The terminal solid solubility of hydrogen in Zircaloy-4 and Opt-ZIRLO with a DSC

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1. Introduction

Due to low neutron absorption cross section, good mechanical properties at high temperature and proper corrosion resistance; zirconium-based materials have been used commonly for nuclear core structural components. When the hydrogen content in cladding exceeds the terminal solid solubility (TSS) of hydrogen, the brittle hydrides can be precipitated. The brittle hydrides can threaten the integrity of cladding such as hydride re-orientation **[1]** or DHC **[2]** in dry storage conditions as well as in reactor operating conditions. In addition, it is known that the terminal solid solubility of hydrogen in zirconium alloys for dissolution (TSSD) and precipitation (TSSP) has a significant hysteresis. Thus, the TSS of hydrogen in zirconium alloys is an important factor and accurate knowledge of the TSS is required for evaluation of cladding integrity. In this study, the TSSD and TSSP for Zircaloy-4 and Opt-ZIRLO were measured.

2. Experimental

2.1 Materials

For the present TSS measurements, commercial Zircaloy-4 and Opt-ZIRLO claddings were used. The chemical composition of materials used in this research is shown in Table 1. The specimens were charged with hydrogen at 400 °C by a modified Sieverts apparatus. After hydrogen charging, the heat treatment was performed at same temperature for 5-10 hours to ensure uniform distribution of hydride and the specimens were slowly cooled down to room temperature at cooling rate of 0.5-1 °C/min. After the DSC measurements, the hydrogen concentrations in all the samples were chemically analyzed by a hydrogen determinator (LECO RH-404) which uses an inert gas fusion method with an uncertainty of 4 wppm and it ranged 40-741 wppm.

Table 1. Chemical compositions of Zry-4 and Opt-ZIRLO (unit: weight %)

Material	Nb	Sn	Fe	Cr	Zr
Zircaloy-4	-	1.3	0.2	0.1	Bal.
Opt-ZIRLO	1.0	0.7	0.1	-	Bal.

2.2 Differential scanning calorimetry

In this study, the TSSD and TSSP temperatures of the samples were measured using the DSC technique (Heat flux DSC Netzsch 200 F3). The DSC is based on the measurement of the difference in the heat exchange between the sample and reference during heating or cooling. There is a measurable change in the amount of heat in the sample when the hydrides dissolve or precipitate. Prior to DSC measurements, the instrument was calibrated using metal standard samples (In, Sn, Zn). The DSC measurements were conducted in purified N_2 at the flow rate of 50 cm^3/min. In all the measurements, the maximum temperature was chosen to be 580 °C and heating/cooling rate was 20 °C/min.

3. Results and discussion

3.1 TSSD and TSSP

In a typical DSC heating curve (Fig. 1), the heat flow decreases as heat is absorbed by the specimen during the hydrides dissolution which is an endothermic reaction. After the hydrides dissolution is completed, the heat absorbed is not necessary and the curve swing upward. For this broad peak, there are three characteristic temperatures which can be selected as the TSSD temperature: the peak temperature (PT), the maximum slope temperature (MST) and the completion temperature (CT). In this study, MST was adopted as the temperature for complete hydride dissolution considering a good reproducibility and agreement with the reference data **[3-8]**.

The analysis of the DSC cooling curve is similar to the DSC heating curve, and correspondence is made to the MST in the cooling curve. Because sharp DSC peaks can be obtained in the TSSP, there are no great evaluation errors depending on the characteristic temperatures.

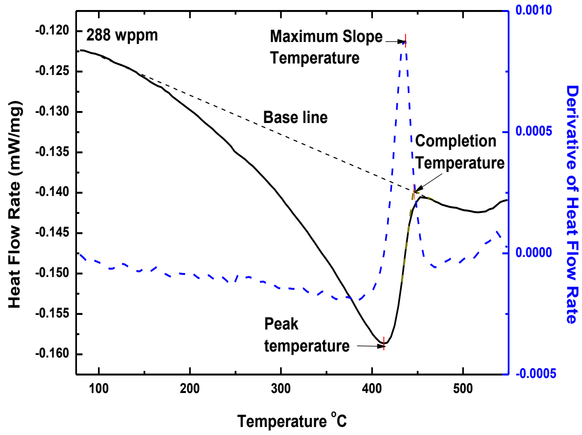

Fig. 1. Typical DSC heating curve

The present TSS results are shown in Fig. 2 and the best-fit TSS curves from this experiment of Zry-4 and Opt-ZIRLO are represented by the following equations:

TSSD of Zry-4: $C = 2.255 \times 10^{5} \exp(-39{,}101/RT)$ (1)

TSSP of Zry-4: $C = 4.722 \times 10^{4} \exp(-26{,}843/RT)$ (2)

TSSD of Opt-ZIRLO: $C = 6.893 \times 10^{4} \exp(-31{,}860/RT)$ (3)

TSSP of Opt-ZIRLO: $C = 1.963 \times 10^{4} \exp(-21{,}611/RT)$ (4)

where C is hydrogen concentrations in wppm, R is the gas constant and T is the absolute temperature.

