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Heat Capacity Measurement of Oxygen-Dissolved V–Ti Alloys[1]

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The heat capacities of $(V_{1-y}Ti_y)O_x$ alloys ($x = 0.13$ to 0.18, $y = 0.06$ to 0.23) were measured in the temperature range from 380 to 900 K with a differential scanning calorimeter. A λ-type peak corresponding to the order–disorder phase transition was observed in the heat capacity curves of each $(V_{1-y}Ti_y)O_x$ alloy ($x \leqq 0.18$, $y \leqq 0.09$). The baseline of the measured heat capacity was estimated with the harmonic term and the anharmonic term of the lattice vibration. The entropy changes at the phase transition were determined by subtracting the baseline mentioned above from the measured heat capacities. The experimental entropy changes were in good agreement with those calculated theoretically, based on the arrangement of oxygen and the limited coordination number of oxygen around vanadium. There were no peaks in the heat capacity curves for the samples with compositions $y \geqq 0.16$. Introduction of titanium, which has a larger ionic radius than that of vanadium, may disturb the ordering of oxygen around the metal.

KEY WORDS: heat capacity; order–disorder phase transition; V–Ti alloy; λ-type transition.

1. INTRODUCTION

Vanadium has been regarded as a candidate material for the first wall of nuclear fusion reactors because of its high melting point and small neutron absorption cross section. Vanadium has, however, high reactive activity against gas impurities, especially oxygen, in plasma, and there exist few data on the mechanical and thermodynamic properties of vanadium as an

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industrial material. For sufficient mechanical strength at high temperature and improved corrosion resistance, vanadium is alloyed with other metals such as titanium and/or chromium. The mechanical properties and behavior of hydrogen dissolution of vanadium alloys have been studied, but there are few studies of thermal properties for vanadium alloys.

As for the mechanical properties of vanadium alloys, ultimate tensile strength (UTS) curves were observed to change nonmonotonically with temperature [1, 2]. As for thermal properties, the heat capacities of the binary vanadium–titanium alloys such as $V_{0.70}Ti_{0.30}$, $V_{0.60}Ti_{0.40}$, and $V_{0.50}Ti_{0.50}$ were measured with a pulse-heating calorimeter in the temperature range from 77 to 300 K by Gololobov et al. [3]. With increasing titanium content, the heat capacity of vanadium–titanium alloys increased monotonically.

We previously measured the heat capacities of the ternary vanadium–titanium–chromium alloys $V_{0.80}Ti_{0.05}Cr_{0.15}$, $V_{0.90}Ti_{0.05}Cr_{0.05}$, and $V_{0.775}Ti_{0.15}Cr_{0.075}$ with a differential scanning calorimeter in the temperature range from 480 to 900 K [4]. No peak corresponding to the phase transition was observed in the heat capacity curve of each alloy.

The purpose of this work is to measure the heat capacities of oxygen dissolved vanadium–titanium alloys and to discuss the origin of the phase transition.

2. EXPERIMENTAL PROCEDURE

2.1. Sample Preparation and Characterization

For the sample preparation, vanadium (99.7% pure, Hirano Hikozaemon Shoten, Japan) and titanium (99.9% pure, Niraco, Japan) metals and titanium dioxide powder (99.99% pure, Rare Metallic Co., Japan) were used. The samples were made by melting them several times with an arc furnace in argon gas atmosphere purified by titanium sponge (99.5% Nacalai Chemicals, Japan). After melting, the surface of the sample button was polished, sealed in a quartz tube, annealed 1 week at 1273 K, and then cooled to room temperature over a period of 3 days. X-ray diffraction (XRD) analysis indicated the presence of a single phase for each sample. XRD data were obtained using an automatic powder diffractometer (RINT 2200 Ultima, Rigaku, Japan).

2.2. Heat Capacity Measurement

Heat capacities of the oxygen-dissolved vanadium–titanium alloys were measured with a differential scanning calorimeter (DSC-220, Seiko

Instruments, Japan) installed in a glove box over the temperature range from 400 to 900 K in a purified argon gas flow. Heating and cooling rates were 10 K · min^{-1}. For the temperature calibration, melting points of tin and indium were used. Three kinds of sample pans were used for the different temperature ranges, an aluminum pan (480 to 630 K), an aluminum pan with a sapphire base sheet (630 to 750 K), and a platinum pan (750 to 880 K). As the reference material for the heat capacity measurement, an NBS Al_2O_3 pellet was used.

