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Vaporization behavior of (Np,Pu)N

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Abstract

Knudsen effusion mass spectrometric analysis of neptunium–plutonium mixed nitride, (Np,Pu)N, was carried out in the temperature range of 1270–2010 K. The pressures of Np(g) over the solid solutions showed a similar temperature dependence with that of Np(g) over Np(l). On the other hand, there were two stages for the temperature dependence of Pu(g) over the solid solutions. The pressures of Pu(g) at higher temperatures showed a similar temperature dependence with the case of congruent vaporization of PuN and depended on the Pu/(Np+Pu) ratio in the solid phase. The pressures of Pu(g) at lower temperatures showed a similar temperature dependence with that over Pu(l). © 1998 Elsevier Science S.A.

Keywords: Vaporization behavior; Knudsen effusion mass spectrometry; Temperature dependence; (Np,Pu)N

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1. Introduction

Feasibility studies for transmuting minor actinides by fast reactors and accelerators have been conducted in several countries from the viewpoint of a better management of high level nuclear waste [1,2]. One of the incentives to nitride fuel for transmutation is the probable formation of solid solutions among actinide mononitrides with an extensive composition as well as superior thermal and neutronic properties. At present, however, thermodynamic information on mononitride solid solutions has been quite scarce, except for (U,Pu)N, which has been developed as an advanced fuel for fast reactors. Therefore, it is essential to prepare mononitride solid solutions containing minor actinides and determine their properties for the application of nitride fuel to transmutation. Vaporization behavior is one of the key properties for understanding fuel behavior at high temperatures. As for the vaporization behavior of NpN, it has been reported recently by us that NpN decomposes into Np(l) and N_2(g), as UN does [3]. On the other hand, it has been reported that PuN vaporizes congruently [4]. This report concerns the mass spectrometric investigation of (Np,Pu)N solid solutions.

2. Experimental

2.1. Sample preparation

Solid solutions of (Np,Pu)N were prepared by heating mixtures of NpN and PuN, synthesized by carbothermic reduction from the oxides. The details of carbothermic reduction and the characteristics of the starting materials were described in earlier papers [5,6]. The mononitrides, NpN and PuN, were mixed in an agate mortar at molar ratios of Np/(Np+Pu) of 0, 0.5, 0.75 and 1.0. The mixed powders were pressed into green pellets under a pressure of about 300 MPa and heated again for allow the formation of solid solutions at 2023 K in a N_2–8% H_2 mixed gas stream for 90–180 ks. Then the products were subjected to X-ray diffraction and chemical analyses for characterization.

Typical results of characterization are summarized in Table 1. According to X-ray diffraction patterns, no phase other than NaCl-type mononitride was observed and the separation of the diffraction lines into $K\alpha_1$ and $K\alpha_2$ at high angles was fairly good. Therefore, it is considered that the formation of a solid (Np,Pu)N solution was completed in all cases. The lattice parameter increased with PuN content in the solid solutions, but the change in the lattice parameter deviated positively from Vegard's law between NpN and PuN [7]. The solid solutions are considered to have an almost stoichiometric composition, and the impurity levels of oxygen and carbon could be kept at less than 500 ppm. In this study, sample preparation was carried out in gloveboxes with a high-purity argon gas atmosphere.

2.2. Mass spectrometric measurement

The vapor species from samples were measured by

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Table 1
Characteristics of (Np,Pu)N solid solutions

Sample	NpN	$Np_{0.75}Pu_{0.25}N$	$Np_{0.5}Pu_{0.5}N$	$Np_{0.25}Pu_{0.75}N$	PuN
Lattice parameter (nm)	0.48971	0.48997	0.49025	0.49016	0.49052
Nitrogen content (wt.%)	5.65	–	–	–	5.57
Oxygen content (wt.%)	0.03	–	–	–	0.04
Carbon content (wt.%)	0.05	–	–	–	0.03

using a quadrupole mass spectrometer (AGA-360, ANELVA Ltd.) with a Knudsen effusion cell in the temperature range of 1270–2010 K. Details of the apparatus used were described in an earlier paper [8]. The cell was made of W with an orifice of 1.0 mm in diameter. The temperature was measured by two sets of W/Re3-25 thermocouples, inserted into the upper and lower positions of the Ta holder containing the Knudsen-cell, and calibrated by comparing the temperature with the melting point of Pd.

