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Heat capacity and phase transition of Zircaloy-4

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Abstract

Heat capacity from 300 K to 1100 K and enthalpy change of the phase transition of Zircaloy-4 between 1080 K and 1270 K were measured with a triple-cell-type differential scanning calorimeter and a twin-type drop calorimeter. Heat capacities measured with these two apparatuses were in good agreement with each other, and they were several % less than the other literature values. They were also in good agreement with the values calculated by assuming the additivity of the contributions of the elements and the values of pure zirconium. On the phase transition, two peaks were observed in the temperature range from 1080 K to 1270 K. The first peak was assigned to a eutectic temperature of the Zr–Fe system or the Zr–Cr system, and the second peak was considered to come from the α–β phase transition of Zr affected by Sn and O. The enthalpy change of the α–β phase transition (ΔH_{tr}) was determined to be 4.12 ± 0.35 kJ mol^{-1}, which was in good agreement with literature values for pure Zr. © 1997 Elsevier Science B.V.

1. Introduction

Zirconium alloys are widely used as a cladding material for light water reactors because of their low neutron absorption cross section. In Japan, two kinds of zirconium alloys are utilized; Zircaloy-2 (1.5%Sn, 0.12%Fe, 0.05%Ni, 0.1%Cr) for BWR and Zircaloy-4 (1.5%Sn, 0.15%Fe, 0.1%Cr) for PWR. Thermophysical property data of these alloys are very important for the evaluation of the reliability and the safety of the reactor systems. In particular, heat capacity is a very important parameter to evaluate the thermochemical behavior of the nuclear fuel assembly. However, there are very limited data sets obtained up to the present [1,2]. In addition, the data above the operation temperature are required to analyze the accidental behavior of the fuel assembly.

We have developed several kinds of calorimeters including a high-temperature laser flash calorimeter, a twin-type calorimeter and a specially designed differential scanning calorimeter (DSC) with a triple-cell systems to measure heat capacity, enthalpy, etc., and obtained the heat capacities of several kinds of nuclear materials with very high accuracy [3–5].

In this study, we measured the heat capacity of Zircaloy-4 by the two different methods of DSC and drop calorimetry and investigated the phase transitions. The former is useful to detect and measure a sharp change in heat capacity on phase transition, and the latter is good at determining absolute values of enthalpy change and derived heat capacity values. In the measurements, it was confirmed that both results obtained by these two methods were in very good agreement with each other.

2. Experimental

2.1. Specimen

The Zircaloy-4 specimens were made of a commercial cladding material supplied by Nuclear Development Co. (NDC), and the size was 7.1 mm∅ × 35 mm for Drop calorimetry and 3.5 mm∅ × 2 mm for DSC. The chemical composition is listed in Table 1. These specimens were polished with emery paper, cleaned in an ultrasonic bath, and heat-treated at 1073 K for 20 h under 1×10^{-5} Pa for removal of hydrogen, before set in the sample holders for measurement.

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Table 1
Chemical composition of Zircaloy-4

Element	Concentration (wt%)
Sn	1.558
Fe	0.220
Cr	0.117
Fe+Cr	0.337
O	0.132
Zr	BALANCE

2.2. Measurement

Enthalpy-change measurements were carried out with a twin-type, high temperature drop calorimeter. Basically the structure of the twin-type drop calorimeter is almost the same as that given in literature [6,7]. But, the calorimeter was modified for high-temperature measurement up to 1500 K. The schematic drawing of the apparatus is shown in Fig. 1. The temperature of the isothermal jacket was kept at 323 ± 0.5 K and NBS reference material of Al_2O_3 (SRM-720) was utilized to determine the apparatus constant in the temperature range of 300–1500 K. Heat capacity of Zircaloy-4 was obtained by the following two methods;

(1) differentiation of enthalpy expressed by polynomial as $H(T) - H(T_0) = AT^2 + BT + C + DT^{-1}$, and

(2) modified QLLR (quasi-local linear regressions) method.

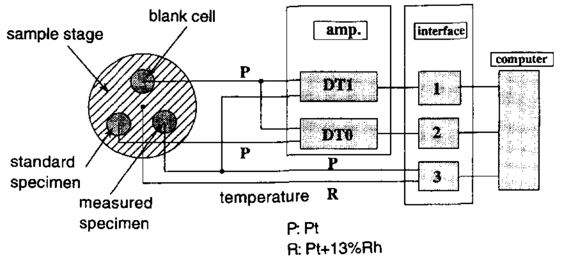

Fig. 2. Block diagram for DSC measurement.

The latter is to obtain a heat capacity value by averaging the slopes between one point and four neighboring points of enthalpy measured as a function of temperature [8].

