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Effect of thermal history on the terminal solid solubility of hydrogen in Zircaloy-4

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ABSTRACT

The terminal solid solubility (TSS) of hydrogen in zirconium alloys has a hysteresis. The TSS of hydrogen in Zircaloy-4 during cooling and heating were studied using differential scanning calorimetry (DSC) with a hydrogen content of 40–731 wppm. A significant hysteresis gap was observed between the TSS for dissolution (TSSD) and precipitation (TSSP). It was confirmed that the hydrogen dissolution temperature was unaffected by the previous thermal history in comparison with the hydride precipitation temperature. The TSSP temperature increased with a decrease in the maximum temperature, but a significant temperature gap remained even when the maximum temperature was equal to the TSSD temperature. The terminal solid solubility of hydrogen in Zircaloy-4 can be represented by the following equations.

TSSD: $C = 2.255 \times 10^5 \exp(-39101/RT)$.

TSSP: $C = 4.722 \times 10^4 \exp(-26843/RT)$.

TSSP2: $C = 8.612 \times 10^5 \exp(-30583/RT)$.

Based on the experimental results hydrogen solubility path depending on the previous thermal history was proposed.

Introduction

Zirconium alloys have been used as reactor component materials owing to a low neutron absorption cross section, high corrosion resistance, and proper mechanical properties at high temperature. Hydrogen pick-up in zirconium alloy is one of the most important issues in reactor operation [1]. Typical nuclear cladding discharged from the pressurized water reactor has 200–600 wppm of hydrogen depending on the burn-up [2]. Most of the hydrogen can dissolve in Zr-matrix at high temperatures. However, the brittle hydrides can be precipitated during the cool-down which can reduce the ductility of the cladding [3], and

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threaten the integrity of cladding such as hydride re-orientation [4] or delayed hydride cracking (DHC) [5,6]. Interestingly the TSS of hydrogen in zirconium alloys for dissolution (TSSD) and precipitation (TSSP) have a hysteresis. This hysteresis can affect the DHC behavior and hydride re-orientation.

Consequently, the terminal solid solubility (TSS) of hydrogen in zirconium and its alloys has been measured using a variety of techniques: diffusion equilibrium [7–10], dilatometry [11–15], internal friction and dynamic elastic modulus [16–19], small-angle neutron diffraction [20], differential scanning calorimetry (DSC) [15,16,21–25], and synchrotron X-ray diffraction [26]. Kearns [8] reviewed the previous investigations [7,11,27–30] and performed experiment with employing diffusion method to determine the TSS of hydrogen in zirconium alloys. His best fit of the data often used as a standard TSSD for zirconium and Zircaloy-2 and Zircaloy-4. The other methods such as internal friction, DSC and dilatometry are dynamic methods to measure the hydrogen thermal behaviors during the temperature transient.

However, most of the works on the TSS of hydrogen in zirconium alloys are about the TSSD rather than the TSSP. In addition, there are no available data on TSSP2 of hydrogen in Zircaloy-4. The TSSD of hydrogen in zirconium alloy seems to be less sensitive to the 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, a holding time at the peak temperature and a cooling rate; therefore, the published data on TSSP is considerable scatter. The objectives of this study are to confirm the TSS of hydrogen in Zircaloy-4 and evaluate the maximum temperature effect on the TSSP. The DSC method was employed to measure the TSS of hydrogen in Zircaloy-4 owing to simplicity and reproducibility.

Experimental

Materials

Cold worked stress-relieved (CWSR) Zircaloy-4 finally annealed at 470 °C for 5 h 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 Sieverts-type apparatus. After hydrogen charging, the heat treatment was performed at 400 °C for 5–10 h to ensure a uniform distribution of hydride. As a result, 40–1121 wppm of hydrided specimens were obtained. All of the hydrogen concentrations were analyzed by a hydrogen determinator (LECO RH-404), which uses an inert gas fusion method. The error of the determinator is less than 5 wppm.

Table 1 – Chemical composition of Zircaloy-4 (unit: weight%).

Element	Sn	Fe	Cr	C	O	Si	Zr
Weight	1.32	0.21	0.11	0.013	0.13	0.0092	Balance

Differential scanning calorimetry

Basically, DSC measures the changes in the difference in the heat exchange between the sample and the reference. The change in the heat flow signal indicates an exothermic or endothermic reaction when a phase transformation occurs. Fig. 1 shows a typical DSC heat flow and its derivative heat flow curves of hydrided Zircaloy-4 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. In this work, the TSS of hydrogen in Zircaloy-4 was measured using a heat flux DSC (Netzsch 200 F3). The calibrations were conducted prior to the experiment using metal standard samples (In, Sn and Zn). DSC measurements were carried out in purified N_2 at a flow rate of 50 cm^3/min. Generally, DSC is more sensitive at higher heating/cooling rates but such rates tend to slightly increase the TSSD temperature and decrease the TSSP temperature. It is known that the effect of heating rate on the dissolution of hydrogen is negligible [21,22], whereas the effect of cooling rate on the precipitation is more susceptible. Considering these effects, TSS measurements were conducted at cooling and heating rate of 20 °C/min. Most samples were heated to peak temperature of 550 °C. The dwell time at the peak temperature was 5 min and then cooled to 40 °C. Some high hydrogen containing specimens were heated to 580 °C. Each specimen was experienced four identical thermal cycles. All the data were used to calculate the mean TSS values excluding that of first heating cycle. Additional tests were conducted to investigate the hydrogen behavior during thermal cycling and effect of the maximum temperature.

Determination of the TSSD and TSSP temperatures

There are three important temperatures for determining the TSS: peak temperature, completion temperature, and maximum slope temperature. The peak temperature (PT) is the maximum or minimum point in the heat flow curve and the maximum slope temperature (MST) is the point of maximum deviation of the heat flow. The completion

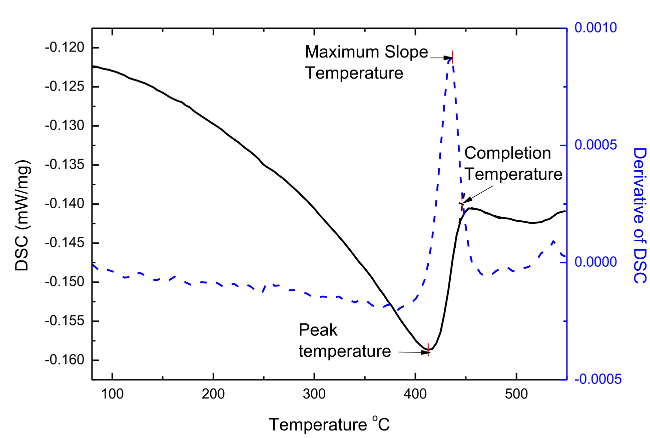

Fig. 1 – DSC curve and its time derivative of Zircaloy-4 specimen with a hydrogen content of 288 wppm during heat-up.