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Thermophysical and thermodynamic properties of actinide mononitrides and their solid solutions

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Abstract

The recent investigations on the thermophysical and thermodynamic properties of actinide mononitrides, which are essential for the development of nitride fuel, are described. The thermal conductivities of UN, NpN and PuN are found to have a tendency to increase gradually with temperature, while to decrease with the atomic number of the actinide element component because of the decrease of electronic contribution. The solid solutions of the mononitrides show a temperature dependence similar to those of two component nitrides each and possess intermediate thermal conductivity values. Knudsen–effusion mass spectrometric measurements of UN, NpN, and PuN have been performed. Predominant vapor species observed were only elemental metals except nitrogen gas. It is considered that UN and NpN form liquid phases and show the partial pressures of metal gas species close to those over pure respective metals, while PuN evaporates congruently. © 1998 Elsevier Science S.A.

Keywords: Nitride; Actinide; Uranium; Neptunium; Plutonium; Lattice parameter; Thermal expansion; Heat capacity; Thermal conductivity; Vapor pressure; Thermodynamics

1. Introduction

Nitride is a candidate material of advanced fuels and targets for fast reactors [1] and for transmutation of minor actinide elements such as Np, Am and Cm [2] because of its advantageous thermal and neutronic properties. The thermophysical and thermodynamic properties of actinide mononitrides; i.e., UN, NpN, PuN and AmN, are essential in fuel designs and evaluation of fuel behavior. Excellent reviews of nitride fuel have been given by Matzke [1] and Blank [3] up to now. Furthermore, the properties of UN have been reviewed by Hayes et al. [4] from the viewpoint of the development for space reactors. It is, however, obvious that more information should be necessary for the development of nitride fuel.

The research of nitride fuel, which includes fuel fabrication technology, property measurements and irradiation tests, has been carried out at Japan Atomic Energy Research Institute (JAERI) [5]. Additional information has been provided on the properties such as thermal conductivity and evaporation behavior of actinide mononitrides and their solid solutions through the research in Refs. [6–16]. Furthermore, some papers on nitride fuel were also presented from India [17,18]. This report summarizes the recent investigations on the thermophysical and thermodynamic properties, comparing with the previous reviews.

2. Experimental

2.1. Sample preparation

Samples of actinide mononitrides such as UN, PuN and NpN for property measurements were separately synthesized by carbothermic reduction of the dioxides with graphite in a N_2–H_2 mixed gas stream at about 1750 K [6,7]. In the case of the fabrication of dense discs or pellets, the mononitride was ground, compacted and sintered in an Ar–H_2 mixed gas atmosphere followed by heat-treatment in a N_2–H_2 mixed gas stream. The preparation of the solid solutions was carried out by sintering the mixture of the respective mononitride. The sample preparation was performed in gloveboxes with an atmosphere of Ar gas purified to the levels of 1–2 ppm oxygen and 2–5 ppm water.

Mononitride samples were subjected to chemical and

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X-ray diffraction analyses [19]. The content of impurity oxygen in samples synthesized by carbothermic reduction was always less than 0.1 wt.% and residual carbon was found to decrease generally from about 0.20 wt.% for UN to 0.05 wt.% for PuN with the atomic number of actinide elements because the solubility of carbon in the mononitride phase under a N_2 atmosphere decreases with the atomic number and the removal of dissolved carbon is not easy compared with that of free carbon [7].

The samples prepared by us were confirmed by X-ray diffraction analyses to consist only of a NaCl-type fcc-structured mononitride phase and the lattice parameters were consistent with the literature. The formation of the solid solutions was also checked by X-ray diffraction analyses.

2.2. Property measurements

The thermal conductivity of nitride samples was determined from the heat capacity, density and thermal diffusivity measured by a laser flash method at the temperature range of 740 K to 1,630 K in a vacuum by use of thin disc samples. The details of the experimental procedure were described in earlier papers [8,20]. The partial pressures of metal gas species over nitrides were determined by a Knudsen–effusion quadrupole mass spectrometer. The details of the equipment and the measurement conditions were described in earlier papers [9,21]. The thermodynamic treatments of the data on vapor pressures were carried out by applying the literature data on nitrogen pressures, because precious determination of nitrogen pressures over nitrides is impossible in our case.

3. Literature data, results and discussion

3.1. Lattice parameter and thermal expansion

The published data on the lattice parameters of UN, NpN and PuN, which have a NaCl-type face-centered cubic structure, seem to be consistent with each other perhaps because the actinide mononitrides are so-called line compounds at low temperatures and the solubility of impurity oxygen in the mononitride phases is relatively low compared with the case of monocarbide.

