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Letter to the Editors

Vaporization behavior of NpN coloaded with PuN

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Abstract

The partial pressures of Np(g) and Pu(g) over NpN(s) coloaded with PuN(s) were measured by means of quadrupole mass spectrometer equipped with a Knudsen-cell in the temperature range of 1950–2070 K. The partial pressures of Np(g) were much lower compared with the case of mass-spectrometric measurement of NpN(s). The partial pressures of Pu(g) agreed well with those over PuN(s) which evaporated congruently. The partial pressure of N_2(g) was estimated from the measured partial pressure of Pu(g) based on the assumption of the congruent vaporization process of PuN(s). The free energy of formation of NpN(s) evaluated from the pressures of Np(g) and N_2(g) in this study almost agreed with that of NpN(s) previously reported. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Solid solution of actinide mononitrides is considered as one of the promising fuel materials for advanced fast reactors [1] and actinide burning reactors [2]. However, information on their thermophysical properties is scarce. Among them, the vaporization behavior is essential for understanding the irradiation behavior of such a material at elevated temperatures. The authors previously investigated the vaporization behavior of NpN(s) by means of a mass spectrometer equipped with a Knudsen-cell in the temperature range of 1690–2030 K, where it was indicated that NpN(s) may decompose into liquid Np metal, Np(l), and N_2(g) as UN(s) does [3]. Further, the Gibbs energy of formation of NpN(s) was evaluated in this temperature range using the N_2(g) pressure over NpN(s) + Np(l) derived by extrapolating the experimental data given by Olson and Mulford [4]. But the temperature range where Olson and Mulford measured the N_2(g) pressure was much higher, from 2480 to 3100 K. So we have carried out a mass-spectrometric study on NpN(s) accompanied by PuN(s) to confirm our previous results. It is well known that PuN(s) evaporates congruently [5]. In addition, the N_2(g) pressure over PuN(s) is expected to be much higher than that over NpN(s). When NpN(s) and PuN(s) coexist in a Knudsen-cell, the ambient nitrogen partial pressure could be governed by the nitrogen pressure derived from PuN(s). The purpose of this study is, therefore, to investigate the vaporization behavior of NpN(s) + PuN(s) and to ascertain that the free energy of formation of NpN(s) evaluated previously is reasonable.

2. Experimental

2.1. Sample preparation

The samples of NpN(s) and PuN(s) were prepared by carbothermic reduction of the dioxides, NpO_2 and PuO_2, respectively. The details of the preparation and characteristics of the starting materials were described in earlier papers [6,7]. The samples were subjected to X-ray diffraction analyses before the mass-spectrometric measurements. The lattice parameters agreed well with the reported values within an experimental error.

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2.2. Mass-spectrometric measurements

The vapor pressures over the sample were measured in the temperature range from 1970 to 2070 K by using a AGA-360 quadrupole mass spectrometer (Anelva) equipped with a Knudsen-cell contained in a Ta holder. The details of the apparatus used in the present study were described in an earlier paper [8]. The Knudsen-cell was made of tungsten with an orifice of 1.0 mm in diameter. The NpN(s) and PuN(s) lumps were put into the Knudsen cell in such a fashion that they could not touch each other during the mass-spectrometric measurement. The temperature was measured with two sets of W/Re 3-25 thermocouple inserted into small holes at the upper and lower positions of the Ta holder.

3. Results and discussion

3.1. Ionization efficiency curve

Ionic species, Np^+, Pu^+, NpO^+ and PuO^+, were detected in this study. Ionization efficiency curves of these vapor species are plotted in Fig. 1. To avoid fragmentation of the oxide ion species, an ionization potential of 12 eV was applied for all the vapor species in the present study.

3.2. Vapor pressures

3.2.1. Method for determining partial pressures

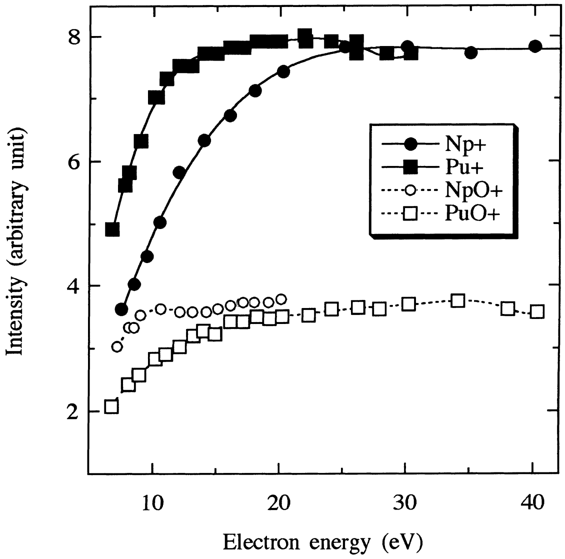

Fig. 1. Ionization efficiency curves of Np^+, Pu^+, NpO^+ and PuO^+ ions.

