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HEAT CAPACITY MEASUREMENT OF ZrO_x and $(Zr_{1-y}Nb_y)O_x$ FROM 325 TO 905 K

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Heat capacities of zirconium-oxygen alloys, ZrO_x ($x = 0.17, 0.20, 0.28$ and 0.31), and those of niobium doped alloys, $(Zr_{1-y}Nb_y)O_x$ ($x = 0.17$ and 0.28, $y = 0.005$ and 0.01), were measured from 325 to 905 K by an adiabatic scanning calorimeter. Two kinds of heat capacity anomalies were observed for all samples. The anomaly at higher temperatures was assigned to be due to an order-disorder rearrangement of oxygen atoms. Another anomaly at lower temperatures was due to a non-equilibrium phenomenon. The entropy change due to the order-disorder transition for Zr–O solid solution at higher temperature obtained from this experiment was compared with the theoretical value. The transition temperature, transition enthalpy and entropy changes due to the order-disorder transition decreased with increasing niobium contents, indicating that arrangement of oxygen atoms in lower temperature phase may be partially disordered by the interaction between niobium and oxygen atoms.

Keywords: adiabatic scanning calorimeter, heat capacities, zirconium-oxygen and zirconium-oxygen niobium doped alloys

Introduction

An α–zirconium metal dissolves oxygen atoms up to 30 at.% in the octahedral interstices of the hcp metal lattice, forming ordered structures at higher oxygen compositions. Hirabayashi *et al.* [1–5] have determined the crystal structure in the ordered phases by X-ray, electron and neutron diffraction methods. According to their studies there are three phases in zirconium-oxygen alloys; the completely ordered phase α'', the intra layer disordered phase α' and the completely disordered phase α. Marked changes in various physical properties such as electrical resistivity [6, 7, 9, 10], microhardness [8] and the diffusion coefficient of oxygen [11] with temperature and composition have been observed due to the order-disorder transition of oxygen atoms in zirconium-oxygen alloys. Arai and Hirabayashi [6] measured the heat capacities of the ZrO_x ($x = 0.16$~0.41) alloys and obtained entropy changes for the transition, whose values are considerably

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small compared with the case of titanium-oxygen [12] and hafnium-oxygen alloys [13]. They also calculated the theoretical transition entropy change for the order-disorder transition in titanium-oxygen and hafnium-oxygen alloys from the structure analysis, but did not calculate for zirconium-oxygen alloys.

In this paper, the heat capacities of ZrO_x (x = 0.17, 0.20, 0.28 and 0.31) and $(Zr_{1-y}Nb_y)O_x$ (x = 0.17 and 0.28, y = 0.005 and 0.01) were measured from 325 to 905 K in order to clarify the transition mechanism from the transition temperatures, transition enthalpy and entropy changes for the order-disorder transitions.

Experimental

Sample preparation

Samples of zirconium-oxygen alloys with O/Zr ratios of 0.17, 0.20, 0.28 and 0.31 were prepared as follows; zirconium metal sponge of 99.5% purity and zirconium dioxide powders of 99.99% purity were mixed in an appropriate ratio and melted a few times using a plasma jet furnace under Ar gas stream. The cast sample obtained was sealed in a quartz tube, annealed 3 days at 1273 K, and cooled to room temperature over a period of 3 days. The sample was crushed into pieces less than 3 mm in a size using a stainless-steel mortar. The crushed sample of about 16 g was sealed in a quartz vessel filled with He gas of 20 kPa, and annealed at 873 K for 2 weeks, then 500 K for 2 weeks and cooled slowly to room temperature to obtain a highly ordered phase. An X-ray diffractometry showed that all the samples were α-Zr–O single phase. The O/Zr ratio of the sample was determined from the weight gain by oxidizing it to ZrO_2 at 1273 K in air for 1 week.