On the other hand, heat capacity was directly measured with a differential scanning calorimeter with a triple-cell system. This apparatus was a newly designed and fabricated one, and it has a blank cell as well as the ones for a standard specimen and a measured specimen. A block diagram for DSC measurement is illustrated in Fig. 2. From the differential output between the standard cell and the blank cell and the one between the specimen cell and the blank cell, we can calculate the average heat capacity of the specimen in a temperature range by 'enthalpy method', or continuous heat capacity values by 'scanning method'. More detailed information of this apparatus is given in literature [9].

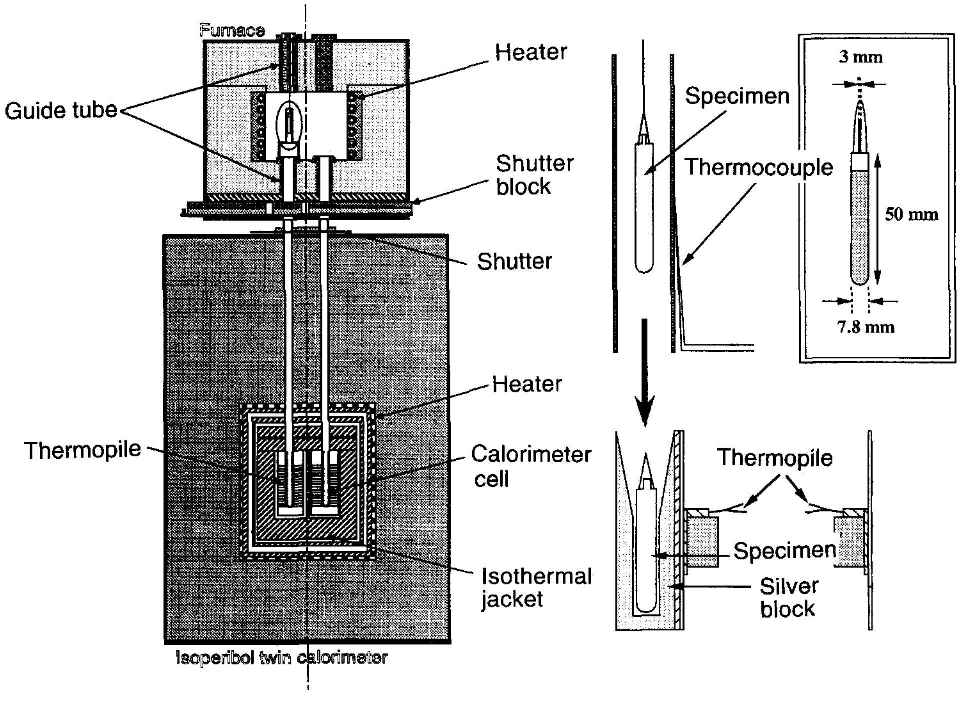

Fig. 1. Schematic drawing of twin-type drop calorimeter.

3. Results and discussion

3.1. Heat capacity of Zircaloy-4 in the temperature range of 300–1000 K

The result of enthalpy change measured by drop calorimetry is shown in Fig. 3. Above 1000 K, there were observed some phase transitions. Below 1000 K, fitting of the present data was carried out using the methods of least squares, which gave the result

$$[H(T)-H(323\text{ K})]/\text{kJ mol}^{-1} = -7.9517+23.324(T/\text{K})+4.1201\times10^{-3}(T/\text{K})^2 + 3.8771\times10^{-7}(T/\text{K})^3$$

for the 300–1000 K temperature range. The deviation of the experimental values from the calculated ones are within 1%.

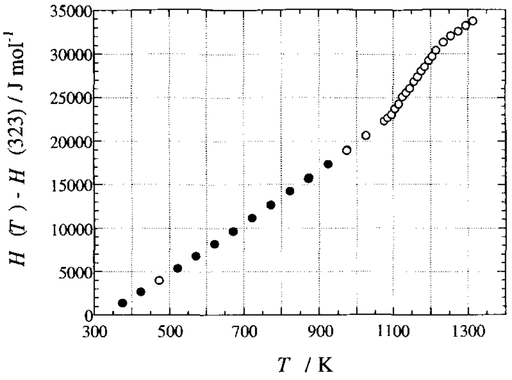

Fig. 3. Enthalpy of Zircaloy-4. Open circles and solid circles indicate different runs.