Calculation of the partial pressure of Pu(g) from the ion current was carried out by a modified integral method [9,10] and the following approximating equation was used:

$$P_{Pu}(T_i) = \frac{\Delta W}{a\Delta t_i}\sqrt{\frac{2\pi RT}{M_{Pu}}} \times \left[M_{Pu} I_i^{Pu^+}\sqrt{T_i}\Delta t_i/\sigma_{Pu}\gamma_{Pu}\right] \Bigg/ \left[\sum_k \left\{\left(I_k^{Pu^+} + I_k^{PuO^+}\right) M_{Pu}/\sigma_{Pu}\gamma_{Pu} + \left(I_k^{Np^+} + I_k^{NpO^+}\right) M_{Np}/\sigma_{Np}\gamma_{Np}\right\}\sqrt{T_k}\Delta t_k\right], \quad (1)$$

where ΔW is the weight difference in the sample between before and after the mass spectrometric measurement, a the cross-section of the orifice, Δt_i the time interval of temperature T_i, I_i the ion current at T_i, R the gas constant, M the mass number of gas species, σ the effective relative cross-section of ionization and γ the isotopic abundance ratio. This equation was derived using the following assumption. The efficiency of the electron multiplier [11] was corrected for the mass dependence by a factor of the reciprocal of square root of the mass number. The sensitivity of mass filter [12] was not taken into account for the little weight difference between the Pu- and Np-bearing vapor species. Though the ionization cross-sections of σ_{Pu} and σ_{PuO} are reported by several investigators, considerable disagreement exists in the values for these ionization cross-sections [13]. So the ionization cross-sections of σ_{NpO} and σ_{PuO} were assumed to be equal to σ_{Np} and σ_{Pu}, respectively, because of the smaller ionization cross-section for σ_O compared to those for σ_{Np} and σ_{Pu}. Clausing correction [14] was not made assuming that the effect of orifice-channel length was negligible. The effect of the vaporization coeficient [15] was not considered since the sample consisted of the porous lumps and the ratio of sample surface/orifice area was large enough to assure the prevalence of equilibrium condition.

The effective relative ionization cross-section of an ion species such as Pu, σ_{Pu}, was estimated from the ionization efficiency curve using the following relationship [16]:

$$\sigma_{Pu} = \sigma_{Pu}(\text{maximum})\frac{I_{Pu} + (12\ \text{eV})}{I_{Pu} + (\text{maximum})}, \quad (2)$$

where σ_{Pu}(maximum) and also σ_{Np}(maximum) were taken from the table by Mann [17].

The partial pressure of Np(g) was calculated by using the following equation [9]:

$$P_{Np}(T_i) = \frac{I_i^{Np^+}\sigma_{Pu}\gamma_{Pu}\sqrt{M_{Np}}}{I_i^{Pu^+}\sigma_{Np}\gamma_{Np}\sqrt{M_{Pu}}} P_{Pu}(T_i). \quad (3)$$

3.2.2. Vaporization mechanism of NpN(s) accompanied with PuN(s)

The determined partial pressures of Np(g) and Pu(g) are plotted in Fig. 2 as functions of the reciprocal absolute temperature. The temperature dependence of the partial pressures could be expressed in the form of $\log P = A - B/T$ as the following equations:

$$\log P_{\mathrm{Np}}(\mathrm{g})\ (\mathrm{Pa}) = 12.4 \pm 0.4 - 27800 \pm 900/T, \qquad (4)$$

$$\log P_{\mathrm{Pu}}(\mathrm{g})\ (\mathrm{Pa}) = 9.02 \pm 0.38 - 17000 \pm 800/T, \qquad (5)$$

where the equations are corresponding to least-squares fitting in the temperature range of 1970–2070 K.

Fig. 2 shows that the partial pressure of Pu(g) obtained in this study agrees well with that over PuN(s) given by Kent and Leary [18] and that the vapor pressure of Np(g) observed in this study is much lower than that of Np(g) over liquid Np metal given by Ackermann and Rauh [19], contrary to the case of mass-spectrometric measurement of NpN(s) [3]. In the present experimental condition, there is a possibility that the interaction of the gas and solid phase such as Pu(g) and NpN(s) results in the formation of the solid solution (Np,Pu)N(s) leading to the change of partial pressures. In the case of (Np,Pu)N(s) solid solution, indeed, it is known that Pu partial pressure strongly depends on the Pu content [10]. So if the compositional change of the sample occurs during the measurement, the ion currents of Np^+ and Pu^+ must change with time. However, no significant time dependence of these ion currents was observed during the measurement. Therefore, it is considered that the influence of the formation of the solid solution (Np,Pu)N(s) could be negligible in this case. Since the partial pressure of Pu(g) agrees well with that in the case of congruent vaporization of PuN(s) and the vapor pressure of Np(g) suggests that no liquid phase occurs, the vaporization mechanism could be expressed by the following reactions:

