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ANOMALIES IN HEAT CAPACITY MEASUREMENTS OF RuO_2–TiO_2 SYSTEM

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Abstract

DSC was used for heat capacity measurements of pure RuO_2 in the temperature range from 300 to 1170 K of solid solutions corresponding to the compositions of $(Ti_{1-x}Ru_x)O_2$ ($x \leq 0.15$ and $x \geq 0.85$) and in the temperature range from 300 to 1550 K of pure TiO_2. The analysis of experimental data obtained within ±2% of accuracy has shown that the characteristic temperatures representing the harmonic lattice vibrations do not strongly depend on the chemical composition x. It was demonstrated that non-harmonic heat capacity is strongly correlated to x. The existence of additional excess heat capacity was observed with the mixed oxide solid solution samples of low Ru content and explained by the defect formation model.

Keywords: DSC, heat capacity, mixed oxide TiO_2–RuO_2, RuO_2, TiO_2

Introduction

The interest to TiO_2–RuO_2 oxide system has recently increased, mainly due to its application as photocatalysts, chemically durable electrodes, electro-resistor films, for electrodes or dielectric devices [1–4]. TiO_2 and RuO_2 have rutile structure containing similar tetravalent cations, the radii of which differ in the range of 0.01 nm. The electron configuration difference between Ti and Ru, however, caused differences in physical and chemical properties on the oxides; TiO_2 is dielectric or semi-conductive, while RuO_2 is one of the typical high conductive compounds. It is of interest to know how thermal properties of solid solutions in this system are correlated to the characteristics of the pure RuO_2 and TiO_2 oxides. It should be mentioned that the reliable heat capacities, which are considered as typical intrinsic properties of substances, can not be found in the literature for this system except pure TiO_2. In this paper the high-temperature heat capacity measurements of this system are compared, focusing on the anomalies of values measured.

Experimental

Sample preparation

Powders of commercial TiO_2 and RuO_2 (supplied by Kojyundo kagaku Co. and Furuya Kinzoku Co., respectively, of chemical purity above 99.9%) were heat-

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treated at 1570 and 1220 K for 4 h, respectively. The oxide mixtures of corresponding chemical compositions were heated twice at the temperatures from 1220–1570 K in order to prepare homogeneous solid solutions. The heat-treated powders were characterized by means of X-ray diffraction patterns and thermogravimetry measurements: the single rutile phase corresponding to solid solution was found in the samples of $(Ti_xRu_{1-x})O_2$ for $x\leq 0.15$ and $x\geq 0.85$, whereas mixture phase was found for $0.15<x<0.85$. Hence, homogeneous solid solutions of the rutile structure and the pure RuO_2 and TiO_2 were used for the heat capacity measurements. It should be noticed that pure RuO_2 and the solid solutions began to dissociate at higher temperature than 1220 K, therefore, the heat capacity measurements were carried out below 1170 K in this work.

Methods and measurements

Heat capacities were measured in the temperature range of 293 to 303 K using heat compensating DSC (Perkin Elmer, Type Pyris), and in the temperature range from 350 to the temperatures of 1550 K for TiO_2 and 1170 K for other samples, respectively using the heat flow DSC device (Setaram, Type MDHTC). Sapphire powders were used as the reference material, and heat capacities were calculated by comparing the heat flux intensities of a sample to those of the reference. The optimization was done as a result of the preliminary experiments concerning to masses, volumes, and particle sizes of samples, scanning rates (heat and cool), cell positions, and atmospheres. The sample masses were 25–30 mg (about 50% of cell volume) for the measurement by Perkin Elmer DSC, Type Pyris, and 0.8–1.2 g (60–80% of cell volume) for the SETARAM DSC, Type MDHTC. The additional modifications of the MDHTC DSC Type (vertically equipped with a cylindrical graphite heater) were made in order to reduce the convection disturbance occurred during temperature scanning.

Theoretical background

The molar heat capacity, C_p , of solids at high temperatures can be expressed by the following formula;

$$C_p=\{3nR-(3nR/20)\theta^2/T^2\}+AT+B(T) \quad (1)$$

where T is absolute temperature, n is the number of atoms in the chemical formula, and 3 for TiO_2 and RuO_2, R is molar gas constant, θ is the characteristic temperature corresponding to the harmonic lattice vibrations [5], and A is constant. The term in the first brackets of Eq. (1) is the first approximation of Debye function [5]. The term AT is related to the dilatometric and the other residual anharmonic lattice vibrations, and/or electric contribution, and the term $B(T)$ is the excess heat capacity related to the defect formation enthalpy, or formation of electron-hole pairs [8].