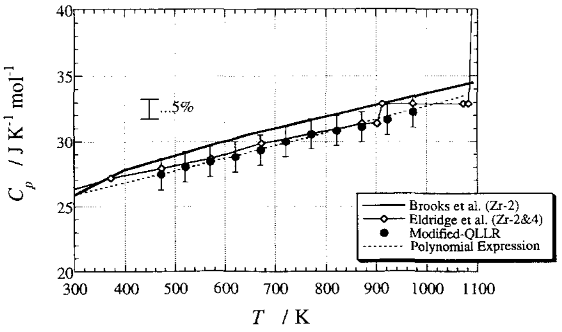

Fig. 4. Heat capacity of Zircaloy-4 obtained by drop calorimetry with literature values.

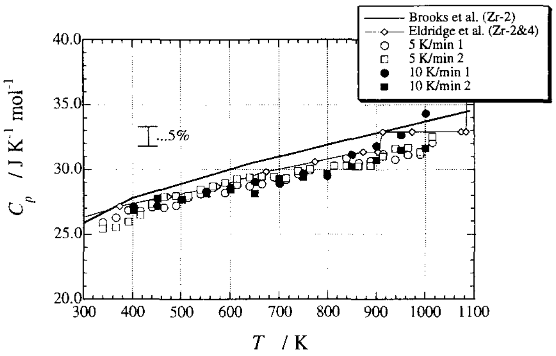

Fig. 5. Heat capacity of Zircaloy-4 obtained by DSC with literature values.

The derived heat capacity values from the enthalpy data are shown in Fig. 4. The heat capacity is consequently given by the equation

$$C_p/\text{J K}^{-1}\text{ mol}^{-1} = 23.324+8.2402\times10^{-3}(T/\text{K}) + 11.6313\times10^{-7}(T/\text{K})^2.$$

The enthalpy obtained here was 1% lower than the values for Zircaloy-2 and Zircaloy-4 recommended by Eldridge et al. [1] below 900 K, and 3% lower than the values for Zircaloy-2 by Brooks et al. [2].

Fig. 5 shows heat capacity data obtained by DSC using the enthalpy method with the temperature scanning rate of 5 K min^{-1} and 10 K min^{-1}. The values were expressed by the equation

$$C_p/\text{J K}^{-1}\text{mol}^{-1} = 24.374+7.6134\times10^{-3}(T/\text{K}) - 1.2592\times10^{5}(T/\text{K})^{-2}$$

within the deviation of ±2.5%.

The results were summarized in Fig. 6 with the comparison of the literature values of pure zirconium. The two series of heat capacity data obtained by the different two

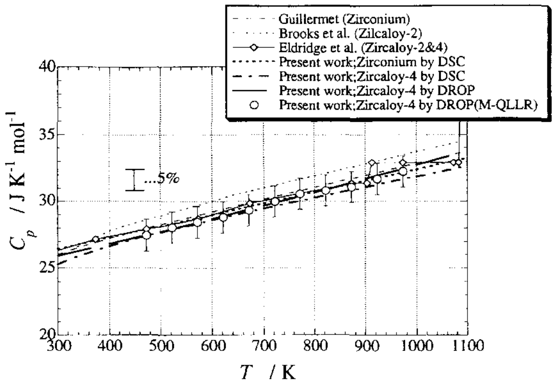

Fig. 6. Heat capacities of Zircaloy-4 and pure zirconium.

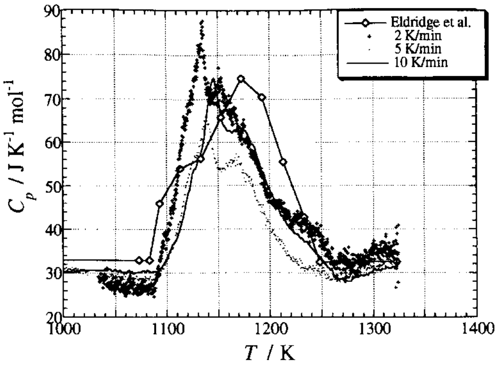

Fig. 7. Heat capacity in phase transition temperature range obtained by DSC with three temperature scanning rate.

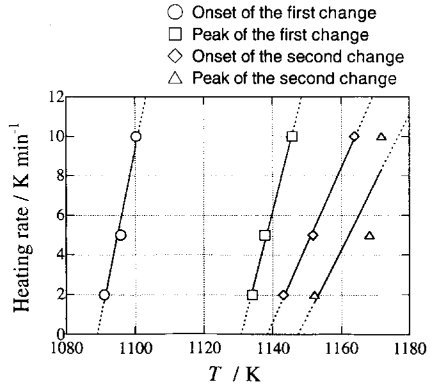

Fig. 9. Onset temperatures and peak temperatures as a function of temperature scanning rate.

methods were quite in good agreement with each other, and a few % lower than the literature values. These experimental values were also in good agreement with the values of pure zirconium obtained by Guillermet [10] and by our group [11], which is expected by the calculation assuming the additivity of the contributions of the elements (only 0.2% in difference between Zircaloy-4 and zirconium).

