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Heat capacity of $(Cr_{1-x}Ni_x)_3Te_4$ (x=0–0.2) at high temperatures

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Abstract

Heat capacities of $(Cr_{1-x}Ni_x)_3Te_4$ (x=0–0.2) were measured from 325 to 920 K by using an adiabatic scanning calorimeter. Heat capacity anomalies due to the order–disorder of chromium atoms and vacancies were observed for all $(Cr_{1-x}Ni_x)_3Te_4$ (x=0–0.1) samples around 800–900 K. The transition temperatures, transition enthalpy and entropy changes decreased with increasing doped nickel contents. The order–disorder transition mechanism will be discussed on the basis of entropy analysis. For $(Cr_{1-x}Ni_x)_3Te_4$ (x=0.15 and 0.2) samples, another heat capacity anomaly in addition to the order–disorder transition mentioned above was observed around 600–700 K, probably due to the order–disorder transition in NiAs-type crystal structure. From X-ray and heat capacity results, the solubility limit of nickel to Cr_3Te_4 was determined to be around x=0.1.

Keywords: Heat capacity; Order–disorder transition; Cr_3Te_4; Ni_3Te_4; NiAs-type crystal structure

1. Introduction

Tellurium is a corrosive element having a fission yield of about 1% in fast breeder reactor and may attack the inner surface of fuel cladding made of stainless steel [1,2]. For the evaluation of the reaction between stainless steel cladding and tellurium, the thermodynamic data in the iron–chromium–nickel–tellurium system are necessary. Heat capacity data are available mainly for binary iron–, nickel– and chromium–telluride systems [3] and only for ternary compound $(Cr_{1-x}Fe_x)_3Te_4$ [4]. We observed heat capacity anomalies for all $(Cr_{1-x}Fe_x)_3Te_4$ (x=0–0.1) samples around 900 K due to the order–disorder transition of chromium atoms and vacancies [4]. The transition temperatures, transition enthalpy and entropy changes decreased with increasing doped iron contents. This transition mechanism was interpreted on the basis of entropy analysis that some of the nearest neighbor chromium vacancies neighboring iron sites may not contribute to the order–disorder transition. The solubility limit of iron to Cr_3Te_4 was determined to be between x=0.04 and 0.1 which was in good agreement with x=0.08 obtained from magnetic susceptibility measurement [5]. Another heat capacity anomaly in addition to the order–disorder transition was observed around 700 K for $(Cr_{0.9}Fe_{0.1})_3Te_4$ sample, probably due to the order–disorder transition in NiAs-type structure.

In this study, the heat capacity of $(Cr_{1-x}Ni_x)_3Te_4$ was measured in the temperature range from 325 to 920 K by an adiabatic scanning calorimeter to know how the thermodynamic data vary with increasing nickel content and the solubility limit of nickel in Cr_3Te_4. The effect of doped nickel on the order–disorder transition is compared with the effect of doped iron as reported in our previous study.

2. Experimental

2.1. Sample preparation

The starting materials used for sample preparation were high-purity chromium (99.99%), nickel (99.9%) and tellurium (99.999%). The chromium, nickel and tellurium having the desired concentrations were mixed, put into a silica capsule and finally sealed under vacuum. The sample was heated to 1273 K over a period of 7 days, kept at this temperature for 2 days, annealed at 1073 K for 2 days, and cooled to room temperature. The sample obtained was finely crushed in n-hexane and sealed in another silica capsule. The sealed sample was heated to 1073 K over a period of 2 days and kept at this temperature for 5 days. This sample was slowly cooled to 673 K, kept at this

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temperature for 10 days and then slowly cooled to room temperature.

X-ray powder diffraction patterns for the composition $x=0$–0.1 at room temperature showed the existence of a single phase with monoclinic Cr_3S_4-type structure, but the peak intensities of $x=0.1$ were slightly different from other compositions ($x=0$–0.04). Samples with the compositions $x=0.15$ and 0.20 were identified as the mixture of monoclinic Cr_3S_4-type and NiAs-type crystal structures.

2.2. Heat capacity measurement

Heat capacities of $(Cr_{1-x}Ni_x)_3Te_4$ ($x=0$, 0.01, 0.02, 0.04, 0.1, 0.15 and 0.2) and Ni_3Te_4 were measured in the temperature range 325–920 K by using an adiabatic scanning calorimeter and the details of the experiment are described elsewhere [4]. In this calorimeter the power supplied to the sample was measured continuously, and the heating rate was kept constant regardless of the type and amount of the sample. The heating rate chosen was 2 K min^{-1}, and the measurement was carried out under a pressure of about 130 Pa of air by using the sample of 16–20 g sealed in a quartz vessel filled with helium gas at 20 kPa in order to get a good thermal conduction. The heating rate and adiabatic control were usually maintained within ±0.005 K min^{-1} and ±0.01 K, respectively. The precision and accuracy of the heat capacity measurement was conducted within ±3% and ±2%, respectively.