Doped samples of $Zr_{1-y}Nb_yO_{0.17}$ and $Zr_{1-y}Nb_yO_{0.28}$ (y = 0.005 and 0.01) were prepared by using similar method to undoped zirconium-oxygen alloys. The Nb/Zr ratio of the sample was determined by fluorescent X-ray analysis. It was found from the plots of the lattice constants against niobium contents that all the samples except $Zr_{0.99}Nb_{0.01}O_{0.17}$ were single phase of α–Zr(Nb)–O.

Heat capacity measurement

Heat capacities of ZrO_x and $(Zr_{1-y}Nb_y)O_x$ were measured by an adiabatic scanning calorimeter [14]; in this calorimeter the power supplied to the sample was measured continuously, and the heating rate was kept constant regardless of the kind and amount of the sample. The heating rate chosen was 2 $\mathrm{deg \cdot min^{-1}}$, and the measurement was carried out between 325 and 905 K under a pressure of about 130 Pa of air. The heating rate and adiabatic control were usually maintained within ±0.005 $\mathrm{deg \cdot min^{-1}}$ and ±0.01 K, respectively. The heat capacity mea-surement was conducted within an imprecision of ±2%.

Results and discussion

Heat capacity of Zr–O *solid solution*

The results of the heat capacity measurement of ZrO_x ($x = 0.17$, 0.20, 0.28 and 0.31) are shown in Fig. 1. The solid line in the figure is a base line of heat capacity which is determined by the heat capacity analysis as will be shown later.

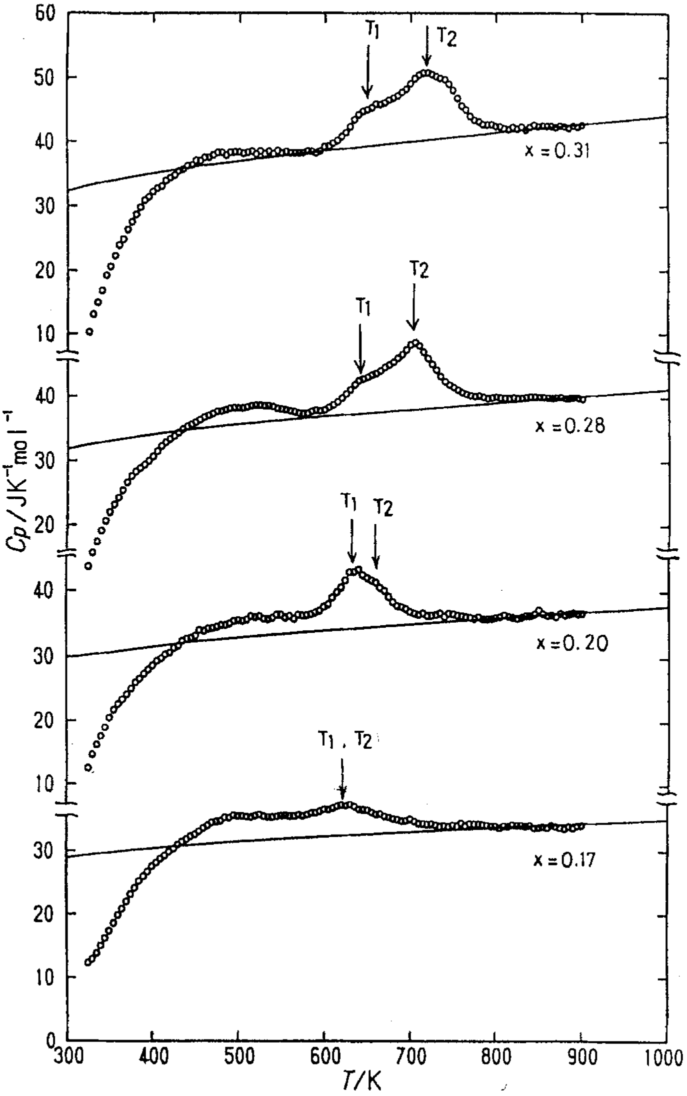

Fig. 1 Heat capacities of ZrO_x ($x = 0.17$, 0.20, 0.28 and 0.31). The solid line is a base line of heat capacity

Two kinds of heat capacity anomalies are seen for all samples in the figure; the broad peak at about 500 K (we designate it the low temperature heat capacity anomaly in this paper) and two sharp peaks (T_1 and T_2) seen in the temperature range from 600 to 750 K (we designate it the high temperature heat capacity anomaly).