Results and discussion

Reliability estimation of experimental data

The thermal equilibrium in the dynamic calorimetric measurements cannot be supposed, because heat transfers may occur not only between the sample holder and the basal plane of a pan, but also between the gas inside the calorimeters and the pan wall having temperature gradients. Therefore, it is indispensable to find empirically optimization conditions of measurements. Figure 1 shows the sample mass dependence of the experimental C_p data measured by DSC, Type Pyris at the dynamic helium flow of 20 ml min^{-1} and the heating rate of 5 K min^{-1}. It is shown in Fig. 1 that the sample mass higher than 20 mg is needed to obtain the experimental heat capacity

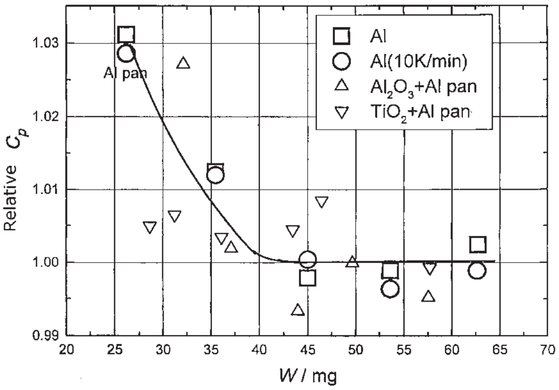

Fig. 1 Sample mass dependence of heat capacity measurements for various samples under the conditions of scanning range of 293–303 K. (Heating rate of 5 K min^{-1} and the He flow rate of 20 ml min^{-1} were used for the measurements by Perkin Elmer, Type Pyris)

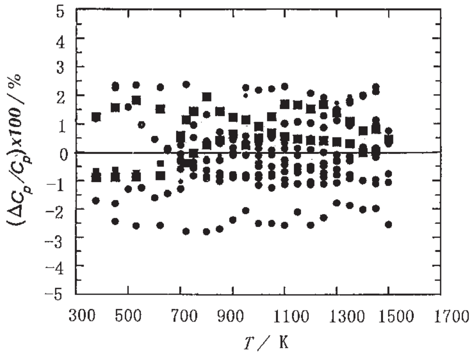

Fig. 2 Reproducibility of heat capacity measurements for sapphire of 0.9 to 1.2 g under the conditions of scanning range of 1250 to 330 K. (Cooling rate of 3.5 K min^{-1} and He static gas closed in a chamber were used for the measurements by SETARAM, Type MDHTC)

date with the dispersion lower than ±1%. Figure 2 shows that the reproducibility of data measured by means of SETARAM DSC, Type MDHTC is ±2.5% over the range of 350 to 1500 K under the optimization conditions described above.

Results of measurements

The heat capacity values we have obtained for pure TiO_2 and RuO_2 are compared with the literature data in Fig. 3. Our experimental data for TiO_2 (rutile) were consistent with the literature values within ±2%. The accuracy of these experiments was nearly the same. Figure 3 shows that the disagreement among the literature data of RuO_2 is higher than 7%. Our data were consistent with those summarized by Barin [6] within the limit of 3% inaccuracy. It should be, however, noticed that the heat capacity data

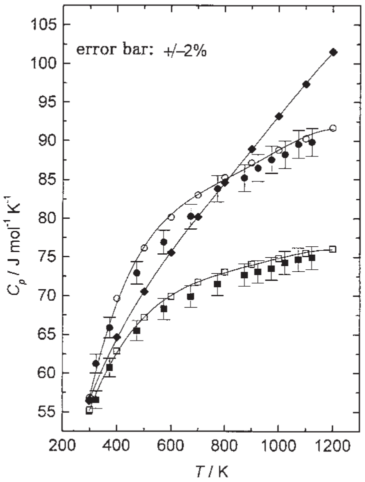

Fig. 3 Molar heat capacities of TiO_2 and RuO_2; ▪ – this work on TiO_2, • – this work on RuO_2, □ – after Ref. [6] on TiO_2, O – after [6] on RuO_2, ♦ – after [7] on RuO_2

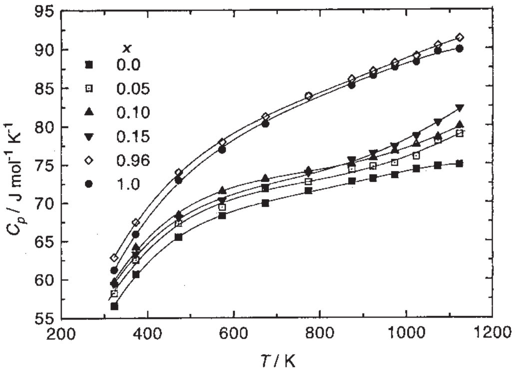

Fig. 4 Molar heat capacities of TiO_2–RuO_2 system, x in $(Ti_{1-x}Ru_x)O_2$

published by Barin [6] and by Cordfunke *et al.* [7] on RuO_2 were not properly measured at the elevated temperatures, but estimated in the range of over 298 and 757 K, respectively. The measurements presented in [7] were carried out using adiabatic calorimetry in the temperature range from 5 to 350 K and the drop calorimetry in the temperature range from 410 to 757 K, respectively. Values of heat capacities obtained in the present work are summarized in Fig. 4. It can be seen from Fig. 4 that the molar heat capacities increase with the increasing component of Ru in the oxide solid solution. In the $(Ti_xRu_{1-x})O_2$ solid solutions for $x \leq 0.15$ the noticeable increase of C_p was observed in the temperatures higher than 850 K.