3.2. Phase transition in the temperature range of 1080 K–1270 K

Fig. 7 shows the heat capacity obtained by DSC with three temperature scanning rates. Two peaks were observed between 1080 K and 1270 K. The similar two peaks were also observed by drop calorimetry using the modified QLLR-method as shown in Fig. 8. Eldridge et al. also reported a heat capacity increase with a shoulder in the same temperature range [1]. The absolute value of the heat capacity in the phase transition in each measurement was not correctly expressed in Fig. 7 because of the difference in sensitivity in each measurement. From this figure, the onset temperatures of both changes are plotted against temperature scanning rate in Fig. 9, where the extrapolation of each plot gives the phase transition temperatures of 1089 K and 1138 K.

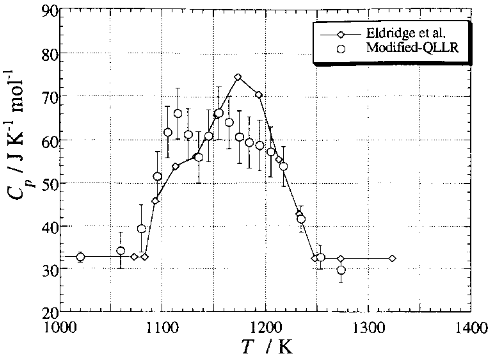

Fig. 8. Heat capacity in phase transition temperature range obtained by drop calorimetry using the modified QLLR-method.

According to the phase diagrams of Zr–Fe [12] and Zr–Cr [13], the eutectic temperatures of Zr–Fe and Zr–Cr are 1068 K and 1109 K, respectively, and the phase diagrams of Zr–O [14] and Zr–Sn systems [15] indicate that the α–β transition temperature of pure zirconium (1136 K) increases by the effects of additive tin and oxygen. From these facts, it is concluded that the first change comes from the eutectic reaction in the Zr–(Fe + Cr) system and the second change is due to the α–β transition of pure zirconium affected by tin and oxygen.

Fig. 10 shows the enthalpy data in the phase transition region. From this figure, enthalpy change of this phase transition was obtained to be 4.12 ± 0.35 kJ mol^{-1} by averaging the enthalpy difference between the α phase and the β phase. This value is in good agreement with the value for pure zirconium, 4.02 ± 0.35 kJ mol^{-1} in JANAF thermochemical tables [16], and 3.94 ± 0.35 kJ mol^{-1} by Hultgren [17]. Since the contribution of the first change is

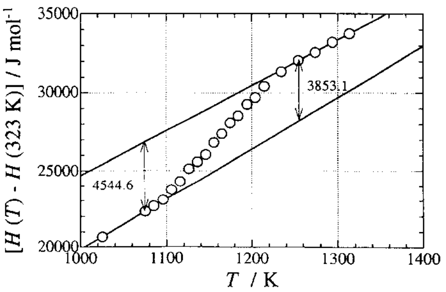

Fig. 10. Temperature dependence of enthalpy in the phase transition range.

quite small due to the small amount of iron and chromium contained in the alloy, this agreement is quite reasonable.

4. Conclusion

Heat capacity from 300 K to 1100 K and enthalpy change of phase transition of Zircaloy-4 between 1080 K and 1270 K were measured with a triple-cell-type differential scanning calorimeter and a twin-type drop calorimeter.

(1) Heat capacities measured by drop calorimetry and DSC were expressed by

$$C_p/\mathrm{J\,K^{-1}\,mol^{-1}} = 23.324 + 8.2402 \times 10^{-3}(T/\mathrm{K}) + 11.6313 \times 10^{-7}(T/\mathrm{K})^2$$

and

$$C_p/\mathrm{J\,K^{-1}\,mol^{-1}} = 24.374 + 7.6134 \times 10^{-3}(T/\mathrm{K}) - 1.2592 \times 10^{5}(T/\mathrm{K})^{-2},$$

respectively, which are in good agreement with each other, and they were several % less than the other literature values. They were also in good agreement with the values calculated by assuming the additivity of the contributions of the elements and the values of pure zirconium.

(2) On the phase transition, two peaks were observed in the temperature range from 1080 K to 1270 K. On-set temperatures of these two peaks determined with the differential scanning calorimeter were 1080 K and 1140 K. The first peak was assigned to a eutectic temperature of the Zr–Fe system or the Zr–Cr system, and the second peak was considered to come from the α–β phase transition of Zr affected by Sn and O. The enthalpy change of the α–β phase transition (ΔH_{tr}) was determined to be 4.12 ± 0.35 kJ mol^{-1}, which was in good agreement with literature values for pure Zr.

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