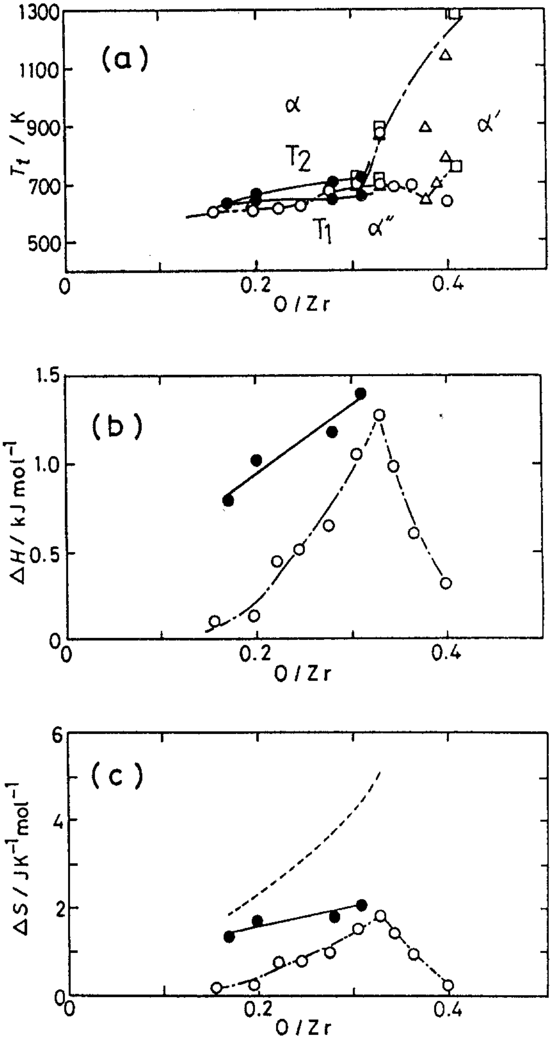

Fig. 2 Transition temperatures (a), transition enthalpy (b) and transition entropy (c) changes of ZrO_x as a function of O/Zr ratios. ● —— ● : heat capacity in this work, O — · — O :heat capacity by Arai and Hirabayashi [6], Δ : electrical resistivity by Arai and Hirabayashi [6], □: neutron diffraction by Hirabayashi *et al.* [4]. ———— : theoretical line (dS_1)

(i) Low temperature heat capacity anomaly

The low temperature heat capacity anomalies about 500 K seen in Fig. 1 have been observed in our laboratory for V–O [15, 16] and Ti–O solid solutions [17]. These anomalies are considered as exo- and endothermic reactions by the relaxation of thermal non-equilibrium states as explained qualitatively elsewhere [16].

(ii) High temperature heat capacity anomaly

Two high temperature heat capacity anomalies (T_1 and T_2) in the temperature range from 600 to 750 K seen in Fig. 1 are thought to be due to the order-disorder rearrangement of the interstitial oxygen atoms in zirconium host lattices, the transition temperatures of T_1 and T_2 correspond to phase transition from the completely ordered phase α'' to the intra layer disordered phase α′ and that from the intra layer disordered phase α' to the completely disordered phase α, respectively, and their results in this paper together with those by Arai and Hirabayashi [6] are shown in Fig. 2(a). To estimate the transition enthalpy and entropy changes, it is needed to obtain the base line of the heat capacity which is determined by the same procedures as described in our previous paper [16].