3. Results and discussion

3.1. Heat capacity of $(Cr_{1-x}Ni_x)_3Te_4$ ($x=0$–0.10)

The results of heat capacity measurement of $(Cr_{1-x}Ni_x)_3Te_4$ ($x=0.01$, 0.02, 0.04 and 0.10) are shown in Fig. 1. An anomaly in the heat capacity is seen around 800–900 K for all monoclinic $(Cr_{1-x}Ni_x)_3Te_4$ samples, probably due to the order–disorder transition of chromium atoms and vacancies which was reported for undoped Cr_3Te_4 by Grønvold [3] and for doped $(Cr_{1-x}Fe_x)_3Te_4$ ($x=0$–0.1) samples by the present authors [4]. As seen in Fig. 1, the order–disorder transition temperature decreases and the shape of the peak becomes slightly broader with increasing the nickel contents. Another small anomaly in heat capacity is seen near 300 K for all samples in Fig. 1.

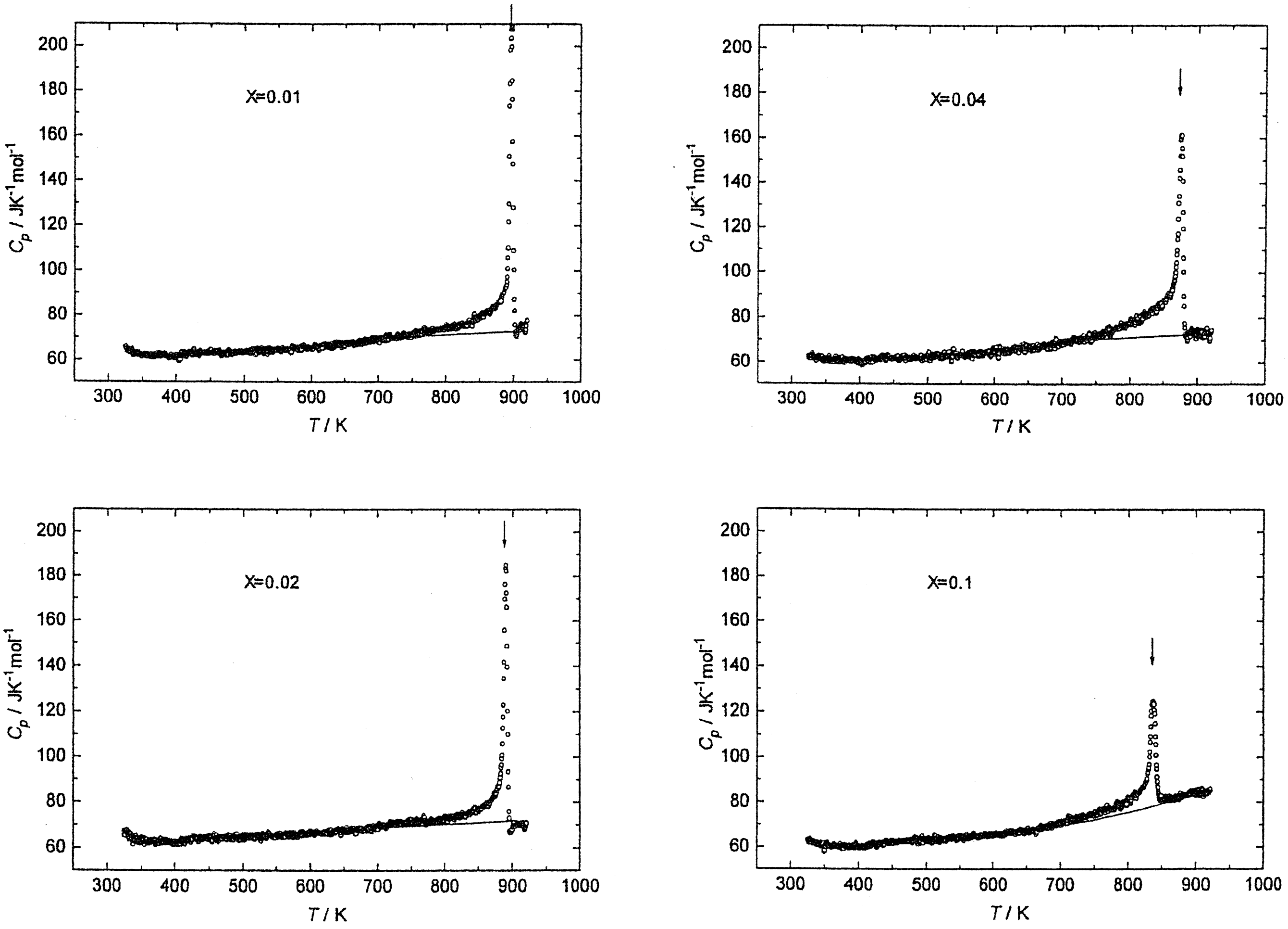

Fig. 1. Heat capacities of $(Cr_{1-x}Ni_x)Te_{1.33}$ ($x=0.01$–0.10) as a function of temperature.

This phase transition corresponds to ferromagnetic to paramagnetic transition measured by magnetic susceptibility [5]. The increase of heat capacity for $x=0.10$ is seen especially above 800 K in Fig. 1, although this abnormal behavior is not seen for $x=0.01$–0.04. The similar increment of heat capacity is observed for Ni_3Te_4, as will be shown in Fig. 3 later. Therefore, this increase may be caused by small amount of Ni_3Te_4 impurity in the sample. From X-ray and heat capacity results, the solubility limit of nickel in Cr_3Te_4 was determined to be around $x=0.1$.

In order to estimate the transition enthalpy and entropy changes from heat capacity data, it is necessary to get the base line of heat capacity, C_p. The base line was determined by the least square method of heat capacity data without phase transition as a function of temperature using the following equation:

$$C_p(T) = A + BT + C/T^2 \tag{1}$$

where T is the absolute temperature and A–C are the coefficients of polynominal terms in Eq. (1). As seen in Fig. 1, the order–disorder phase transition for the composition of $x=0.01$–0.04 is considered to be finished because of a sharp peak. For the calculation of the base line, Eq. (1) was applied to heat capacity data in the temperature range of 500–700 K for the composition of $x=0.01$–0.04. On the other hand, the base line of $x=0.1$ is similar to that of Ni_3Te_4, and the following function is used for this composition:

