



Heat capacity measurements of V–Ti–Cr ternary alloys

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Abstract

Heat capacities of $V_{0.80}Ti_{0.05}Cr_{0.15}$, $V_{0.90}Ti_{0.05}Cr_{0.05}$ and $V_{0.775}Ti_{0.15}Cr_{0.075}$ were measured in the temperature range from 480 to 900 K with a differential scanning calorimeter. No peak corresponding to the phase transition was observed in the heat capacity curve of each alloy. From Gibbs free energies of formation calculated from the measured heat capacities and the estimated standard enthalpies of formation, $V_{0.80}Ti_{0.05}Cr_{0.15}$ was determined to be the most stable among these alloys. © 1997 Elsevier Science B.V.

1. Introduction

Vanadium has been regarded as a candidate material for the first wall of fusion reactor, because of its high melting point and small neutron absorption cross-section. Vanadium has, however, high activity against gas impurities in plasma, and there exist few data on the mechanical and thermodynamic properties of vanadium as an industrial material. For keeping enough mechanical strength at high temperature and improving corrosion resistance, vanadium is alloyed with other metals. Mechanical properties and behavior of hydrogen dissolution of vanadium alloys have been studied, but thermal properties of vanadium alloys have not been studied.

As for the mechanical properties of vanadium alloys, ultimate tensile strength (UTS) curves were observed to change non-monotonically with temperature [1,2]. Loomis et al. [1] reported that the UTS curve of $V_{0.80}Ti_{0.05}Cr_{0.15}$ exhibited several different changes depending on the temperature range and that of $V_{0.775}Ti_{0.15}Cr_{0.075}$ increased in the range from 520 to 670 K. Satou et al. [2] also reported that UTS of $V_{0.90}Ti_{0.05}Cr_{0.05}$ decreased from 200 to 600 K except for an increase in the range from 600 to 800 K.

As the thermal property, the heat capacities of the binary alloys, $V_{0.70}Ti_{0.30}$, $V_{0.60}Ti_{0.40}$ 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, heat capacity of V–Ti alloy increased monotonically.

The purpose of this work is to measure the heat capacities of V–Ti–Cr alloys and to discuss the presence of the phase transition related to the non-monotonical change of UTS curve.

2. Experimental

2.1. Sample preparation

For the sample preparation, vanadium (99.7% pure, Hirano Hikozaemon Shoten, Japan), titanium and chromium (99.9% and 99.5% pure, respectively, Niraco, Japan) metals were used. The samples were made by melting them several times with an arc furnace in argon atmosphere purified by titanium sponge (99.5% Nacalai Chemicals, Japan). After melting, the surface of the sample button was polished. The compositions of the samples were determined to be $V_{0.80}Ti_{0.05}Cr_{0.15}$, $V_{0.90}Ti_{0.05}Cr_{0.05}$ and $V_{0.775}Ti_{0.15}Cr_{0.075}$ by XMA.

2.2. Method for heat capacity measurement

Heat capacities of the V–Ti–Cr alloys were measured with a differential scanning calorimeter (Seiko Instruments, Japan) installed in a globe box over the temperature range from 400 to 900 K in a purified argon gas flow. Both heating and cooling rates were 10 K min^{-1} . For the temperature calibration, melting points of Sn and In were used. Three kinds of sample pans were used for the

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different temperature ranges, an aluminium pan (480–630 K), an aluminium pan with a base of sapphire sheet (630–750 K) and a platinum pan (750–880 K). As the reference material for the heat capacity measurement, a NBS Al_2O_3 pellet was used.

3. Results and discussion

3.1. Heat capacity measurements

The heat capacity of $\text{V}_{0.80}\text{Ti}_{0.05}\text{Cr}_{0.15}$ obtained in this study is shown in Fig. 1. There seems no peak in the heat capacity curve, and the heat capacity increases monotonically. The heat capacities of $\text{V}_{0.90}\text{Ti}_{0.05}\text{Cr}_{0.05}$ and $\text{V}_{0.775}\text{Ti}_{0.15}\text{Cr}_{0.075}$ are shown in Figs. 2 and 3, respectively. In these figures, no anomaly in the heat capacity curve was either seen for each sample. It is, therefore, concluded that non-monotonical change in the UTS curves reported in the literature [1,2] is not related to the phase transition.