The heat capacity of ZrO_x is expressed by the sum

$$C_p = C_h + C_d + C_e + C_{ah} + \Delta C \,, \tag{1}$$

where C_h is the harmonic term of the lattice vibration, C_d the dilational term, C_e the electronic term, C_{ah} the anharmonic term of the lattice vibration and ΔC the excess heat capacity due to the order-disorder transition.

The harmonic term of the lattice vibration for ZrO_x can be calculated from

$$C_h = 3R \cdot D\ \theta_D/T \cdot (1 + x) \tag{2}$$

where $D(\theta_D/T)$ is the Debye function. Debye temperatures, θ_D, of ZrO_x (x = 0.17, 0.20, 0.28 and 0.31) samples are calculated from a linear relationship between the Debye temperature and the O/Zr ratio to be 351, 365, 400 and 411 K, respectively [18].

The dilational term of the molar heat capacity, C_d, can be estimated from Nernst-Lindemann equation [19], which is expressed as

$$C_d = A \cdot \frac{T_m}{T} \cdot C_p^2 \tag{3}$$

where A is the universal constant, 0.00255 $K \cdot mol \cdot J^{-1}$, and T_m the melting point of ZrO_x.

The electronic and anharmonic terms of the molar heat capacity of ZrO_x are not available. We assume that the excess heat capacity, ΔC, due to the order-disorder transition is negligibly small in the temperature range from 800 to 900 K for all samples. The electronic and anharmonic terms are then calculated from the experimental heat capacity data, C_p, and the values of C_h and C_d in this temperature range by using the following equation,

$$(C_e + C_{ah}) = C_p - (C_h + C_d) = (\gamma + b) \cdot T \qquad (4)$$

where γ and b are the coefficients of the electronic and anharmonic terms, respectively. The value of this sum is calculated from linear regression line of Eq. (4) in the temperature range from 800 to 900 K and their results are shown in Table 1. The base line of the heat capacity shown in Fig. 1 is calculated as the sum of Eqs (2)–(4).

The excess heat capacities for ZrO_x due to the two order-disorder transitions are estimated with the similar way to our previous study by the present authors [17] and the results of transition temperature (T_t), transition enthalpy (ΔH) and entropy (ΔS) changes are shown in Figs 2(a), (b) and (c), respectively , as a function of the O/Zr ratio.

Table 1 The coefficients of the electronic and anharmonic terms, $(\gamma + b)$, for ZrO_x samples

O/Zr	$(\gamma + b)$ ($\times 10^{-3}$) / $J \cdot K^{-2} \cdot mol^{-1}$
0.17	4.25
0.20	6.36
0.28	7.83
0.31	9.67

In Fig. 2(c), dS_1 is the theoretical entropy change due to the order-disorder transition of oxygen atoms from the ordered phase (α"–ZrO_x type [4], the crystal structure of the ordered phase is shown in Fig. 3) to the completely disordered phase (α), and the theoretical value is calculated from the following equation by using Stirling's approximation

$$dS_1 = k \ln ({}_{N}C_{Nx}) - k \ln ({}_{N/3}C_{Nx})$$

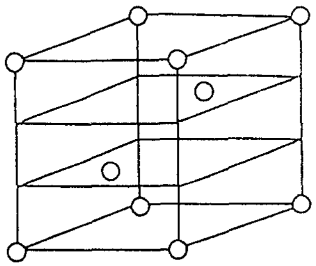

Fig. 3 Crystal structure of the completely ordered phase (α"–ZrO_x type) [4]. Only oxygen atoms are shown in the figure