$$C_p(T) = A + BT + C/T + D/T^2. \tag{2}$$

The base line of $x=0.10$ is calculated from heat capacity data at temperatures of 400–600 K and 900–920 K by using Eq. (2). The base lines obtained in this study are shown in Fig. 1. Transition temperatures, transition enthalpy and entropy changes obtained in this study are shown in Table 1. Transition temperatures, transition enthalpy and entropy changes decrease with increasing doped nickel contents.

We proposed two models for the effect of doped M atoms on the order–disorder phase transition of $(Cr_{1-x}M_x)_3Te_4$. In the model 1, the order–disorder transition entropy was calculated on the assumption that the M atoms substitute randomly for chromium atoms in the layers containing vacancy and the M atoms are also independent of the order–disorder transition, as follows:

$$\begin{aligned}
&\text{For } Cr_{1-x}M_xTe_{1.33}\\
&\quad = (2/3)\big[CrTe\{Cr_{\{(1/2)-(3x/2)\}}M_{3x/2}\square_{1/2}Te\big],\\
&\Delta_{trs}S = (2/3)k\ln({}_{\{1-(3x/2)\}N}C_{N/2})\\
&\quad = (2/3)R[\{1-(3x/2)\}\ln\{1-(3x/2)\}\\
&\qquad - \{(1/2)-(3x/2)\}\ln\{(1/2)-(3x/2)\}\\
&\qquad - (1/2)\ln(1/2)]
\end{aligned} \tag{3}$$

where ${}_NC_n$ is the number of combinations of n elements among N and is given by ${}_NC_n = N!/\{n!(N-n)!\}$.

In the model 2, transition entropy is calculated on the assumption that the M atoms substitute randomly for chromium atoms in the layers containing vacancy and the nearest neighbor chromium vacancies neighboring the M sites are independent of the order–disorder transition, and it is expressed by the following equation:

$$\begin{aligned}
&\text{For } Cr_{1-x}M_xTe_{1.33}\\
&\quad = (2/3)\big[CrTe\{Cr_{\{(1/2)-(3x/2)\}}\square_{\{(1/2)-3x\}}(M_{3x/2}\square_{3x})Te\}\big],\\
&\Delta_{trs}S = (2/3)k\ln({}_{\{1-(9x/2)\}N}C_{\{(1/2)-3x\}N})\\
&\quad = (2/3)R[\{1-(9x/2)\}\ln\{1-(9x/2)\}\\
&\qquad - \{(1/2)-3x\}\ln\{(1/2)-3x\}\\
&\qquad - \{(1/2)-(3x/2)\}\ln\{(1/2)-(3x/2)\}]
\end{aligned} \tag{4}$$

