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Thermodynamic study on UPd_3 and $U(Pd_{0.85}Rh_{0.15})_3$

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Abstract

The heat capacities of UPd_3 and $U(Pd_{0.85}Rh_{0.15})_3$ were measured over the temperature range between 290 and 1500 K by direct heating pulse calorimetry, which is a direct method for heat capacity measurements. The measured heat capacities of UPd_3 were smaller than the literature values up to 900 K. The heat capacities of $U(Pd_{0.85}Rh_{0.15})_3$, obtained for the first time, were a little larger than those of UPd_3, but showed a similar temperature dependence. Since the oxygen partial pressures for the oxidation of UPd_3 and $U(Pd_{0.85}Rh_{0.15})_3$ alloys were calculated from the heat capacities to be higher than that for $MoO_2(s)$, UPd_3 and $U(Pd_{0.85}Rh_{0.15})_3$ are not expected to be oxidized during the irradiation of UO_2 fuel. © 1997 Elsevier Science B.V.

1. Introduction

The intermetallic compounds MMe_3, where M = U and transuranium elements (TRU), and Me = Pd, Rh and Ru, are important because of their potential formation during nuclear fission in the fuels, and the possible generation of an insoluble residue in dissolved solution of spent fuels [1]. To understand the formation and the thermodynamic stability of MMe_3 alloys, thermodynamic quantities are very useful. Very little is known about the thermophysical properties of MPd_3 and nothing about $M(Pd,Rh)_3$. For each UMe_3 (Me = Pd or Rh), a few heat capacity measurements have been reported over the temperature range between 1 and 900 K [2–4].

In this study, the heat capacities of UPd_3 and $U(Pd_{0.85}Rh_{0.15})_3$ were measured over the temperature range between 290 and 1500 K by means of direct heating pulse calorimetry.

2. Experimental

The mixtures of U and Pd, or U, Pd and Rh, each being 99.9% pure, were shaped into cylindrical rods of about 4–6 mm in diameter and about 50–60 mm in length, using an arc melting furnace in a purified argon atmosphere. The arc melting processes were repeated several times. The cylindrical rods of the alloys obtained were then annealed at 1373 K for 30 h in vacuum. X-ray diffraction analysis indicated the presence of a single phase (hexagonal $TiNi_3$ structure) for each alloy.

The heat capacities of these alloys were measured by using a direct heating pulse calorimeter, described in detail previously [5]. In this calorimeter, a sample rod is at first heated to a desired temperature by an external platinum heater. After attaining an equilibrium condition (i.e., constant desired temperature), an electric current is applied to the sample rod for a short period (usually 1 s) from a regulated dc power supply. The temperature rise of the sample (generally 2–5 K) is measured by a Pt/Pt–13%Rh thermocouple. In this calorimeter, the sample rod is surrounded by double concentric cylindrical thermal shields made of molybdenum. To reduce the error in the measured heat capacity due to heat leak from the sample at high temperatures, the molybdenum shields are heated by using batteries to the same temperature as the sample (i.e., to attain an adiabatic condition). The electric potential drop, the current and the temperature rise in the sample rod are measured simultaneously to obtain the heat capacity of the sample. The heat capacity measurements were conducted within an error of ±3%.

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3. Result and discussion

3.1. Heat capacity

The heat capacity of UPd_3 measured in this study over the temperature range of 288–1351 K is shown in Fig. 1 together with the previous result for UPd_3 by Burriel et al. [4]. Although the temperature dependence of the heat capacity of UPd_3 obtained in this study is close to that of Burriel et al. [4] below 900 K, our heat capacity values increased rapidly above 900 K, where heat capacity data have not been reported previously. In Fig. 2, the heat capacity of $U(Pd_{0.85}Rh_{0.15})_3$ is compared with that of URh_3 (Cordfunke et al. [3]) and that of UPd_3 (this study). The heat capacity of $U(Pd_{0.85}Rh_{0.15})_3$ was found to be larger than that of UPd_3 but has a similar temperature dependence. As seen in Fig. 2, the experimental heat capacity of $U(Pd_{0.85}Rh_{0.15})_3$ is close to that calculated from our UPd_3 data and the URh_3 value [3] using the additivity law for data below 900 K. For temperatures above 900 K, a rapid increase in the heat capacity due to defect formation is seen with temperature.