3. Results

3.1. Ionization efficiency curve

As ion species, Np^+, NpO^+, Pu^+ and PuO^+ were detected in this study. Fig. 1 shows the ion efficiency curve for these species. Ion currents of these species have saturated by 10 eV, as shown in the figure, so an ionization potential of 10 eV was applied in the present study, to avoid the fragmentation of oxide ion species, such as PuO^+ and NpO^+. Ion intensities of NpO^+ and PuO^+ were about one forth and one twentieth smaller than those of Np^+ and Pu^+, respectively, except at the initial heating stage. No attempt was made to determine the temperature dependence of the pressure of $N_2(g)$ because of high background at the mass number of 28.

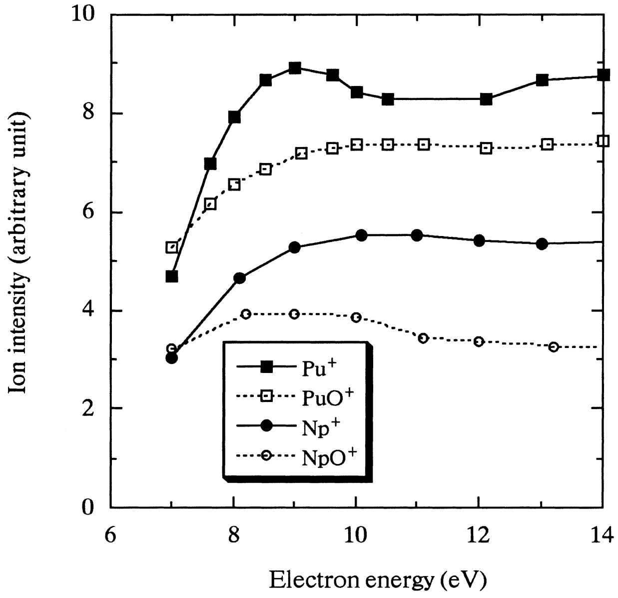

Fig. 1. Ionization efficiency curves for Np^+, NpO^+, Pu^+ and PuO^+.

3.2. Vapor pressures

3.2.1. Method for determining partial pressures

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

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

where ΔW is the weight difference in the sample before and after the mass spectrometric measurement, a is the cross-section of the orifice, Δt_i is the time interval of temperature T_i, I_i is the ion current at T_i, R is the gas constant, M is the mass number of gas species, σ is the maximum ionization cross-section and γ is the isotopic abundance ratio. On the other hand, the partial pressure of Np(g) was calculated by the following equation;

$$P_{Np}(T_i) = \frac{I_i^{Np^+} \sigma_{Pu}\gamma_{Pu}\sqrt{M_{Np}}}{I_i^{Pu^+} \sigma_{Np}\gamma_{Np}\sqrt{M_{Pu}}} P_{Pu}(T_i) \tag{2}$$

In this study, the efficiency of the electron multiplier was corrected for the mass dependence by a factor of the reciprocal of the square root of the mass number and σ_{PuO} and σ_{NpO} were assumed to be equal to σ_{Np} and σ_{Pu}, respectively. σ_{Np} and σ_{Pu} were taken from the table by Mann [10].

3.2.2. Partial pressures of Np(g) and Pu(g) over (Np,Pu)N

The partial pressures of Np(g) and Pu(g) over the solid solutions are plotted in Fig. 2 as a function of the reciprocal absolute temperature. This figure indicates that partial pressures of Np(g) over the solid solutions show a similar temperature dependence with that of Np(g) over liquid neptunium metal, as given by Ackermann and Rauh [11], as in the case of NpN [3]. Slight differences in the partial pressure of Np(g) among the solid solutions were observed.