$$\mathrm{NpN(s)} = \mathrm{Np(g)} + 1/2\mathrm{N_2(g)}, \qquad (6)$$

$$\mathrm{PuN(s)} = \mathrm{Pu(g)} + 1/2\mathrm{N_2(g)}. \qquad (7)$$

3.3. Standard Gibbs energy of formation of NpN

The partial pressure of N_2(g) over NpN(s) is needed for obtaining the Gibbs energy of formation of NpN(s) besides the partial pressure of Np(g). So the partial pressure of N_2(g) over NpN(s) + PuN(s) was derived from the partial pressure of Pu(g) obtained in this study using the following relation based on the congruent vaporization of PuN(s) [5]:

$$P_{\mathrm{N_2}} = 0.5\sqrt{M_{\mathrm{N_2}}/M_{\mathrm{Pu}}}\ P_{\mathrm{Pu}}. \qquad (8)$$

The standard Gibbs energy of formation of NpN(s) was determined from the vapor pressure measured for Np(g), the pressure of N2(g) derived from Eq. (8) and the Gibbs energy of formation of Np(g) obtained from the table given by Oetting et al. [20] as follows:

$$\Delta_f G(T)(\mathrm{Np,g})\ (\mathrm{J/mol}) = 426\,000 - 98.6T (1900\text{–}2100\ \mathrm{K}). \qquad (9)$$

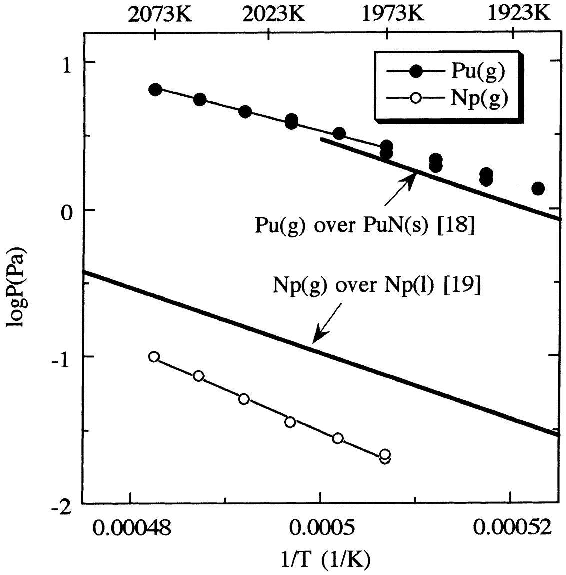

Fig. 2. Temperature dependence of the partial pressures of Np(g) and Pu(g) over NpN(s) + PuN(s).

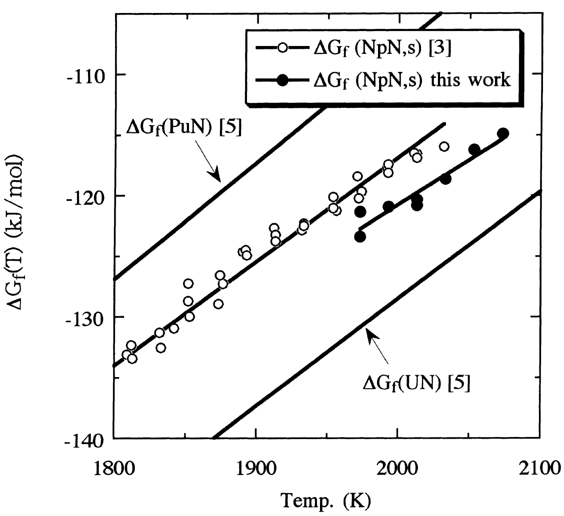

Fig. 3. Free energy of formation of NpN(s) compared with those of UN(s) and PuN(s).

In Fig. 3 the Gibbs energy of formation of NpN(s) is plotted, together with the previously reported one [3] and those of UN(s) and PuN(s) given by Matsui and Ohse [5]. The least-squares treatment of the data gives the following equation:

$$\Delta_f G(T)(\mathrm{NpN, s})\ (\mathrm{J/mol}) = -269\,000 \pm 17\,000 + 74.0 \pm 8.4T. \tag{10}$$

The Gibbs energy of formation of NpN(s) obtained in this study agrees fairly well with that reported previously [3]. Further it was reconfirmed that Gibbs energy of formation of NpN(s) is located between those of PuN(s) and UN(s).

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