The heat capacity (C_p) can be expressed by the sum

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

where C_h is the harmonic term of the lattice vibration, C_d is the dilational term, C_{ah} is the anharmonic term of the lattice vibration, C_e is the electronic term and C_{ex} is the excess heat capacity due to the defect formation. Hence the excess heat capacity, C_{ex}, can be generally obtained by subtracting the sum of the terms, C_h, C_d, C_{ah} and C_e, from the measured heat capacity C_p. The harmonic term C_h can be expressed as

$$C_h = 3RD(\theta_D/T), \tag{2}$$

where $D(\theta_D/T)$ is the Debye function and θ_D is the Debye temperature. The Debye temperature for $U(Pd_{0.85}Rh_{0.15})_3$ was calculated by using the following equation [6]:

$$\frac{1}{\theta_{AB}^3} = \frac{p}{\theta_A^3} + \frac{q}{\theta_B^3}, \tag{3}$$

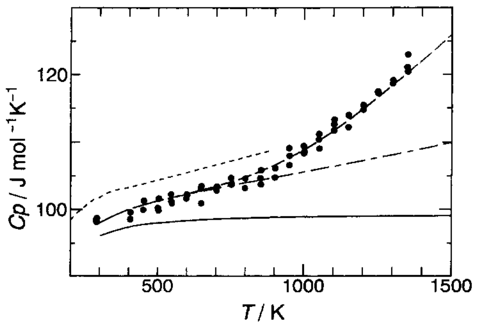

Fig. 1. Heat capacity of UPd_3. ●: present result; ---: Burriel et al. [4]; ————: C_h; – · –: $C_h + C_d + C_{ah} + C_e$; — — —: $C_h + C_d + C_{ah} + C_e + C_{ex}$.

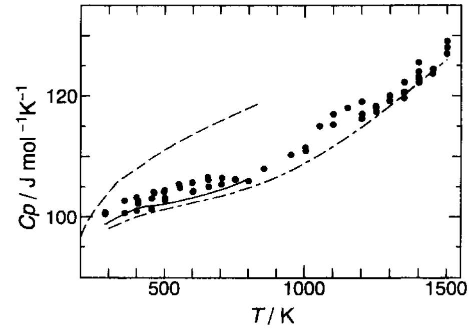

Fig. 2. Heat capacity of $U(Pd_{0.85}Rh_{0.15})_3$. ●: present result; ---: URh_3 by Cordfunke et al. [3]; ————: $0.85C_p$ (UPd_3; in this study)+$0.15C_p$ (URh_3 [3]); – · –: UPd_3 (in this study).

where AB represents the alloy, and p and q are the mole fractions of element A and B, respectively. The Debye temperature of $U(Pd_{0.85}Rh_{0.15})_3$ was thus estimated as 239 K from the Debye temperature of UPd_3 [4] and URh_3 [3]. The heat capacity of UPd_3 at temperatures below 360 K has been reported to be represented by the following equation [4]:

$$C_p = 3nR\left(1 - \theta_D^2/20T^2\right) + (a + b + \gamma)T, \tag{4}$$

where a, b and γ are the coefficients of the dilational, the anharmonic and the electronic heat capacity, respectively. By using the coefficients $(a + b + \gamma)$ in Eq. (4) an equation for our data on the heat capacity of UPd_3 was obtained for 290 to 700 K, where the increase in the heat capacity due to defect formation is thought to be negligibly small. The equation, thus obtained is given as follows:

$$\left(C_p/\text{J mol}^{-1}\ \text{K}^{-1}\right) = 95.1973 + 1.1411 \times 10^{-2}(T/\text{K}) - 1.5373 \times 10^4(\text{K}/T)^2. \tag{5}$$

In the case of $U(Pd_{0.85}Rh_{0.15})_3$ the equation for the heat capacity was obtained here by using the additivity law from Eq. (4) for UPd_3 and a similar equation for URh_3 [3] as follows:

$$\left(C_p/\text{J mol}^{-1}\ \text{K}^{-1}\right) = 97.4917 + 1.2431 \times 10^{-2}(T/\text{K}) - 1.8744 \times 10^4(\text{K}/T)^2. \tag{6}$$

The excess heat capacity, C_{ex}, was estimated for UPd_3 and for $U(Pd_{0.85}Rh_{0.15})_3$ from the difference between the experimental values and Eq. (5) or Eq. (6). The excess heat capacity is generally represented as

$$C_{ex} = \left(\Delta S_f \Delta H_f^2/RT^2\right)\exp(-\Delta H_f/2RT), \tag{7}$$

where ΔS_f is the entropy and ΔH_f the enthalpy of defect formation. From Eq. (7) the enthalpy of defect formation was determined to be 138 kJ/mol for UPd_3 and 128 kJ/mol for $U(Pd_{0.85}Rh_{0.15})_3$, respectively. Several heat capacity terms, such as C_h, $C_h + C_d + C_{ah} + C_e$ (Eq. (5) for UPd_3 and Eq. (6) for $U(Pd_{0.85}Rh_{0.15})_3$) and $C_h + C_d + C_{ah} + C_e + C_{ex}$, are compared in Figs. 1 and 3 with the experimental data.

