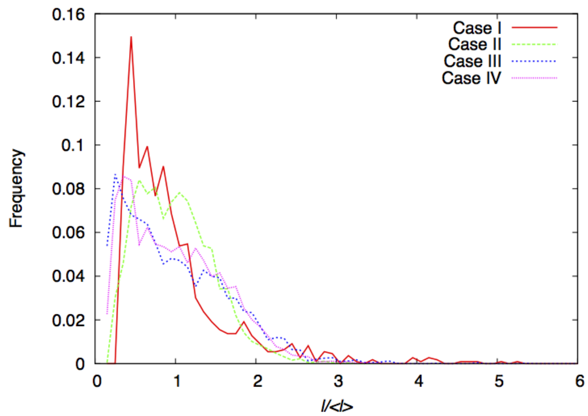

Fig. 3. Distribution of the normalized precipitate lengths (l) with respect to the average length ($< l >$) for four cases.

TABLE II. Quantitative analyzed results of the distribution in Fig. 2.

Case	Ave (μm)	Dev.	Skewness	Kurtosis
I	5.34	4.39	3.72	23.93
II	8.93	4.29	1.29	10.19
III	17.94	11.97	1.93	11.35
IV	13.50	8.11	1.19	7.68

comes broader as hydrogen concentration and heat treatment temperature increases.

References

1. D. Northwood and U. Kosasih, "Hydrides and delayed hydrogen cracking in zirconium and its alloys," *International Metals Reviews*, vol. 28, no. 1, pp. 92–121, 1983.
2. J. Root and R. Fong, "Neutron diffraction study of the precipitation and dissolution of hydrides in zr-2.5 nb pressure tube material," *Journal of Nuclear Materials*, vol. 232, no. 1, pp. 75–85, 1996.
3. E. Tulk, M. Kerr, and M. Daymond, "Study on the effects of matrix yield strength on hydride phase stability in zircaloy-2 and zr 2.5 wt% nb," *Journal of Nuclear Materials*, vol. 425, no. 1, pp. 93–104, 2012.
4. J. Kearns, "Terminal solubility and partitioning of hydrogen in the alpha phase of zirconium, zircaloy-2 and zircaloy-4," *Journal of Nuclear Materials*, vol. 22, no. 3, pp. 292–303, 1967.
5. D. Khatamian, "Effect of β-zr decomposition on the solubility limits for h in zr–2.5 nb," *Journal of alloys and compounds*, vol. 356, pp. 22–26, 2003.