The theoretical values for the two models, together with the experimental values for $(Cr_{1-x}M_x)_3Te_4$ (M=Ni and Fe) are shown in Fig. 2 as a function of x. The slope of $(Cr_{1-x}Ni_x)_3Te_4$ obtained in this experiment lies to model

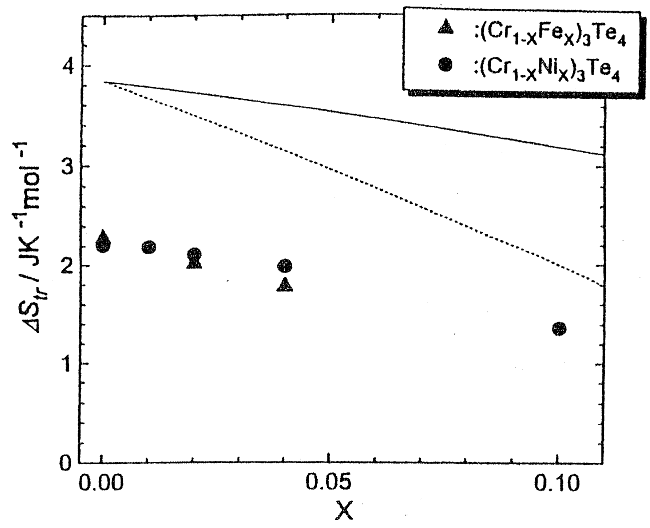

Fig. 2. Transition entropy changes for $(Cr_{1-x}M_x)Te_{1.33}$ (M=Ni and Fe). $(Cr_{1-x}Ni_x)_3Te_4$ (●); $(Cr_{1-x}Fe_x)_3Te_4$ (▲); model 1 (—) and model 2 (- - -).

Table 1
Transition temperature (T_{trs}), transition enthalpy ($\Delta_{trs}H$) and entropy ($\Delta_{trs}S$) changes for $(Cr_{1-x}Ni_x)Te_{1.33}$, i.e. $(Cr_{1-x}Ni_x)_3Te_4$

x	T_{trs} (K)	$\Delta_{trs}H$ (kJ mol^{-1})	$\Delta_{trs}S$ (J K^{-1} mol^{-1})	References
0	903	2.28	2.52	Grønvold [3]
0	904	2.00	2.29	Yasui et al. [4]
0.01	896	1.89	2.19	This work
0.02	890	1.80	2.11	This work
0.04	875	1.69	1.99	This work
0.10	837	1.10	1.36	This work

1, while that of $(Cr_{1-x}Fe_x)_3Te_4$ lies between models 1 and 2 as shown in the previous study [4]. The ionic radius of nickel is near to that of chromium than iron. Thus the stress by substituting nickel for chromium can be smaller, compared to substitution of iron for chromium.

