Determination of Terminal Solid Solubility of Hydrogen in Zirconium Alloys

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1. Introduction

Zirconium alloys are widely used as the material for the fuel cladding and the structural components of nuclear power plants. Hydrides in zirconium alloys is a major parameter in assessing the potential for delayed hydride cracking in the embrittlement of fuel cladding and other structural components. Many studies on the measurements of TSSD during heating and TSSP during cooling have been carried out for Zr and its alloys, and various measuring techniques have been used. However, there is considerable scatter in the published TSS data. This may be attributed partly to the different experimental techniques used such as diffusion gradient[1,2], dilatometry[3], differential scanning calorimetry[4,5], dynamic elastic modulus[4,6], and so on.

In this study, TSSD and TSSP of commercial Zircaloy-4 and advanced zirconium alloy which were hydrogenated up to a level of 225 ppm, were derived by differential scanning calorimetry (DSC), and best fit equations were presented. Moreover, the average precipitation rates of zirconium hydrides from the super-saturated state were assessed from the widths of the DSC peak obtained during cooldown.

2. Experimental

2.1 Materials

Zircaloy-4 and advanced zirconium alloy A were used for TSS measurements. The chemical composition of the specimens is shown in Table 1. Advanced alloy A developed for high burnup fuel cladding include Nb element. The hydrogen contents of the as-received materials were 5-10 ppm.

Table 1. Chemical composition of specimens

(wt %)

Material	Nb	Sn	others	Zr
Zry-4		1.3	0.3	balance
A-alloy	1.0	1.0	2.3	balance

2.2 Hydrogen charging

The specimens were hydrided by 3-electrode electrochemical hydrogen charging method. Hydrogen charging was carried out on pickled specimens at room temperature in sulfuric acid (1 N, aerated medium). The intensity of -5mA was applied to previously pickled specimens. The size of the specimen was 25 ㎜ long and 9.5 ㎜ in diameter. The specimens was pickled in $H_2SO_4/HNO_3/HF$ solution. After hydrogen charging, the specimens were homogenized for 26 hours at 430□ in pure Ar. The hydrogen concentrations of the specimens were analyzed by the hot extraction method using LECO hydrogen analyzer. Average hydrogen concentrations ranged from about 50 to 220 ppm.

2.3 Differential scanning calorimetry

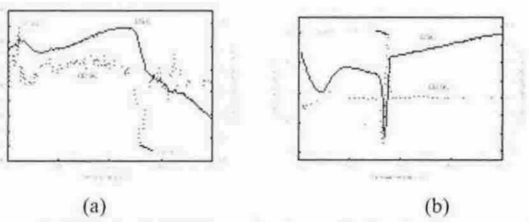
The measurement of the terminal solid solubility of hydrogen in zirconium alloy was carried out using the Differential Scanning Calorimetry (DSC) technique. A Netzsch DSC 404C was used to perform the measurements. The instrument is based on the measurement of thermal response of a specimen compared to a reference when the two are heated up or cooled down uniformly at a constant heating or cooling rate. The resulting differential heat flow detects the dissolution or precipitation of hydrides in the samples.

The DSC measurements were carried out in purified Ar at the flow rate of 50 ㎤/min. A specimen was hold 60 minutes at 40 □, and then heated up to 600 □ from 40 □. And after the specimen was hold 60 minutes at 600 □ and cooled down 40 □. This procedure was repeated 3 cycles. In this study the heatup and cooldown rate was 10 □/min.

3. Results and Discussion

3.1 TSSD and TSSP

Figure 1 shows the typical DSC curves for Zircaloy-4 containing 134 ppm hydrogen, obtained during 3rd heatup and cooldown cycle. Three temperatures are noted in DDSC curve; the peak temperature, the maximum slope temperature and the completion temperature. There are no established rules and experimental evidence for declaring which temperature best represents the temperature for complete hydride dissolution. In this study the maximum slope temperature was adopted as TSSD temperature from the narrow peak in the DDSC curve.



(a) (b)

Figure 1. Typical DSC and time derivation curves from Zircaloy-4 obtained during (a) heatup and (b) cooldown (134 ppm H, heating/cooldown rate: 10 □/min).

The results of TSS measurement obtained in this study are plotted in Figure 2. There is no difference in TSSD and TSSP between Zircaloy-4 and advanced zirconium alloy A containing Nb. Some papers reported almost no alloy effect on TSSD and TSSP. It it not clear whether there exists some difference in solubility between Zr and Zircaloys [5].

Relationship between hydrogen solubility and temperature of Zircaloy-4 and advanced Zr alloy A is given by following equations.

$C_{TSSD} = 2.45 \times 10^5 \exp(-39642/RT)$
$C_{TSSP} = 4.83 \times 10^4 \exp(-27040/RT)$

The activation energy for the hydride dissolution is 39 kJ/mol. Other workers reported the activation energies of 31-45 kJ/mol.

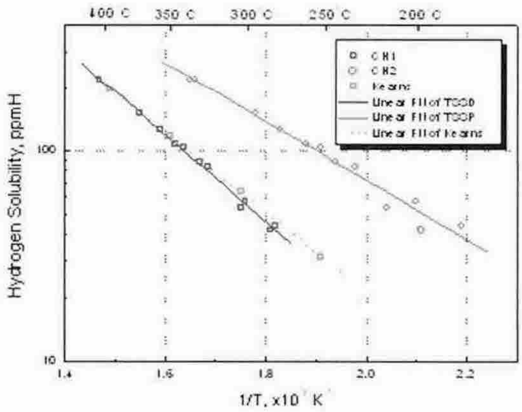


Figure 2. TSSD and TSSP for Zircaloy-4 and advanced alloy A versus reciprocal temperature obtained using DSC

3.2 *Hydride precipitate*

When zirconium hydride precipitates for the first time from a completely dissolved state of hydrogen, super saturated amounts of hydrogen tend to precipitate during a shorter time, presenting a sharp DSC peak as seen in Figure 2(b). Figure 3 shows the average precipitation rate of hydride for Zircaloy-4.

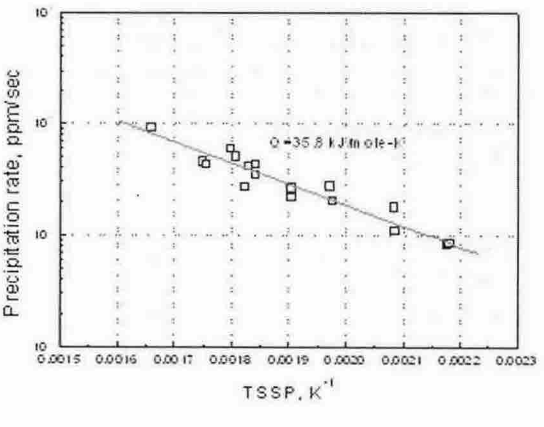


Figure 3. Average precipitation rate of hydride as a function of temperature derived from the DSC peak on cooldown.

4. Conclusion

The terminal solid solubility of Zircaloy-4 and advanced zirconium alloy A was measured using DSC. Specimens were charged by electrochemical hydrogen charging method, and hydrogen concentrations of the specimens ranged from about 50 to 220 ppm. There was no differences in TSSD and TSSP between Zircaloy-4 and advanced zirconium alloy A. The activation energy of the precipitation rate was approximately consistent with reported values of hydrogen coefficients of zirconium alloys.

Acknowledgement

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