Terminal Solid Solubility of Hydrogen in Zircaloy-4 by Differential Scanning Calorimetry

Ju-seong Kim and Yong-soo Kim*
Department of Nuclear Engineering, Hanyang University, Seoul, 133-791, Korea
**Corresponding author: yongskim @hanyang.ac.kr*

1. Introduction

During dry storage of spent nuclear fuel the brittle hydrides can be precipitated which can reduce the ductility of the cladding, and threaten the integrity of cladding such as hydride re-orientation or delayed hydride cracking. The terminal solid solubility (TSS) of hydrogen in zirconium alloy for dissolution (TSSD) and precipitation (TSSP) has the hysteresis. It is known that the TSSD of hydrogen in zirconium seem to be less sensitive to previous thermal history but the TSSP is strongly dependent on the thermal history. The extent of the hysteresis depends on the temperature history such as peak temperature, holding time at the peak temperature and cooling rate.

2. Experimental

2.1 Material

Cold worked stress-relieved (CWSR) Zircaloy-4 which was finally annealed at 470 °C for 5 hours was used for the present TSS measurements. Table 1 shows the chemical composition of Zircaloy-4. Hydrogen charging was conducted at 400 °C by a modified Sieverts apparatus. As a result, 40–1121 wppm of hydrided specimen was obtained. All of the hydrogen concentrations were analyzed by a hydrogen determinator (LECO RH-404) which uses an inert gas fusion method.

2.2 Differential scanning calorimetry

In this work, the TSS of hydrogen in Zircaloy-4 was measured using heat flux DSC (Netzsch 200 F3). The calibrations were conducted prior to the experiment using metal standard samples (In, Sn and Zn). The change in the heat flow signal is an exothermic or endothermic reaction when hydride transformation occurs. Figure 1 shows a typical DSC heat flow and its derivative heat flow curves during heating. As the temperature increases, the hydrogen begins to dissolve and the heat flow curve decreases steadily indicating that the hydrogen dissolution process is an endothermic reaction. DSC measurements were carried out in purified N2 at a flow rate of 50 cm^3/min.

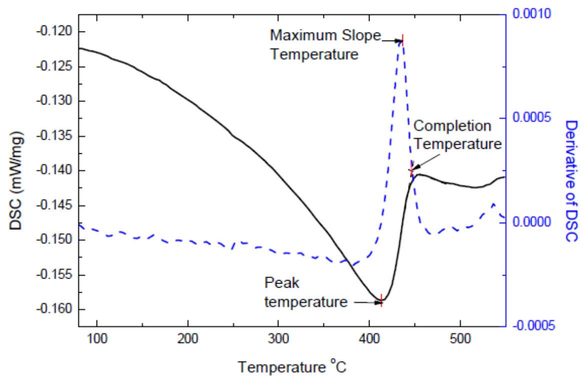

Fig. 1. DSC curve and its time variation of Zircaloy-4 specimen with a hydrogen content of 288 wppm during heat-up.

3. Results and discussions

3.1 Terminal solid solubility for dissolution and precipitation

In order to determine the wide range of TSS of hydrogen in Zircaloy-4, 40-731 wppm of hydrided specimen was used. The DSC results of this work are plotted with references in Fig. 1 and Fig. 2. There is a significant temperature gap between the TSSD and TSSP. The curves from our experiment are

TSSD of Zircaloy 4: $C= 2.255\times10^5 \exp(-39101/RT)$,

TSSP of Zircaloy 4: $C= 4.722\times10^4 \exp(-26843/RT)$,

where C is hydrogen content (wppm), R is the gas constant and T is absolute temperature. The present activation energies of TSSD and TSSP are 39.101 and 26.843 KJ/mole, respectively. The current TSSD line is similar to the reference equilibrium method which is often used as a reference TSSD of Zircaloy-4 [1]. The present activation energy for dissolution is 39.101 KJ/mole which is good agreement with the other TSSD data of 32-39 KJ/mole [2-4]. On the other hand, TSSP data shows significant scatter in Fig. 2 which might be due to the previous thermal history and the different measurement method. Nevertheless, the present data agrees with other TSSP data. The temperature gap between TSSD and TSSP tends to decrease with increasing temperature which corresponds to 50-87 °C in this study.