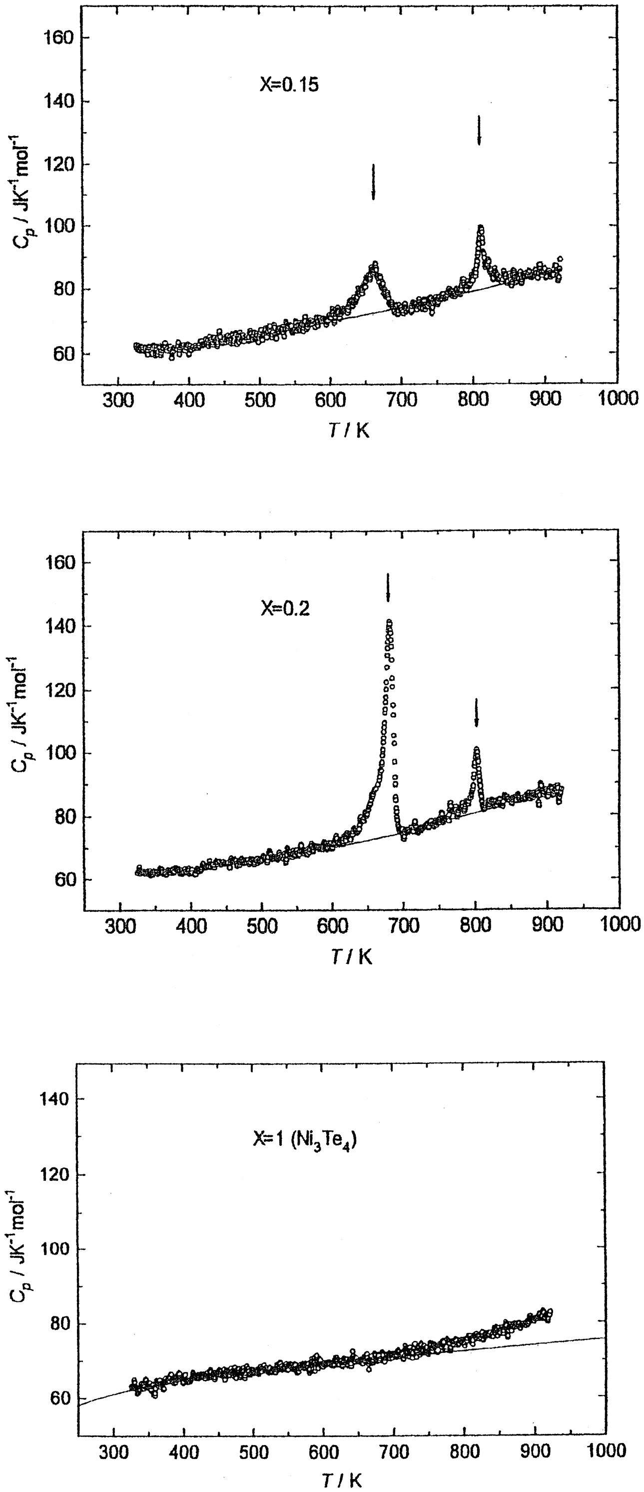

Fig. 3. Heat capacities of $(Cr_{1-x}Ni_x)Te_{1.33}$ ($x=0.15$ and 0.20) and $NiTe_{1.33}$ as a function of temperature.

3.2. Heat capacities of $(Cr_{1-x}Ni_x)_3Te_4$ ($x=0.15$ and 0.2) and Ni_3Te_4

The results of heat capacity measurements of $(Cr_{1-x}Ni_x)_3Te_4$ ($x=0.15$ and 0.2) together with that of Ni_3Te_4 are shown in Fig. 3. An anomaly in the heat capacity is seen around 800 K for both $x=0.15$ and 0.2, probably due to the order–disorder transition of chromium atoms and vacancies, as already discussed for $x=0.01$–0.1. Another heat capacity anomaly in addition to the order–disorder transition was observed around 670 K for $(Cr_{1-x}Ni_x)_3Te_4$ ($x=0.15$ and 0.2) samples, probably due to the order–disorder transition in NiAs-type structure, which was observed for $(Cr_{0.9}Fe_{0.1})_3Te_4$ [4].

4. Conclusions

We measured heat capacities of $(Cr_{1-x}Ni_x)_3Te_4$ ($x=0$–0.2) from 325 to 920 K by using an adiabatic scanning calorimeter and obtained the following conclusions.

(1) For all $(Cr_{1-x}Ni_x)_3Te_4$ ($x=0$–0.1) samples, heat capacity anomalies were observed around 800–900 K. The transition temperatures, transition entropy and entropy changes decreased with increasing nickel content. Effect of nickel content on the order–disorder transition mechanism of chromium atoms and vacancies was discussed on the basis of entropy analysis.

(2) For $(Cr_{1-x}Ni_x)_3Te_4$ ($x=0.15$ and 0.20) samples, another heat capacity anomaly in addition to the order–disorder transition observed for $(Cr_{1-x}Ni_x)_3Te_4$ ($x=0$–0.1) samples was seen around 600 K, probably due to the order–disorder transition in NiAs-type crystal structure.

(3) The solubility limit of nickel in Cr_3Te_4 was determined to be around $x=0.1$ by X-ray and heat capacity data.

References

[1] M.G. Adamson, E.A. Aitken, Proceedings of the International Conference on Fast Breeder Reactor Fuel Performance, Montterly, CA, USA, 1979, p. 536.
[2] M.G. Adamson, E.A. Aitken, T.B. Lindermer, J. Nucl. Mater. 130 (1985) 375.
[3] F. Grønvold, J. Chem. Thermodyn. 5 (1973) 545.
[4] K. Yasui, K. Ishida, T. Tsuji, J. Nucl. Mater. 247 (1997) 345.
[5] Y. Hinatsu, K. Ishida, T. Tsuji, J. Solid State Chem. 120 (1995) 49.