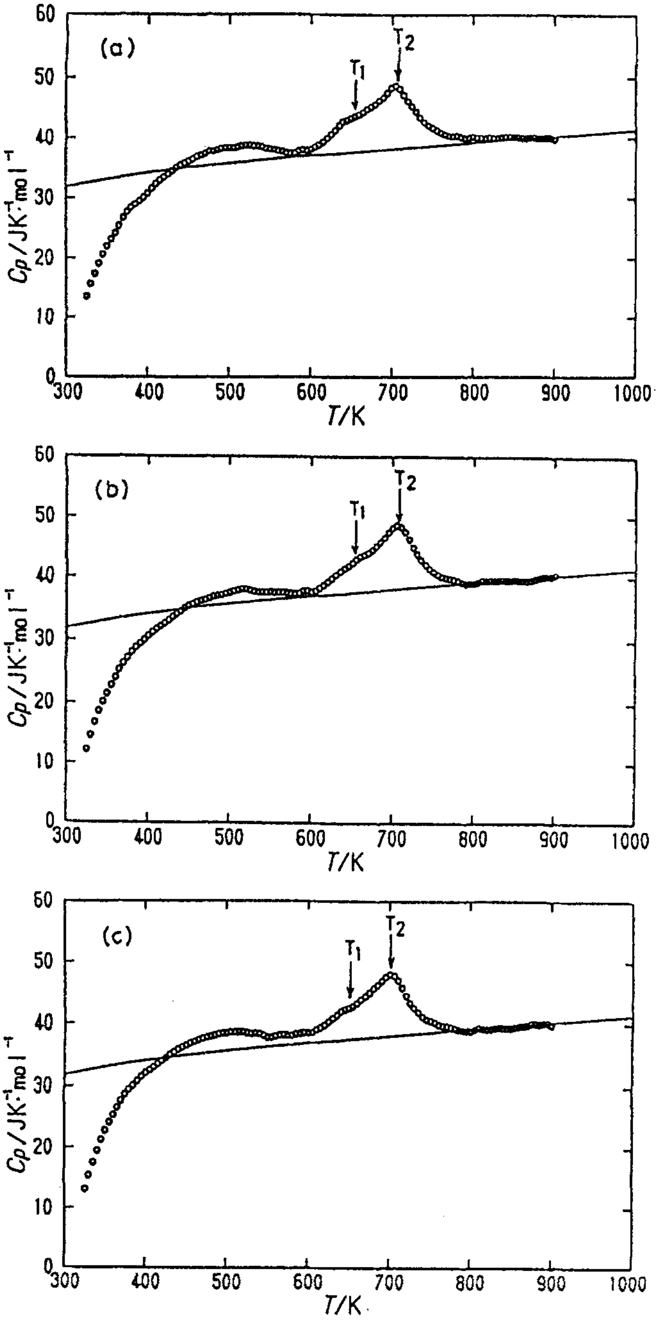

Fig. 4 Heat capacities of $(Zr_{1-y}Nb_y)O_{0.28}$. (a), (b) and (c) are heat capacities for the compositions of $y = 0$, $y = 0.005$ and $y = 0.01$, respectively. The solid line is a base line of heat capacity

$$= -Nk\left\{(1-x)\ln(1-x)-\left(\frac{1}{3}-x\right)\ln\left(\frac{1}{3}-x\right)-\frac{1}{3}\ln 3\right\} \qquad (5)$$

where k is Boltzmann's constant and N Avogadro's number. The average transition temperatures of T_1 and T_2 for each sample in this study are in good agreement with those by Arai and Hirabayashi [6], although their experiments could not resolve two peaks for $ZrO_{0.20}$, $ZrO_{0.28}$ and $ZrO_{0.31}$ samples. However, the transition entropies of each sample in this study are larger than those by Arai and Hirabayashi [6], but smaller than the theoretical values of dS_1. This fact may be