On the other hand, the temperature dependence of Pu(g)

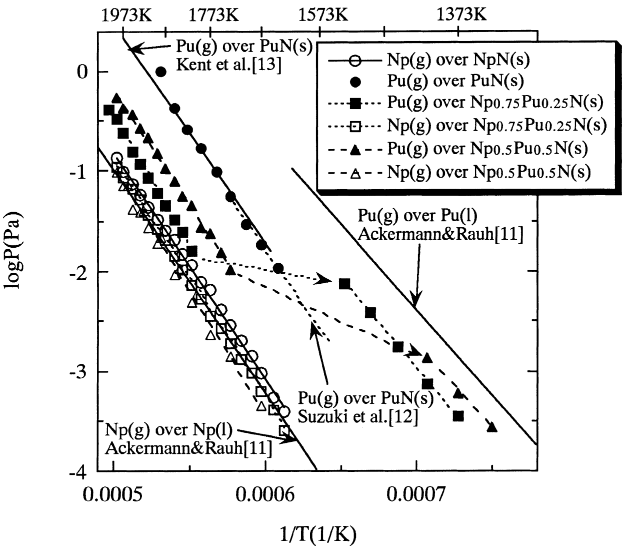

Fig. 2. Vapor pressures of Np(g) and Pu(g) over (Np,Pu)N solid solutions.

over the solid solutions showed different behaviors at higher and lower temperatures. At temperatures higher than about 1850 K, the slope of the logarithmic pressures of Pu(g) versus the reciprocal temperature was similar with that over PuN, given by Suzuki et al. [12] and Kent and Leary [13], and there exists a clear composition dependence among the solid solutions. At temperatures lower than about 1450 K, the partial pressures of Pu(g) showed relatively large values and a similar temperature dependence with that of Pu(g) over liquid plutonium metal was found as that reported previously [11]. The partial pressures decreased with Pu concentration in the sample. At intermediate temperatures, the measured ion intensity of Pu^+ exhibited a time dependence during the measurements.

4. Discussion

It is suggested from the pressures of Np(g) over the solid solutions that the precipitation of liquid phase occurs during the measurements in the same way that NpN does. But the partial pressures of Pu(g) at the concerning temperature were much lower than that over Pu(l), unlike the case of Np(g). Based on the assumption that the Pu–Np system in the liquid state is nearly ideal, it is thought that the Pu concentration in the liquid phase may be very small. The partial pressures of Np(g) over the solid solution showed a slight composition dependence. This might be caused by the increase in the partial pressures of Pu(g).

Since the temperature dependence of the partial pressures of Pu(g) observed at higher temperatures was similar to the case of congruent vaporization of PuN reported by Kent and Leary [13], as shown in Fig. 2, the pressures of Pu(g) observed at higher temperatures are thought to reflect the vapor pressure over the solid phase. Furthermore, there was a composition dependence in the pressure of Pu(g), so we tentatively evaluated the activities of PuN(s) in the pseudo-binary NpN–PuN solid solution at 1873 K from the partial pressures of Pu(g), assuming that the Pu/(Np+Pu) ratio in the solid phase is equal to the initial mixing ratio and that the component of PuN in (Np,Pu)N evaporates congruently. The results are 0.071 for $(Np_{0.75}Pu_{0.25})N$ and 0.163 for $(Np_{0.5}Pu_{0.5})N$. These results suggest that the behavior of the solid solution (Np,Pu)N may largely deviate from that of an ideal solid solution.

The time dependence of the ion current of Pu^+ at the transition stage suggests that the composition of the liquid phase gradually changed with time. Furthermore, it was found that the pressure of Pu(g) over PuN also approached that over Pu(l) with decreasing temperature; at lower temperatures than the temperature range examined in the past, as seen in the solid solutions. This phenomenon may be related to the limited single phase region of PuN at lower temperatures. However, the reasons why the transition stage appeared should be the subjects of future study.

The pressures of Pu(g) over the solid solutions at lower temperatures suggest that the Pu concentration in the liquid phase was much higher than that at higher temperatures. The differences in the partial pressures of Pu(g) observed among the solid solutions will be related to the composition of the liquid phase.

5. Summary

The vaporization behavior of (Np,Pu)N solid solutions was investigated by Knudsen effusion mass spectrometry in the temperature range of 1270–2010 K. The pressures of Pu(g) showed a similar temperature dependence to that of congruent vaporization of PuN and depended on the Pu/(Np+Pu) ratio in the solid phase. The activities of PuN that were evaluated suggest that the behavior of the solid solution (Np,Pu)N may largely deviate from that of an ideal solid solution. On the other hand, the pressures of Np(g) over the solid solutions showed a similar temperature dependence with that of Np(g) over Np(l), and the precipitation of liquid phase is suggested during the measurement. Furthermore, the pressures of Pu(g) at temperatures lower than about 1450 K showed a similar temperature dependence to that over Pu(l).

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