The effect of hydrogen on the heat capacity of Zr-based alloys

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1. Introduction

Zr-based alloys have been widely used as fuel cladding for light water reactors because of their low neutron absorption cross section and good corrosion resistance. Hydrogen, generated mainly from the oxidation reaction between Zr alloy and cooling water is absorbed by the claddings. When the hydrogen concentration in Zr alloys exceeds the terminal solid solubility, the claddings are susceptible to a crack initiation and a propagation. In addition, hydrogen addition in the Zr alloys changes the heat capacity which is important for an evaluation of the fuel temperature under normal, transient and accident reactor conditions. Although there are many papers[1,2] for a heat capacity of zirconium based alloys, papers for that of specimens containing hydrogen are limited.

In this study, the heat capacity of Zircaloy-4, Zr-1Nb-1Sn-0.1Fe was determined from 150℃ to 550℃ by using a DSC. Also, the effect of hydrogen on the heat capacity of two alloys was investigated.

2. Experimental

The hydrogen concentrations of the as-received Zircaloy-4, Zr-1Nb-1Sn-0.1Fe were about 5ppm. Hydrogen was introduced into the specimens by two methods. One was a gas charging at 400 ℃ in an Ar/H2 mixed gas, and the absorbed hydrogen concentrations were controlled by varying the reaction duration. The other was an electrolyte cathodic charging. A platinum anode and an electrolytic of 10vol.% H_2SO_4 + 90vol.% H_2O were used for the cathodic charging. Then the specimens were annealed in separated quartz tubes, sealed under a vacuum, at 673K for 24h to make sure that the hydrogen concentration was uniform in the specimens. The specimens were cut into shapes approximately 4mm square and 0.5 mm thick.

The specimens were measured by using a differential scanning calorimeter (Netzsch DSC-404, high temperature type) to obtain the heat capacities of the specimens. Each specimen was measured for their heat capacities in three consecutive thermal cycle runs. The mean of the last two results of the three runs was chosen to be a result because the first run was affected by the prior thermal history. The DSC measurements were carried out in purified Ar at a flow rate of 50 cm^3 /min.

In all the measurements, the maximum temperature was chosen to be 600℃ and the cooldown/heatup rate was 10℃/min. The hydrogen concentration of the specimens was analyzed after the DSC measurements by the hot vacuum extraction method with an accuracy of ± 3%.

3. Results

3. 1 Heat capacity of as-received Zircaloy-4 and Zr-1Nb-1Sn-01.Fe

The heat capacities of the as-received Zircaloy-4 and Zr-1Nb-1Sn-01.Fe, containing 5ppm, are shown in Fig. 1. The heat capacity of the Zr-1Nb-1Sn-01.Fe is higher than that of the Zircaloy-4. It might be anticipated due to the difference in the Nb addition between the present Zircaloy-4 and the Zr-1Nb-1Sn-0.1Fe. So, the effect of the Nb content was investigated in Zr-xNb(x= 0, 1.5). Fig. 2 shows the heat capacities in Zr-xNb(x= 0, 1.5) The heat capacity was increased with the increase of Nb content. This result may be reasonably accepted because the heat capacity of the Zr-1Nb-1Sn-01.Fe is higher than that of the Zircaloy-4 due to the difference in the Nb content between the Zircaloy-4 and the Zr-1Nb-1Sn-01.Fe.
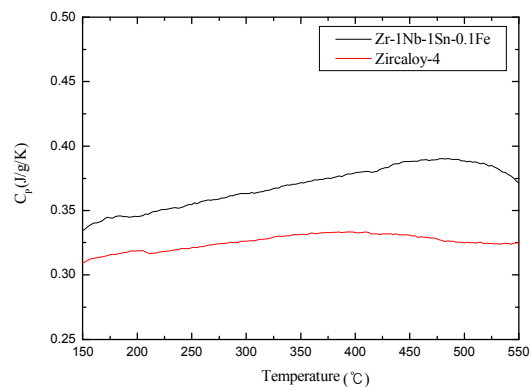

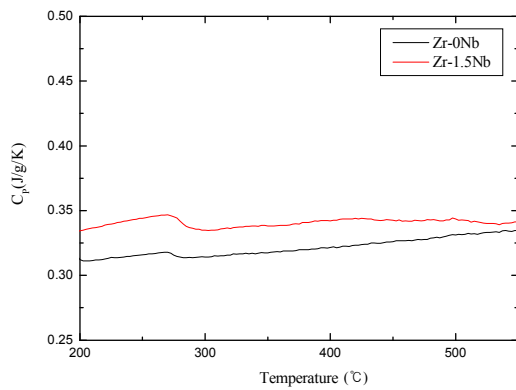Fig. 1. Heat capacity of as-received Zircaloy-4 and Zr-1Nb-1Sn-0.1Fe.