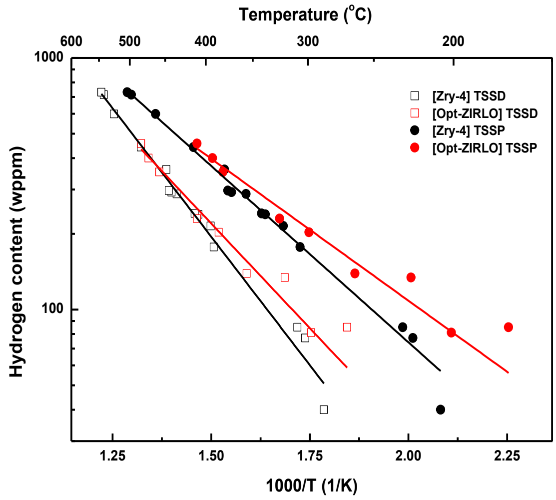

Fig. 2. TSSD and TSSP for Zircaloy-4 and Opt-ZIRLO

The present TSSD (Fig. 3) and TSSP (Fig. 4) results are compared with references **[3-8]**. The current activation energies of the TSSD for Zry-4 and Opt-ZIRLO were 39.1 kJ/mole and 31.9 kJ/mole respectively. The current activation energies of the TSSP for Zry-4 and Opt-ZIRLO were 26.8 kJ/mole and 21.6 kJ/mole respectively. Both the present TSSD and TSSP were similar to the other TSSD results range of 30-38.1 kJ/mole **[3-8]** and TSSP results range of 18.7-34.5 kJ/mole **[3-8]** respectively. However, there was a difference between TSS for Zircaloy-4 and TSS for Opt-ZIRLO. Opt-ZIRLO had a higher terminal solid solubility of hydrogen than Zircaloy-4 at the same temperature for less than about 400 wppm. The activation energy of Zircaloy-4 was relatively high compared with references **[3-8]**, while the activation energy of Opt-ZIRLO was relatively low. Some authors showed that there was no significant difference in either the TSSD or TSSP behavior, although zirconium alloys which have different chemical compositions **[6, 7]**. On the other hands, Slattery **[9]** obtained different TSS behaviors for Zry-4, Zry-2 and Zr-2.5Nb. In this study, based on the present TSS results, it is considered that the chemical composition affects the TSS.

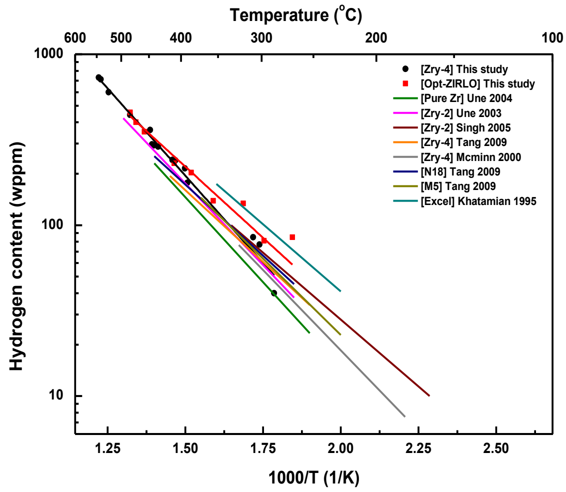

Fig. 3. The present TSSD results with reference data

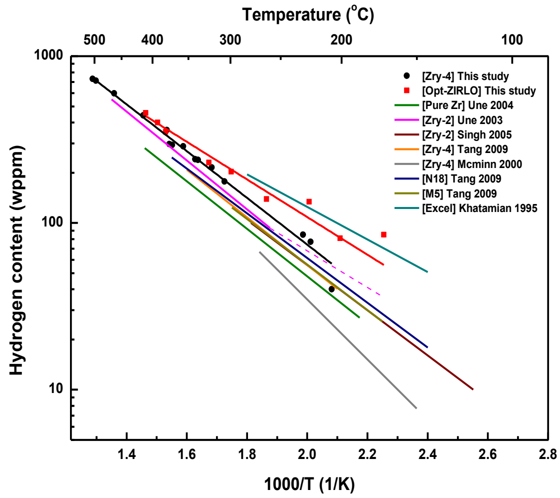

Fig. 4. The present TSSP results with reference data

4. Conclusions

The TSS of hydrogen in Zry-4 and Opt-ZIRLO was investigated with a DSC in this study. The hydrogen concentrations in zirconium alloys ranged 40-741 wppm. Both TSSD and TSSP were similar to literature TSS results. However, Opt-ZIRLO had a higher terminal solid solubility of hydrogen than Zry-4 at the same temperature for less than about 400 wppm. The activation energy of Zircaloy-4 was relatively high compared with references, while the activation energy of Opt-ZIRLO was relatively low. It was considered that the chemical composition affects the TSS.

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