Hydrogen Solubility of Nb-containing Zirconium Alloys

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1. Introduction

Zirconium alloys are widely used as the material for the fuel cladding and the structural components in nuclear power plants. Terminal solid solubility of hydrogen in zirconium alloys is an important parameter in assessing the potential for delayed hydride cracking and hydride blister formation. 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 such as diffusion gradient[1,2], dilatometry[3], differential scanning calorimetry[4,5,7], dynamic elastic modulus[4,6], have been used. A review of published TSS data for Zr and zirconium alloys has revealed considerable scatter.

In this study, TSSD and TSSP of *HANA* claddings developed in KAERI, which were hydrogenated up to a level of 400 ppm, were derived by differential scanning calorimetry (DSC), and compared to those of Zicaloy-4 obtained in previous work. The average precipitation rates of zirconium were also assessed from the widths of the DSC peak obtained during the cooling-down.

2. Experimental

2.1 Materials

Commercial Zircaloy-4 and *HANA* claddings were used for TSS measurements. The chemical composition of the specimens is shown in Table 1. The hydrogen contents of the as-received materials were 5-10 ppm.

Table 1. Chemical composition of specimens

(wt %)

Alloysl	*Nb*	*Sn*	*others*	*Zr*
Zry-4		1.3	0.3	balance
HANA-3	1.5	0.4	0.2	”
HANA-5	0.4	0.8	0.55	”

2.2 Hydrogen charging

The specimens were hydrided by electrochemical hydrogen charging method. Hydrogen charging of Zry-4 was carried out on pickled specimens at room temperature in sulfuric acid (1 N, aerated medium), and *HANA* claddings at 65℃ in sulfuric acid (1 N, aerated medium). The intensity applied to previously pickled Zry-4 and *HANA* specimens was -5mA and -10 mA, respectively. The size of Zry-4 specimen was 25㎜ long and 9.5 ㎜ in diameter and the size of *HANA* specimens was 60 ㎜ long and 9.5 ㎜ in diameter. The specimens were pickled in $H_2SO_4/HNO_3/HF$ solution. After the hydrogen charging, the specimens were homogenized for 26 hours at 430℃ in pure Ar atmosphere. The hydrogen concentrations of the specimens were analyzed by the hot extraction method using a LECO hydrogen analyzer. Average hydrogen concentrations were ranged from about 30 to 400 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 details of the instrument and the measurements were described in reference 7.

3. Results and Discussion

3.1 TSSD and TSSP

Figure 1 shows comparison of TSSD and TSSP for Zry-4 and *HANA* alloys obtained in this study and Kearns TSSD data. There is no difference in TSSD and TSSP between Zry-4 and *HANA* alloys containing Nb. Some papers reported almost no alloy effect on TSSD and TSSP. It is not clear whether there exists some difference in solubility between Zr and Zrys [5].

Relationship between hydrogen solubility and temperature of *HANA* alloys is given by following equations:

$$C_{TSSD} = 1.50 \times 10^5 \exp(-37424/RT)$$
$$C_{TSSP} = 3.63 \times 10^4 \exp(-26133/RT)$$

where, R is the gas constant (8.314 J/K-mol) and T is the temperature in K.

The activation energy for the hydride dissolution of *HANA* alloy and Zry-4 is 37.4 kJ/mol and 38.5 kJ/mol, respectively. Other workers reported the activation energies of 31-45 kJ/mol.

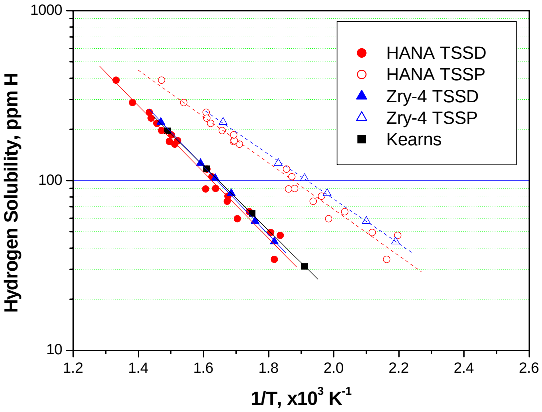

Figure 1. TSSD and TSSP for Zircaloy-4 and HANA alloys versus reciprocal temperature obtained using DSC

3.2 Hydride precipitation

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. The average precipitation rate was calculated from precipitation duration and super-saturated amounts of hydrogen. Figure 2 shows the average precipitation rate of hydride for *HANA* alloys. The average precipitation rate is represented by following equation,

$$H_P = 3.12 \times 10^5 \exp(-36912/RT)$$

The activation energy of 36.9 kJ/mol for *HANA* alloys was well agreement with other values (26-43 kJ/mol).

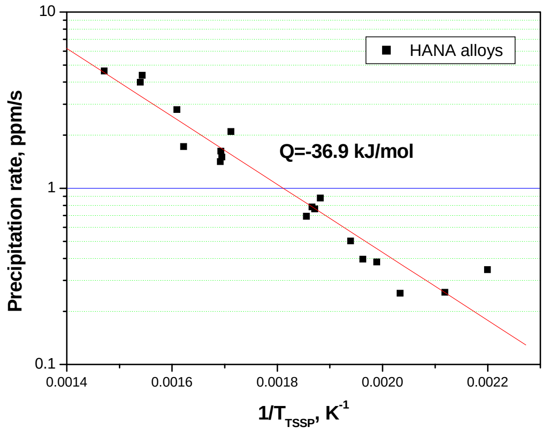

Figure 2. Average precipitation rate of hydride as a function of temperature of TSSP.

4. Conclusion

The terminal solid solubility of *HANA* claddings was measured using DSC and compared with Zircaloy-4 TSS data. Specimens were charged by electrochemical hydrogen charging method, and the hydrogen concentrations of the specimens ranged from about 30 to 400 ppm. There was no difference in TSSD and TSSP between Zry-4 and HANA alloys. The activation energy of the precipitation rate for *HANA* claddings was good agreement with other values of hydrogen diffusion coefficients of zirconium alloys.

Acknowledgement

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