Measured heat capacity (C_p) was evaluated with the harmonic term of the lattice vibration (C_h), the dilational term (C_d), the conduction electron term (C_e) and the inharmonic term of the lattice vibration (C_{ah}). The harmonic molar heat capacity is expressed by the following Debye function $D(\Theta_D/T)$:

$$C_h = 3RD(\Theta_D/T) = 9R(T/\Theta_D)^3 \int_0^x e^x x^4 / (e^x - 1)^2 dx, \quad (1)$$

where $x = \Theta_D/T$, Θ_D is the Debye temperature and R is gas constant. The Debye temperatures for the V–Ti–Cr ternary alloys in Eq. (1) were estimated from the those for

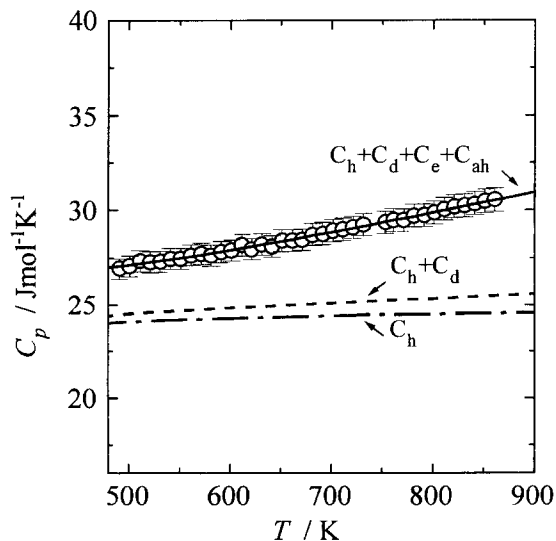


Fig. 1. Heat capacity of $\text{V}_{0.80}\text{Ti}_{0.05}\text{Cr}_{0.15}$.

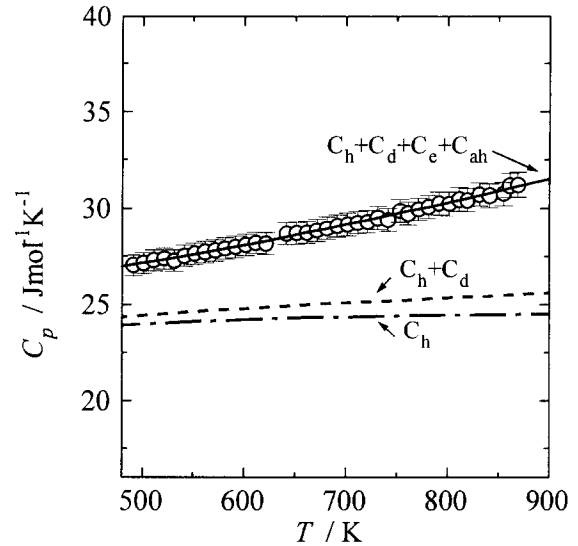


Fig. 2. Heat capacity of $\text{V}_{0.90}\text{Ti}_{0.05}\text{Cr}_{0.05}$.

pure V, Ti and Cr metals measured by Clusius et al. [4,5] and Alers [6], assuming the following equation for the ternary system [7]:

$$\Theta_{ABC}^3 = x\Theta_A^3 + y\Theta_B^3 + (1-x-y)\Theta_C^3. \quad (2)$$

The dilational term is estimated from the empirical equation of Nens–Lindemann [8] using the melting temperature (T_m):

$$C_d = 0.0025 \frac{T}{T_m} C_p^2. \quad (3)$$

The melting points for the V–Ti–Cr ternary alloys in Eq. (3) were calculated by interpolation between two