Fig. 2. Heat capacity of Zr-xNb(x= 0, 1.5)

3. 2 The effect of hydrogen addition on the C_P of the Zircaloy-4

Fig. 3 shows the heat capacities of the Zircaloy-4 with various hydrogen concentrations of 38, 90, 118, 249 and 364 ppm. In the C_P curves, the broad peaks were seen with a peak size and peak terminal temperature depending considerably on the hydrogen concentration. It results from the endothermic reaction of the dissolution of the δhydrides. In a previous paper[3], two type of peaks were observed on the heat capacity curve of the Zircaloy-2 and high Fe Zircaloy ; (1) small peaks around 187℃ and (2) broad peaks due to the endothermic reaction of the dissolution of the δhydrides. For the first low temperature peaks, the phase transition from γhydride (ZrH) to α+δhydride (ZrH$_X$) might be anticipated. There has been an evidence[4] that supports the γto δphase transition around 187℃. But small peaks around 460K in this study were not observed. It may be related with the microstructure of the alloys.
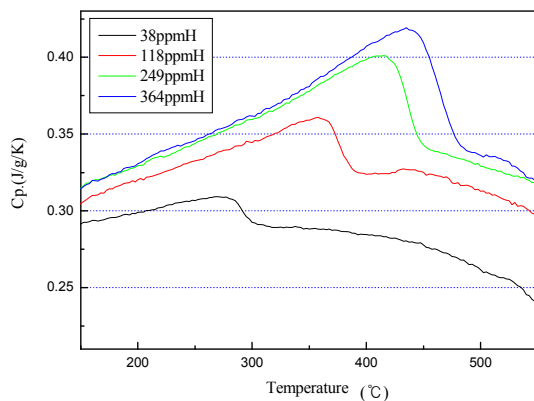

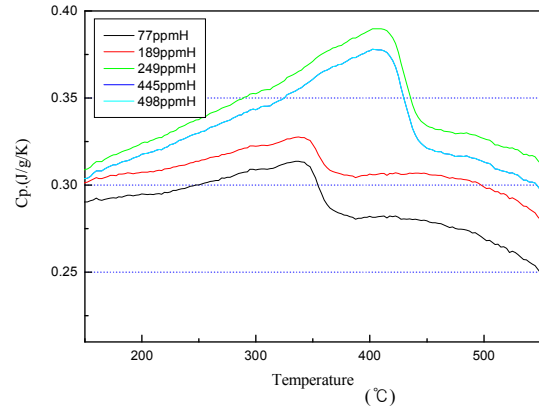Fig. 3. Heat capacities of the Zircaloy-4 with hydrogen concentrations of 38-364ppm.

Fig. 4. Heat capacities of the Zr-1Nb-1Sn-0.1Fe with hydrogen concentrations of 77-498ppm.

Fig. 4 shows the results of the heat capacities of the Zr-1Nb-1Sn-01.Fe with various hydrogen concentrations of 77, 189, 249, 400 and 498 ppm. The same type of broad peaks was observed as those for Zirclaloy-4 in Fig.3.

4. Conclusions

The heat capacity of Zircaloy-4, Zr-1Nb-1Sn-0.1Fe was determined from 150℃ to 550℃ by using a DSC. The heat capacity of the Zr-1Nb-1Sn-01.Fe is higher than that of the Zircaloy-4 due to the difference in the Nb content between the Zircaloy-4 and the Zr-1Nb-1Sn-01.Fe. In the C_P curves of Zircaloy-4 and Zr-1Nb-1Sn-0.1Fe, the broad peaks were seen with a peak size and peak terminal temperature depending considerably on the hydrogen concentration due to the endothermic reaction of the dissolution of the δ hydrides.

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