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Vaporization behavior of neptunium mononitride

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Abstract

Vaporization behavior of NpN(s) was investigated by mass spectrometry with a Knudsen-cell in the temperature range of 1690–2030 K. It is suggested from the vapor pressure measurements that NpN(s) decomposed into Np(l) and N_2(g). The free energy of formation of NpN(s) was evaluated by using the partial pressures of Np(g), the decomposition pressures of N_2(g) reported previously and the free energy of formation of Np(g). The free energy of formation of NpN(s) obtained lay between those of UN and PuN reported in the literature. © 1997 Elsevier Science B.V.

1. Introduction

Minor actinides (Np, Am and Cm), and/or their daughters in spent fuels, are radiotoxic and have fairly long half-lives. As an option for closing the fuel cycle, the concept of transmuting minor actinide elements to lighter nuclides with shorter half-lives has been proposed [1]. Neptunium is one of the key elements among minor actinides because of its large accumulated amount and long half-life compared with those of other elements such as Am and Cm. Actinide mononitrides such as UN and PuN are well known to have superior characteristics for nuclear fuel, i.e., high melting temperature, high heavy metal density, and excellent thermal conductivity. Therefore, a solid solution of actinide mononitrides has been proposed as a potential fuel of the actinide burner reactor [2]. However, information is scarce on the thermophysical properties of minor actinide compounds. On the evaporation behavior of NpN(s) there is only one report by Olson and Mulford who measured the partial pressure of N_2(g) over NpN(s) + Np(l) [3]. The purpose of this study is to determine the partial pressures of Np(g) over NpN(s) and to estimate its thermodynamic functions.

2. Experimental

2.1. Sample preparation

The sample of NpN(s) was prepared by carbothermic reduction of the dioxide, NpO_2. The mixture of NpO_2 and graphite powder with a molar ratio C/NpO_2 of 2.2 was heated in N_2 gas stream at 1823 K and N_2–8%H_2 mixed gas stream at 1723 K. The characteristics of the raw materials and details of preparation method have been described elsewhere [4]. The product of carbothermic reduction was subjected to chemical and X-ray diffraction analyses and these results are summarized in Table 1. It was seen that high-purity NpN sample with near-stoichiometric composition of a single phase was obtained. The lattice parameter of NpN agreed well with the values reported by Novion and Lorenzelli, 0.48979 nm [5], and Olson and Mulford, 0.48987 nm [3].

2.2. Mass spectrometric measurements

The vapour pressures over the sample were measured in the temperature range from 1690 to 2030 K by using a quadrupole mass spectrometer 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 [6]. The Knudsen-cell was made of tungsten metal with an

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Table 1
Results of chemical and X-ray diffraction analyses of NpN sample for mass spectrometric measurements

Chemical analysis			X-ray diffraction lattice parameter of NpN (nm)
nitrogen (wt%)	oxygen (wt%)	carbon (wt%)	
5.69	0.02	0.07	0.48967

orifice of 1.0 mm in diameter. The temperature was measured by two sets of W/Re 3-25 thermocouple inserted into the upper and lower positions of a Ta folder and calibrated by the melting point of Pd.

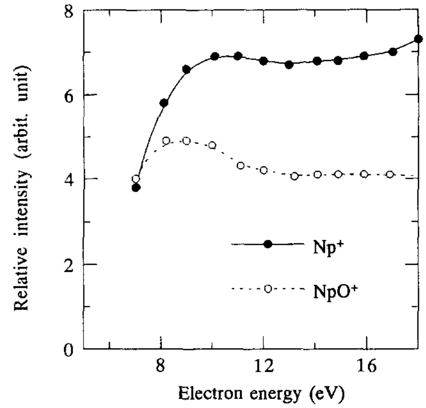

Fig. 1. Ionization efficiency curves for Np^+ and NpO^+ ions over NpN(s).

3. Results and discussion

3.1. *Ionization efficiency curve*

Ionic species, Np^+ and NpO^+ were detected in this study. Fig. 1 shows the ion efficiency curve of these species. Ion currents of these vapour species have already saturated at 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 NpO^+. On the other hand, ion intensity of N_2^+ from the sample could not be measured on account of high background at mass number 28. Therefore, no attempt was made to determine the temperature dependence of N_2^+ ion current.

3.2. *Vapour pressures*

3.2.1. *Method for determining partial pressures*

The determination of the partial pressure of Np(g) has been carried out by the modified integral method [7] and the following approximate equation was used:

$$P_{Np}(T_i) = \frac{\Delta W_{Np} \text{ in NpN}}{a\Delta t(T_i)} \times \frac{I_{Np^+}(T_i)\sqrt{T_i}\,\Delta t(T_i)}{\Sigma_k I_{Np^+}(T_k)(\text{sum})\sqrt{T_k}\,\Delta t(T_k)} \times \sqrt{\frac{2\pi R T_i}{M_{Np}}}, \qquad (1)$$

where ΔW_{Np} in NpN is the whole amount of Np vaporized from the sample during the mass-spectrometric measurement, a is the cross-section of orifice, $\Delta t(T_i)$ is the time interval of temperature T_i, R is the gas constant, M_{Np} is mass number of neptunium and $I_{Np^+}(\text{sum})$ is the sum of I_{Np^+} and $I_{Np^+}(\text{imag})$ which is equivalent to I_{NpO^+} and expressed by the following equation:

$$I_{Np^+}(\text{imag}) = \frac{\sigma_{Np} S_{Np} \sqrt{M_{Np}}}{\sigma_{NpO} S_{NpO} \sqrt{M_{NpO}}} I_{NpO^+}, \qquad (2)$$

where S is the efficiency of the electron multiplier and σ is the maximum ionization cross-section of the gaseous species.