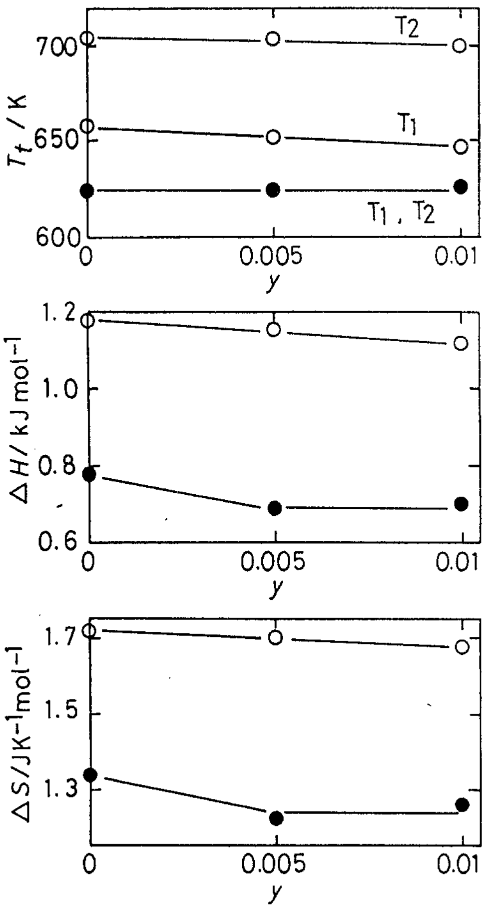

Fig. 5 Transition temperatures (T_t), transition enthalpy (ΔH) and transition entropy (ΔS) changes for $(Zr_{1-y}Nb_y)O_x$ as a function of niobium contents (y). The marks of O and ● show the experimental data for $x = 0.28$ and $x = 0.17$, respectively

explained by assuming the partially ordered phase at low temperature caused by quenching of the sample.

Heat capacity of $(Zr_{1-y}Nb_y)O_x$

Heat capacities of $(Zr_{1-y}Nb_y)O_{0.28}$ ($y = 0$, 0.005 and 0.01) in the temperature range from 325 to 905 K are shown in Figs 4(a), (b) and (c), respectively, where heat capacities of niobium doped samples are in good agreement with those of undoped ZrO_x samples in the temperature range from 800 to 900 K. The transition temperatures (T_1), transition enthalpy (ΔH) and entropy (ΔS) changes of doped samples are shown in Fig. 5 as a function of niobium contents. As can be seen in the figure, the transition temperatures, transition enthalpy and entropy changes decrease slightly with increasing niobium contents. The decreases of transition enthalpy and entropy changes with increasing niobium contents may be explained by the fact that oxygen stabilizes α phase of zirconium, whereas niobium stabilizes β phase: Since niobium substituted for zirconium sites causes partial disordering of oxygen atoms at low temperature phase, the difference of regularity between ordered and disordered states of niobium doped sample is smaller than that of undoped sample. It is also seen in Fig. 5 that the solubility limit of $(Zr_{1-y}Nb_y)O_{0.17}$ sample is around the composition of $y = 0.005$ as expected from the plots of lattice constants against niobium contents.

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Zusammenfassung — Mittels eines adiabatischen Scanning-Kalorimeters wurden im Temperaturbereich 325-905 K die Wärmekapazitäten von Zirkonium-Sauerstoff Legierungen ZrO_x (mit x=0.17, 0.20, 0.28 und 0.31) und von mit Niob versetzten Legierungen $(Zr_{1-y}Nb_y)O_x$ gemessen. Für alle Proben konnten zwei Arten von Wärmekapazitätsanomalien beobachtet werden. Die Anomalie bei höherer Temperatur wird einer Ordnung-Unordnung-Umwandlung von Sauerstoffatomen zugeschrieben. Eine andere Anomalie bei niedrigerer Temperatur steht mit einer Nicht-Gleichgewichtserscheinung in Zusammenhang. Die Entropieänderung der Ordnung-Unordnung-Umwandlung für einen Zr–O Mischkristall aus diesem Experiment wurde mit dem theoretischen Wert verglichen. Umwandlungstemperatur, Umwandlungsenthalpie- und Entropieänderungen der Ordnung-Unordnung-Umwandlung nehmen mit steigendem Niobgehalt ab, was zeigt, daß die Anordnung der Sauerstoffatome in Phasen mit niedrigerer Temperatur partiell durch die Wechselwirkungen zwischen Niob- und Sauerstoffatomen gestört werden kann.