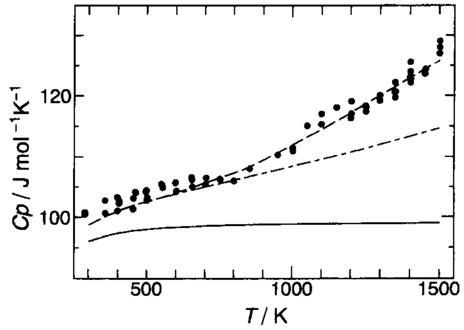

Fig. 3. Heat capacity of $U(Pd_{0.85}Rh_{0.15})_3$. ———: C_h; – · –: $C_h + C_d + C_{ah} + C_e$; — — —: $C_h + C_d + C_{ah} + C_e + C_{ex}$.

3.2. Thermodynamic quantities

The Gibbs energies of formation for UPd_3 and $U(Pd_{0.85}Rh_{0.15})_3$ were calculated from the experimental heat capacities and the enthalpies of formation ($\Delta_f H^\circ_{298}$) and entropy (ΔS°_{298}) at 298 K, and the estimated values by assuming an ideal solution of UPd_3 ($\Delta_f H^\circ_{298} = -524$ kJ/mol [7] and $S^\circ_{298} = 176.4$ J/mol K [4]) and URh_3 ($\Delta_f H^\circ_{298} = -301.2$ kJ/mol [8] and $S^\circ_{298} = 152.2$ J/mol K [3]) for $U(Pd_{0.85}Rh_{0.15})_3$. The Gibbs energy of formation for UPd_3 calculated in this study was in good agreement with that estimated by Cordfunke et al. [9]. The Gibbs energies of formation ($\Delta_f G^\circ_T$) for UPd_3 and $U(Pd_{0.85}Rh_{0.15})_3$ are given in the following equations (Eqs. (8) and (9)), respectively:

$$\left(\Delta_f G^\circ_T/\text{kJ mol}^{-1}\right) = -532.1 + 4.78 \times 10^{-3}(T/\text{K}), \tag{8}$$

$$\left(\Delta_f G^\circ_T/\text{kJ mol}^{-1}\right) = -497.6 + 3.01 \times 10^{-3}(T/\text{K}). \tag{9}$$

The oxygen partial pressures for the oxidation of UMe_3 alloys can be calculated from our Gibbs energies of formation for UPd_3 and $U(Pd_{0.85}Rh_{0.15})_3$ on the basis of the reaction

$$UMe_3(s) + O_2(g) = UO_{2.000}(s) + 3Me(s). \tag{10}$$

The oxygen partial pressures for the oxidation of $UPd_3(s)$ and $U(Pd_{0.85}Rh_{0.15})_3(s)$ were higher than that of $MoO_2(s)$ [10]. Since molybdenum in the fission-produced noble metal alloys is believed to buffer the oxygen potential in irradiated oxide fuel, UPd_3 and $U(Pd_{0.85}Rh_{0.15})_3$ should not be oxidized during the irradiation of $UO_2(s)$. The formation of a UMe_3 phase (M = Pd, Rh and/or a mixture) in oxide fuel is facilitated by reduction of the oxygen potential of UO_{2+x} (i.e., decreasing O/U ratio).

4. Conclusion

The heat capacities of UPd_3 and $U(Pd_{0.85}Rh_{0.15})_3$ were measured between 290 and 1500 K. The heat capacities of UPd_3 determined here had a temperature dependence similar to the literature values below 900 K, but were a little smaller than the literature values. Above 900 K, larger temperature dependences were seen both for UPd_3 and $U(Pd_{0.85}Rh_{0.15})_3$. The heat capacity values of $U(Pd_{0.85}Rh_{0.15})_3$ showed a similar temperature dependence to that of UPd_3 measured in this study but are larger.

Since the oxygen partial pressures for the oxidation of UPd_3 and $U(Pd_{0.85}Rh_{0.15})_3$ alloys, calculated from the Gibbs energies obtained here, were higher than that of $MoO_2(s)$, UPd_3 and $U(Pd_{0.85}Rh_{0.15})_3$ should not be oxidized during the irradiation of UO_2 fuel.

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