3. RESULTS AND DISCUSSION

The results of the heat capacity measurements on $V_{0.94}Ti_{0.06}O_{0.13}$, $V_{0.92}Ti_{0.08}O_{0.16}$, and $V_{0.91}Ti_{0.09}O_{0.18}$ alloys are shown in Figs. 1–3, respectively. The heat capacities of $V_{0.84}Ti_{0.16}O_{0.16}$, $V_{0.79}Ti_{0.21}O_{0.16}$, and $V_{0.77}Ti_{0.23}O_{0.18}$ are shown in Fig. 4. As seen in Figs. 1–3, a λ-type heat capacity anomaly due to an order–disorder transition is observed for each sample, $V_{1-y}Ti_yO_x$ ($0.06 \leqq y \leqq 0.09$ and $0.13 \leqq x \leqq 0.18$). The transition temperatures obtained in this study are summarized in Table I.

The heat capacity at constant pressure C_p is generally expressed by the sum

$$C_p = C_h + C_d + C_{ah} + C_e + \Delta C \qquad (1)$$

where C_h is the harmonic term of the lattice vibration, C_d is the dilatational term, C_{ah} is the anharmonic term of the lattice vibration, C_e is the

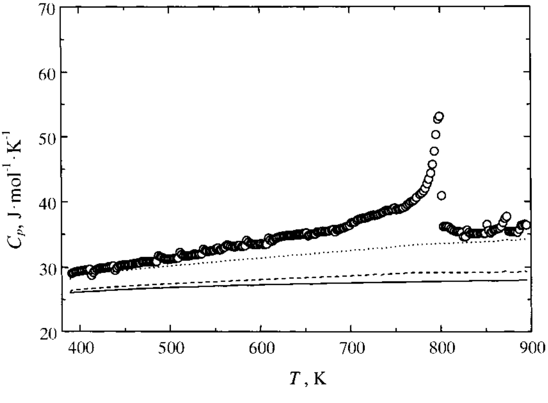

Fig. 1. Temperature dependence of heat capacity for $(V_{0.94}Ti_{0.06})O_{0.13}$. (—) C_h, (---) $C_h + C_d$, (···) $C_h + C_d + C_e + C_{ah}$.

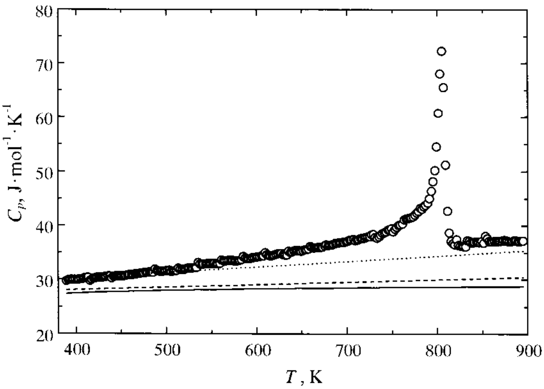

Fig. 2. Temperature dependence of heat capacity for $(V_{0.92}Ti_{0.08})O_{0.16}$. (—) C_h, (---) $C_h + C_d$, (···) $C_h + C_d + C_e + C_{ah}$.

conduction electronic term, and ΔC is the excess heat capacity due to phase transition.

The harmonic molar heat capacity is expressed by the following Debye function $\Delta(\Theta_D/T)$:

$$C_h = (1+x)\,3RD(\Theta_D/T)$$

$$= (1+x)\,9R(T/\Theta_D)^3 \int_0^z e^z z^4/(e^z-1)^2\,dz \tag{2}$$

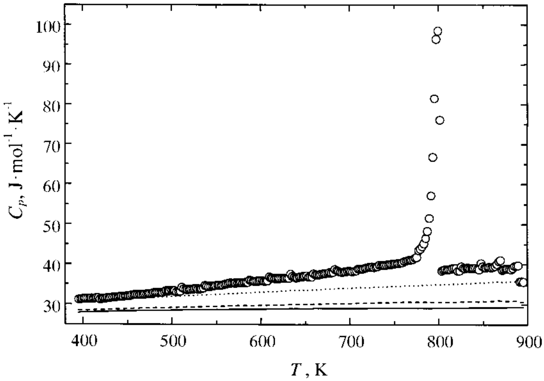

Fig. 3. Temperature dependence of heat capacity for $(V_{0.91}Ti_{0.09})O_{0.18}$. (—) C_h, (---) $C_h + C_d$, (···) $C_h + C_d + C_e + C_{ah}$.