Analysis of experimental data

As shown in Fig. 4, the heat capacity data of the system studied enabled us to construct the linear relationship over the wide temperature range; following expression is obtained by modification of Eq. (1)

$$(C_p - 3nR)/T = -(3nR/20)\theta^2/T^3 + A \qquad (2)$$

The experimental results are plotted in Fig. 5, as temperature dependencies corresponding to Eq. (2). The obtained values of A and θ are plotted in Fig. 6. It is obvious from Fig. 6 that the value of θ was determined to be 700±20 K, that is, does not strongly depend on the chemical composition x of the solid solution. On the other hand, the value of parameter A increased from 0.7±0.5 to 15±0.5 mJ mol^{-1} K^{-2} with increasing x. The strong x dependence of A may be due to either electron contribution or the anharmonic lattice vibrations. As the magnitudes of A on the TiO_2-relating insulating oxides are normally below 1.5 mJ mol^{-1} K^{-2}, we can suppose, by considering the high electron conductivity of RuO_2, that the electronic contribution may occupy the major part of A. Though the linear relations were established over the wide temperatures on both pure TiO_2 and RuO_2, the deviations from the linear relationship

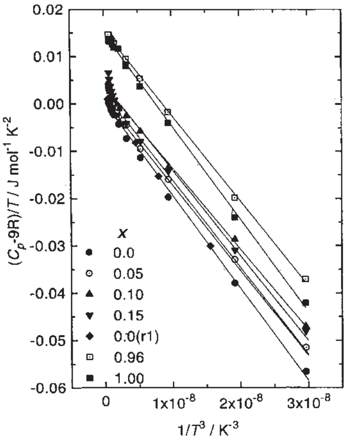

Fig. 5 Plot of $(C_p-9R)/T$ *vs.* $1/T^3$ on TiO_2–RuO_2 system

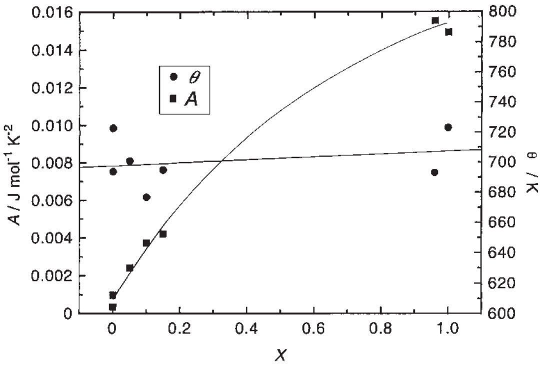

Fig. 6 Composition dependence of harmonic and anharmonic heat capacities on TiO_2–RuO_2 system; θ and A are parameters in Eq. (2), respectively

(caused by excess heat capacities) were observed for the solid oxide solutions at high temperatures. The temperature dependencies presented in Fig. 6 can be expressed by Eq. (3) derived for the defect formation mechanism in the solids [8]

$$\mathrm{Ln}\,(RT^2\Delta C_p)=-\Delta H_f/RT+c \qquad (3)$$

where the term ΔC_p represents the excess heat capacity, denoted in Eq. (1) as $B(T)$, ΔH_f is the enthalpy of defect formation, c is a constant. The linear dependencies in Fig. 7 were found for $(Ti_xRu_{1-x})O_2$ solid solutions with low content of Ru, i.e. for $x\leq0.15$, though this relationship was not always obvious for x=0.05. The value of ΔH_f was estimated to be 1.5±0.5 eV from the linear dependence in Fig. 7. Equation (2) has been normally established for the lattice defect formation. It is of interest that this ΔH_f value is similar to the values published by Inaba *et al.* on vanadium oxide [8], and the value of ΔH_f=2.2 eV for dissociation enthalpy on pure RuO_2 [9]. The further discussion on the defect formation mechanism will be the matter of our next study.

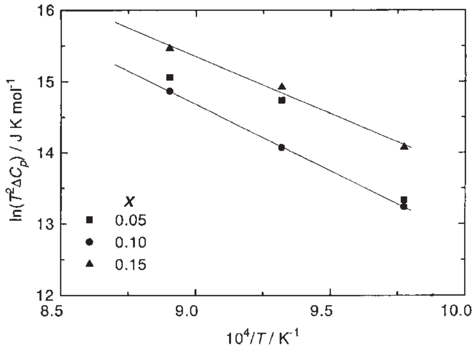

Fig. 7 Plot of $\ln(T^2\Delta C_p)$ *vs.* $10^4/T$, where the heat capacity ΔC_p equals to $C_p-9R+(9R/20)\theta^2/T^2-AT$ (refer to Fig. 5)

Conclusions

Results of DSC measurements of the samples in the system TiO_2–RuO_2 were successfully used for the determination of the heat capacity values of the oxide samples with varying chemical composition.

Temperature dependencies of the heat capacity values were constructed. The effect of chemical composition x on the parameters expressing heat capacity of $(Ti_xRu_{1-x})O_2$ solid solutions was discussed. The strong x dependence of the parameter A was ascribed mainly to the electron contribution. The excess heat capacities observed for $(Ti_xRu_{1-x})O_2$ solid solutions with low content of Ru, i.e. for $x \leq 0.15$ were explained on the basis of the defect formation model.

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