CANDU Pressure tube hydride phase transition phenomenon

Sang-yeob Lim*, SungSoo Kim, Gyeong-Geun Lee
Korea Atomic Energy Research Institute,
111, Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon, Korea
**E-mail: sylim@kaeri.re.kr*

1. Introduction

In CANDU (CANada Deuterium Uranium) heavy water reactors, Zr-2.5Nb materials are used to protect the fuel bundles from exposure to pressurized coolant. Zr-2.5Nb material has excellent corrosion resistance, mechanical properties and low neutron absorption rate, so it can protect the material from the impact of cooling water pressure and flow rate. However, when zirconium material is exposed to pressurized water for a long time, it forms ZrO_2 by the oxidation reaction and generates hydrogen. The generated hydride is absorbed into the base material of zirconium at operating temperature due to the hydrogen pick-up phenomenon of zirconium. Thereafter, when the pressure tube is cooled by the operating conditions, it is precipitated into the zirconium hydride phase inside the base material. Since the precipitation of hydrides results in delayed hydride cracking (DHC, management of hydrides in pressure tube is very important. In this study, the precipitation and dissolution of hydride peaks were observed by in-situ method using a Pohang Light Source (PLS) to observe the hydride formation conditions and phase changes of δ and γ hydrides.

2. Experimental

2.1. Pressure Tube material (Zr-2.5Nb)

The pressure tube material used in the experiment is Zr-2.5Nb alloy. The chemical composition is shown in Table 1. The material of pressure tube was cut into 30 x 100 mm pieces.

Table I: Chemical composition of Zr-2.5Nb (wt%)

Elements	*Zr*	*Nb*	*Fe*	*O*	*N*	*P*
Wt %	*97.4*	*2.5*	*0.05*	*0.097*	*0.007*	*0.003*

2.2. Formation of Hydride

Hydride was formed on the surface of the sample through the electrolytic hydrogen charge method. 1 M sulfuric acid solution was used at a current density of 100mA/cm^2. The solution temperature was controlled to be 85 ± 5℃ for 24 hours. After formation of hydride at the surface of specimen, the specimen is sealed into Pyrex vacuum tubing, and the tubing was heat treated at 350℃ for 24 hours to homogenize the hydrogen. Hydrogen concentration was measured by LECO RH-404 hydrogen analyzer. It was confirmed as 54ppm and 33ppm, respectively.

2.3. DSC analysis

In order to identify the temperature of the hydride dissolution and phase transformation, DSC (Differential scanning calorimeter) is measured to 54ppm and 33ppm sample. NETZSCH DSC 404 F1 device was used. TSSD (Terminal Solid Solubility of Dissolution) and TSSP (Terminal Solid Solubility of precipitation) was measured by DSC analysis.

2.4. PLS XRS analysis

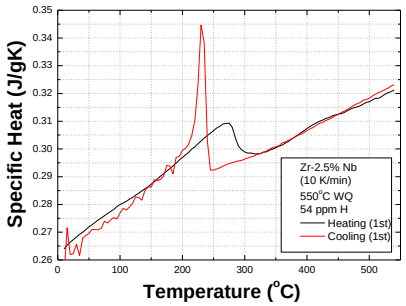
X-ray diffraction was analyzed by using PLS 3D-XRS (X-ray scattering) Beam Line to confirm the initial phase and phase change of hydride formed by water quenching from RT to 290℃. The wavelength used for analyzing diffraction is 1.32 Å.

The γ-hydride peaks of these specimens were analyzed by XRS. It was heated from RT to 290℃. While the specimen heating, In-situ XRS was analyzed.

3. Result and discussion

54 and 33 ppm hydrogen charged material was water quenched. DSC was performed to measure TSSD. The result was measured as 284.5℃ and 249℃ respectively.

(a)



(b)

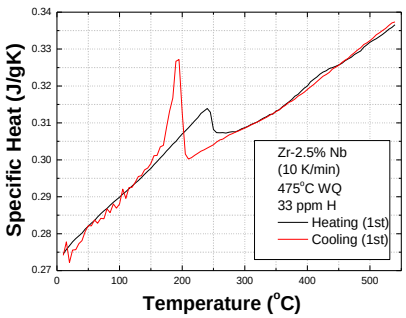
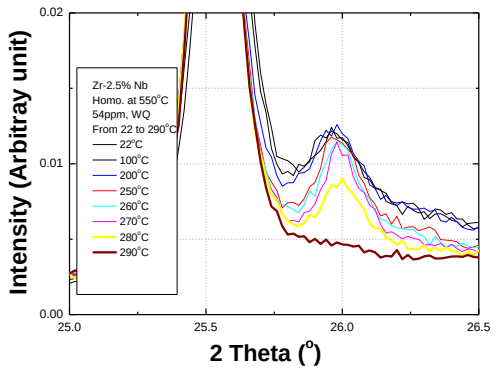


Fig. 1. DSC measured data of heating and cooling. (a) 54ppm (WQ from 550℃) and (b) 33ppm (WQ from 475℃).

DSC results shows the TSSP and TSSD in water quenched specimen with 54 ppm and 33 ppm hydrogen (Fig. 1). The TSSD's are 285℃ (Fig. 1 (a)) and 249℃ (Fig. 1 (b)), respectively.

The γ-hydride peak in 54 ppm specimen was weakened at about 280℃ with heating and the peak was completely disappeared at 290℃ as shown in Fig. 2 (a). Fig 2 (b) shows the results of water quenched 33 ppm hydrogen. The TSSD of specimen with 54 ppm hydrogen in XRS (Fig. 2(a)) is agreed with DSC results shown in Fig. 1 (a).

(a)



(b)

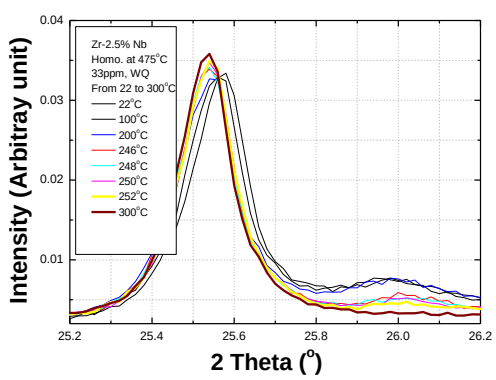


Fig. 2. In- situ PLS 3D-XRS measured data during heating condition. (a) 54ppm (WQ from 550℃) and (b) 33ppm (WQ from 475℃).

After heater off on the stage, sample was cooled by atmosphere of Laboratory environment. XRS was taken after sample temperature was reached at RT. The cooling rate is observed nearly by 30K/min. The γ-hydride is observed by XRS at about 100℃. The γ-hydride peak was not found at around 240℃ in the fast cooled sample. When the specimen is cooled, the δ-hydride was formed at around TSSP of 54 ppm specimen (239℃) as shown in Fig. 1 (a).

The specimen with 33ppm hydrogen shows the same phenomena. But the TSSD of 33ppm measured at 249℃ so peak was weekend at 246℃ and fully disappeared at ~250℃.

4. Conclusions

The water quenching of the hydrogen charged pressure tube forms γ-hydride. The γ-hydride in specimens with 54 ppm and 33 ppm, respectively, dissolves at 284.5℃ and 249℃ completely, determined by DSC. The fast cooling from TSSD forms γ -hydride and the slow cooling from TSSD forms δ-hydride.

Acknowledgments

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