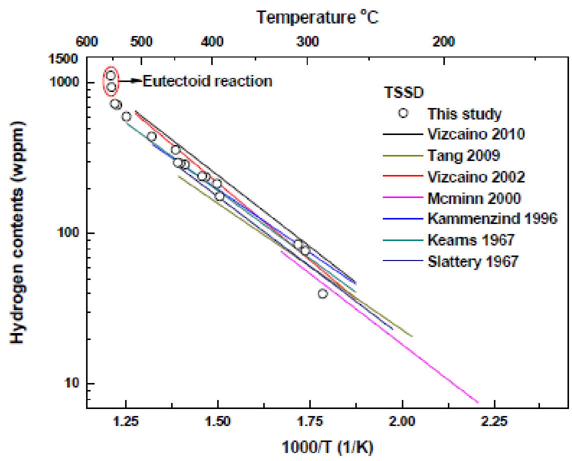

Fig. 2. TSSD of hydrogen in Zircaloy-4 with reference data

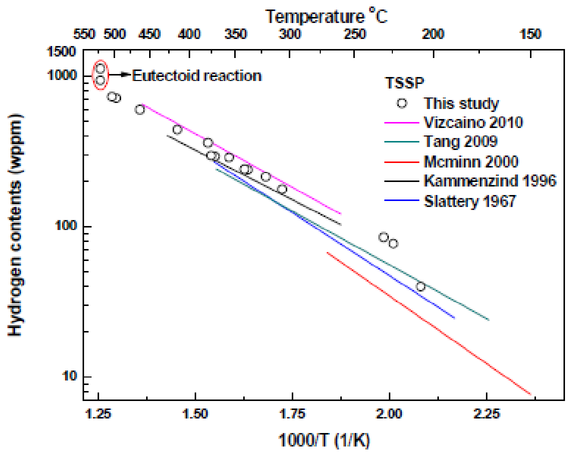

Fig. 3. TSSP of hydrogen in Zircaloy-4 with reference data.

Previous studies showed that increasing the maximum temperature and hold time at the maximum temperature had no effect on the TSSD temperature, whereas the TSSP temperature can be reduced [5-7]. In other words, lowering the maximum temperature increases the TSSP temperature. Pan et al. [6] defined this increased temperature as the TSSP2 temperature. They regarded the broad TSSP2 curve as a growth process and the truncated peak as a nucleation stage of hydride formation in the cooling curve.

Additional tests were conducted in order to find the TSSP2 temperature. The maximum temperature was adjusted just above the TSSD temperature. The difference between two temperatures is less than 4 °C. Figure 7 show the TSS of hydrogen in Zircaloy-4. The temperature gap between TSSP and TSSP2 temperature tends to increase with decreasing hydrogen content; on the other hand, the temperature gap between TSSD and TSSP2 is around 65 °C. The TSSP2 of hydrogen in Zircaloy-4 yields the following relationship.

TSSP2 of Zircaloy 4: $C= 8.612\times10^5 \exp(-30583/RT)$

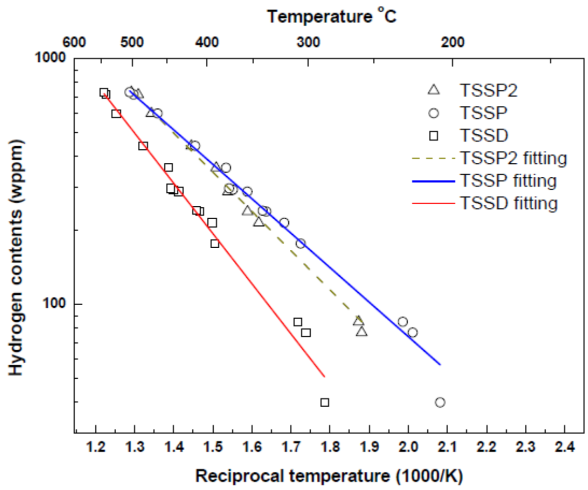

Fig. 4. Terminal solid solubility of hydrogen in Zircaloy-4.

4. Conclusions

The TSS of hydrogen in Zircaloy-4 was studied by the DSC method with 40-731wppm of hydrided specimen. We observed that the solubility limit in alpha-Zircaloy-4 is near 731 wppm and the temperature of eutectoid reaction is around 552.5 °C. The activation energy for dissolution and precipitation is 39.101 KJ/mole and 26.843 KJ/mole, respectively. These values are in good agreement with reference equilibrium TSS data. The temperature gap between two solvus lines is around 50-87 °C at the interesting dry storage temperature range. The activation energy of the TSSP2 is 30.583 KJ/mole and the temperature gap between the TSSD and TSSP2 is 50-66 °C.

REFERENCES

[1] J.J. Kearns, Journal of nuclear materials 22 (1967) 292-303.
[2] B.G. Kammenzind, D.G. Franklin, H.R. Peters, W.J. Duffin, ASTM special technical publication 1295 (1996) 338-369.
[3] R. Tang, X. Yang, International Journal of Hydrogen Energy 34 (2009) 7269-7274.
[4] G.F. Slattery, The Journal of the Institute of Metals 95 (1967) 43-47.
[5] D. Khatamian, Z.L. Pan, M.P. Puls, C.D. Cann, Journal of Alloys and Compounds 231 (1995) 488-493.
[6] Z.L. Pan, I.G. Ritchie, M.P. Puls, Journal of nuclear materials 228 (1996) 227-237.
[7] A. McMinn, E.C. Darby, J.S. Schofield, ASTM special technical publication 1354 (2000) 173-195.