In this study, ΔW_{Np} and $I_{Np^+}(\text{imag})$ were approximated as follows. ΔW_{Np} in NpN was approximately equal to the difference in weight of sample before and after the mass spectrometric measurement, since the weight change originated by vaporizing of all vapor species other than Np-bearing species could be neglected in the total weight

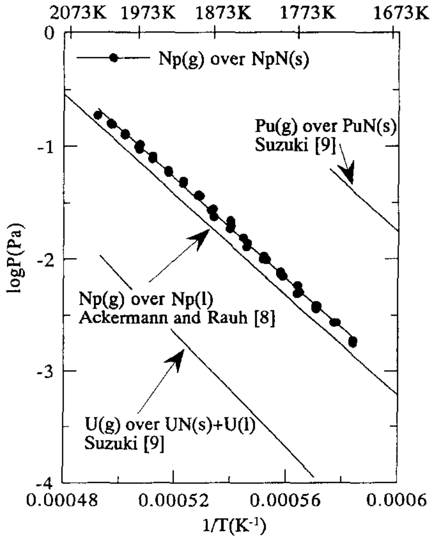

Fig. 2. Temperature dependence of partial pressures of Np(g) over NpN(s), Pu(g) over PuN(s) and U(g) over UN(s) [8,9].

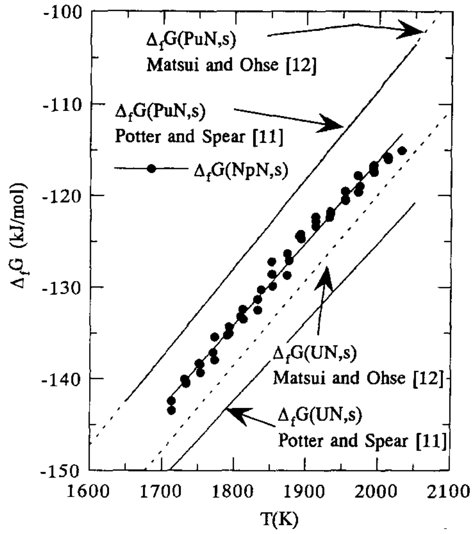

Fig. 3. Free energy of formation of NpN(s) compared with those of UN(s) and PuN(s) [11,12].

change of sample. I_{Np^+}(imag) was approximately equal to I_{NpO^+}, since S was corrected for the mass dependence by a factor of the reciprocal of square root of the mass number and σ_{NpO} was considered approximately equal to σ_{Np}.

3.2.2. *Decomposition mechanism of NpN(s)*

The determined partial pressures of Np are plotted in Fig. 2 as a function of the reciprocal absolute temperature. The partial pressures of Np(g) were expressed in the form of $\log P = A - B/T$ by the following equation:

$$\log P_{\mathrm{Np}}(\mathrm{g})\ (\mathrm{Pa}) = 10.26 - 22200/T, \qquad (3)$$

where the equation was corresponding to a least-squares fit.

It was found that the vapor pressure of Np(g) observed in this study was similar to that of Np(g) over liquid Np metal given by Ackermann and Rauh [8] as represented in Fig. 2. Therefore, the decomposition mechanism was considered as the following reaction:

$$\mathrm{NpN(s)} = \mathrm{Np(l)} + \tfrac{1}{2}\mathrm{N_2(g)}, \qquad (4)$$

$$\mathrm{Np(l)} = \mathrm{Np(g)}. \qquad (5)$$

3.3. *Standard free energy of formation of NpN*

Besides the partial pressures of Np(g), those of N_2(g) over NpN(s) and the standard free energy of formation of Np(g) are needed for obtaining that of NpN(s). Fortunately, Olson and Mulford [3] carried out the measurement of partial pressures of N_2(g) over NpN(s) + Np(l) in the temperature range 2480–3100 K and gave the following equation:

$$\log P_{N_2}\ (\mathrm{Pa}) = 13.199 - (29.54 \times 10^3)/T + 7.87 \times 10^{-18} T^5. \qquad (6)$$

It was assumed that the equation could be extrapolated to the present temperature range concerned. On the other hand, the standard free energy of formation of Np(g), $\Delta_f G(T)$(Np, g), was given by the following equation derived from the values given by Oetting et al. [10]:

$$\Delta_f G(T)(\mathrm{Np, g})\ (\mathrm{J/mol}) = 427000 - 98.99T\ (1700 - 2100\ \mathrm{K}). \qquad (7)$$

From the experimental results and the Eqs. (6) and (7), $\Delta_f G(T)$(NpN, s) could be calculated. In Fig. 3, the temperature dependence of $\Delta_f G(T)$(NpN, s) is plotted, together with $\Delta_f G(T)$(UN, s) and $\Delta_f G(T)$(PuN, s) given by Potter and Spear [11] and Matsui and Ohse [12]. The line for NpN(s) drawn by the least-squares treatment of the data corresponds to the following equation:

$$\Delta_f G(T)(\mathrm{NpN, s})\ (\mathrm{J/mol}) = -295900 + 89.88T. \qquad (8)$$

It was found that the values of $\Delta_f G(T)$(NpN, s) were located between those of $\Delta_f G(T)$(PuN, s) and $\Delta_f G(T)$(UN, s).

4. Conclusion

Vaporization behavior of Np(g) over NpN(s) was investigated by mass spectrometry with a Knudsen-cell. Decomposition of NpN(s) into Np(l) and N_2(g) was suggested from the vapor pressure measurements. The free energy of formation of NpN(s) was calculated from the partial pressures of Np(g) measured in this investigation, the decomposition pressures of nitrogen reported by Olson and Mulford [3] and the free energy of formation of Np(g) reported by Oetting et al. [10]. The free energy of formation of NpN(s) obtained lay between those of UN and PuN reported previously.

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