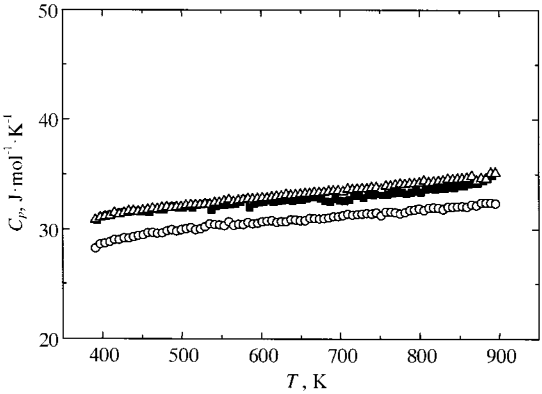

Fig. 4. Temperature dependence of heat capacity for $(V_{1-y}Ti_y)\ O_x$. (△) $(V_{0.84}Ti_{0.16})\ O_{0.16}$, (○) $(V_{0.79}Ti_{0.21})\ O_{0.16}$, (■) $(V_{0.77}Ti_{0.23})\ O_{0.18}$.

where $z = \Theta_D/T$, Θ_D is the Debye temperature, R is the universal gas constant, and x is oxygen-to-metal (vanadium and titanium) ratio. First the Debye temperatures for the vanadium–titanium alloys were calculated from those for pure vanadium and titanium metals measured by Clusius and Franzusini [5], assuming the following equation for the binary system [6]:

$$\Theta^2_{AB} = x\Theta^2_A + (1-x)\,\Theta^2_B \tag{3}$$

The Debye temperatures for the oxygen-dissolved vanadium–titanium alloys were estimated assuming the same linear relation between vanadium and oxygen-dissolved vanadium measured by Sumin et al. [7].

The dilatational term is estimated from the empirical equation of Nernst and Lindemann [8] using the melting temperature (T_m):

$$C_d = 0.0025\,\frac{T}{T_m}\,C_p^2 \tag{4}$$

Table I. Transition Temperature T_r of $V_{1-y}Ti_yO_x$

Sample	T_r (K)
$V_{0.94}Ti_{0.06}O_{0.13}$	799 ± 5
$V_{0.92}Ti_{0.08}O_{0.16}$	803 ± 5
$V_{0.91}Ti_{0.09}O_{0.18}$	799 ± 5

The melting temperatures for the oxygen-dissolved vanadium–titanium alloys in Eq. (4) were calculated by interpolation between two melting points obtained from the phase diagrams of vanadium–titanium and vanadium–oxygen binary systems [9, 10]. The values of C_h and C_d thus calculated, are given in Figs. 1–3. Differences between measured heat capacities C_p and estimated terms $C_h + C_d$ are regarded as the electronic C_e, anharmonic C_{ah}, and the excess terms ΔC of the heat capacity. Both the electronic and anharmonic terms have linear dependence on T at low temperature and can be expressed as

$$C_p - C_h - C_d - \Delta C = C_e + C_{ah} = (\gamma + b)\, T. \tag{5}$$

However, the coefficient of the electronic heat capacity γ of oxygen-dissolved vanadium–titanium alloys changes nonmonotonically with temperature at high temperature, and the γ value was estimated from the data for oxygen-dissolved vanadium [11]. The coefficients used in calculating each heat capacity term are shown in Table II.

The excess heat capacity ΔC can be obtained by subtracting the terms C_{base} of C_h, C_d, C_{ah}, and C_e from the measured C_p. By integrating the excess heat capacity, the changes in enthalpy ΔH and entropy ΔS_{exp} for each sample at the phase transition were calculated using

$$\Delta H = \int (C_p - C_{\text{base}})\, dT \tag{6}$$

$$\Delta S = \int \frac{C_p - C_{\text{base}}}{T}\, dT \tag{7}$$

The results are given in Table III.