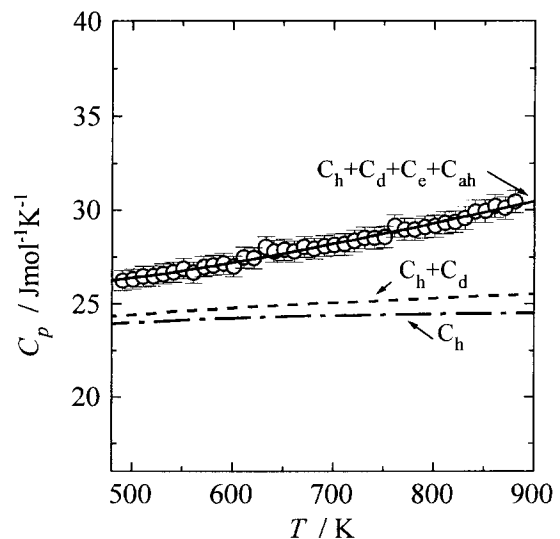


Fig. 3. Heat capacity of $\text{V}_{0.775}\text{Ti}_{0.15}\text{Cr}_{0.075}$.

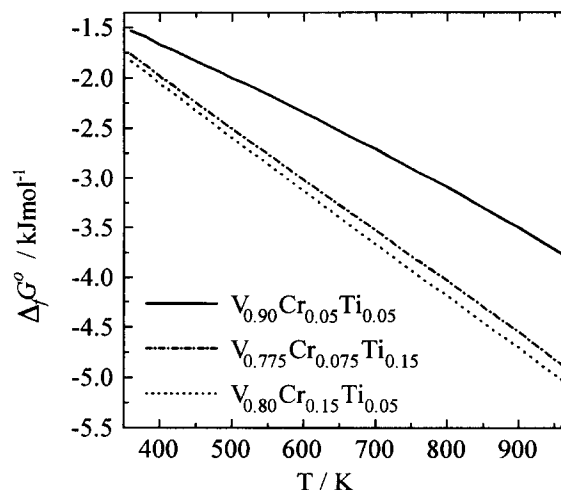


Fig. 4. Gibbs free energy of formation.

melting points obtained from the phase diagrams of V–Ti and V–Cr binary systems [9]. The values of C_h and C_d , thus calculated, are given in Figs. 1–3. Difference between measured heat capacities (C_p) and estimated terms ($C_h + C_d$) is regarded as the electronic (C_e) and inharmonic (C_{ah}) terms of the heat capacity

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

where γ and b are the coefficients of the high-temperature electronic and inharmonic terms of heat capacity, respectively. Since the coefficient of the high-temperature electronic heat capacity of V–Ti–Cr alloys changes non-monotonically with temperature, precise estimation of γ and b could not be made at the moment, but the value of $(\gamma + b)$ is 5.5–6.6 $\text{mJ mol}^{-1} \text{K}^{-2}$, determined in this work was the same order as the value of γ (5.4–9.6 $\text{mJ mol}^{-1} \text{K}^{-2}$) for vanadium by Krikorian et al. [10]. It seems that the magnitude of b is much smaller than that of γ .

3.2. Thermodynamic properties

To evaluate the thermodynamic stability of the V–Ti–Cr alloys, Gibbs free energies of formation were calculated from the measured heat capacities and the standard en-

thalpies of formation. The standard enthalpies of formation for three alloys were estimated from Miedema's model [11]. Gibbs free energies of formation of these alloys are shown in Fig. 4. It is seen that the $\text{V}_{0.80}\text{Ti}_{0.05}\text{Cr}_{0.15}$ alloy is the most stable among these alloys, and that the thermodynamic stability increases with increasing chromium content.

4. Conclusion

No anomalous increase in the heat capacity curve over the temperature range of 480–900 K was seen for three V–Ti–Cr alloys. The non-monotonical change of the mechanical properties with temperature reported in the literature was concluded to be not related to the phase transition. From the Gibbs free energies of formation calculated from the measured heat capacities, $\text{V}_{0.80}\text{Ti}_{0.05}\text{Cr}_{0.15}$ was found to be the most stable among these three alloys. With increasing chromium content, the thermodynamic stability seemed to increase. The contribution of titanium to the thermodynamic stability was smaller than that of chromium.

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