In the previous studies on VO_x $(0.083 < x < 0.13)$ [11] and $Ti_{1-y}V_yO_x$ $(y = 0.016$ and 0.048, $x \approx 0.2)$ alloys [12], the experimental values of entropy change at the transition were in good agreement with those calculated theoretically based on the order–disorder transition of oxygen

Table II. The Debye Temperature Θ_D, Melting Point T_m, and Electronic and Anharmonic Term $\gamma + b$ of the Heat Capacity

Sample	Θ_D (K)	T_m (K)	$\gamma + b$ $(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$
$V_{0.94}Ti_{0.06}O_{0.13}$	480	2100	0.0055
$V_{0.92}Ti_{0.08}O_{0.16}$	510	2100	0.0055
$V_{0.91}Ti_{0.09}O_{0.18}$	530	2100	0.0055

Table III. The Transition Enthalpy ΔH and Entropies Obtained Experimentally ΔS_{exp} and Theoretically ΔS_{cal}

Sample	ΔH $(\mathrm{kJ \cdot mol^{-1}})$	ΔS_{exp} $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	ΔS_{cal} $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$
$V_{0.94}Ti_{0.06}O_{0.13}$	1.28 ± 0.03	2.66 ± 0.02	3.21
$V_{0.92}Ti_{0.08}O_{0.16}$	1.38 ± 0.01	3.54 ± 0.03	3.65
$V_{0.91}Ti_{0.09}O_{0.18}$	1.76 ± 0.02	3.89 ± 0.05	3.91

atoms. Therefore, the anomaly in heat capacity observed for oxygen-dissolved vanadium–titanium alloys in this study was thought to be due to an order–disorder rearrangement of oxygen atoms.

The entropy change assumed to be due to the order–disorder transition can be calculated theoretically as follows. The oxygen atoms are distributed in octahedral sites (O_x, O_y, O_z) in a bct (body-centered tetragonal) metal subcell, where the O_x, O_y, and O_z sites have their neighboring metal atoms along the axes x, y, and z, respectively. Since oxygen atoms occupy only O_z sites in the high temperature (disordered) phase, the number of available oxygen sites is equal to the number of metal atoms N, and the entropy change ΔS is calculated as follows, assuming perfect ordering in the low-temperature phase:

$$\Delta S = k\, ln \frac{N_i}{xN!\,(N - xN)!} - R\{x\, ln\, x + (1-x)\, ln(1-x)\} \tag{8}$$

where N and x are the number of metal sites and the O/(V + Ti) ratio, respectively. The calculated ΔS_{cal} values are also given in Table III.

Although ΔS_{cal} values of $(V_{0.92}Ti_{0.08})\,O_{0.16}$ and $(V_{0.91}Ti_{0.09})\,O_{0.18}$ are seen to be close to the ΔS_{exp} values, the ΔS_{exp} value of $(V_{0.94}Ti_{0.06})\,O_{0.13}$ is smaller than the ΔS_{cal} value. If the number of the available oxygen sites decreases for low titanium and oxygen content, the entropy change of phase transition will decrease. When the number of the available oxygen sites is limited from 6 to 4 per unit cell, the value of ΔS_{cal} is calculated to be $2.77\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, which is in fairly good agreement with the ΔS_{exp} value of $(V_{0.94}Ti_{0.06})\,O_{0.13}$ of $2.66\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$.

For the samples with the composition $y \geqq 0.16$, there were no peaks in the heat capacity curves. By introducing titanium, which has a larger ionic radius than that of vanadium, the ordering of oxygen around the metal is thought to be disturbed.

4. CONCLUSIONS

A λ-type peak corresponding to the phase transition was observed in the heat capacity curves of each $(V_{1-y}Ti_y)O_x$ alloy ($x \leqq 0.18$, $y \leqq 0.09$). The experimental entropy changes were in fairly good agreement with those calculated theoretically based on the order–disorder rearrangement of oxygen and the limited coordination number of oxygen around vanadium. In the samples with compositions $y \geqq 0.16$, there were no peaks in the heat capacity curves probably due to the disturbance of the ordering of oxygen around metal by introducing titanium, which has a larger ionic radius than that of host vanadium.

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