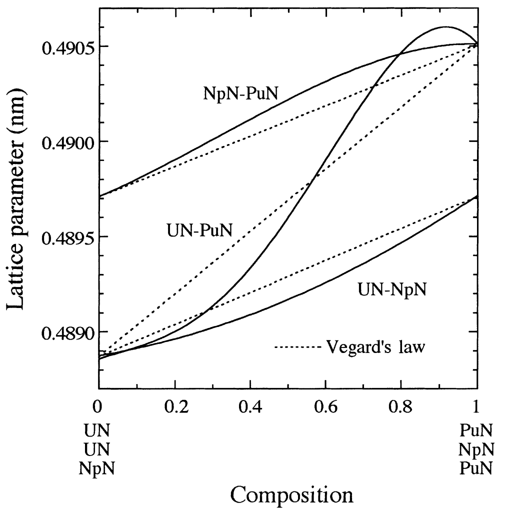

Fig. 1. Lattice parameter of solid solutions of actinide mononitrides

The lattice parameters of the solid solutions of the UN–PuN, UN–NpN and NpN–PuN systems [9–11,22] are shown in Fig. 1, where they deviate from the Vegard's law. It can be pointed out that the lattice parameters of the solid solutions containing UN show a negative deviation in the UN-rich compositions, while PuN has a tendency to enlarge the lattice parameters of the solid solutions with UN and NpN from the Vegard's law. The lattice parameters of the solid solutions increase with the addition of actinide mononitrides having larger lattice parameter, but the characters of UN and PuN are predominant in the solid solutions at their rich composition sides. The relatively large deviation from the Vegard's law suggests that the solid solution of actinides mononitride cannot be treated as an ideal solution.

As for the lattice parameter of PuN, the effect of self-irradiation damage becomes significant during long storage. The increase of the lattice parameter ($\Delta\ a/a$) is represented by the following equation independent of the difference in the isotopic ratio:

$$\Delta a/a = 2.54 \times 10^{-3}\{1 - \exp(-2.128 \times 10^{4}\lambda t)\},$$

where λ is the decay constant (per year) and t the storage time (year) at room temperature [12]. The damage can be recovered by heat treatment at the temperatures over 1500 K. It can be said that heat treatment would be necessary before the property measurements at lower temperatures.

The thermal expansion of UN has been reviewed by Hayes et al. [4] and an equation has been proposed from the assessment of X-ray diffraction data as shown in Fig. 2. The thermal expansion of PuN and (U,Pu)N is also plotted in the figure. The linear thermal expansion coefficient of PuN by Alexander et al. [23] indicates a larger value than that of UN. The values for UN-PuN solid solutions [24,25] are intermediate between those of UN and PuN, and increase with the PuN content. However, the accuracy of the above data was not well known and the temperature range measured was limited. In addition there is no information on the thermal expansion of NpN and the solid solutions. Further investigations would be requested for the thermal expansion of nitrides of transuranium elements.

3.2. Heat capacity

Heat capacity, *Cp*, is essential as one of thermodynamic functions and also necessary for calculation of thermal

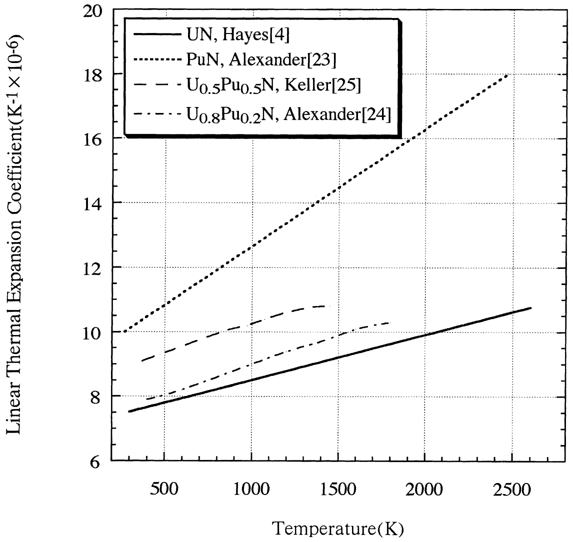

Fig. 2. Linear thermal expansion coefficient of actinide mononitrides

conductivity from the thermal diffusivity. Fig. 3 shows the literature data of the heat capacities of UN, PuN and UN–PuN solid solutions. There is, however, no additional information after the reviews by Blank [3] and Hayes et al. [4].

Hayes et al. [4] have recommended an equation for the heat capacity of UN comparing nine data sets, which seem to agree with each other at low temperatures, but at elevated temperatures the data are limited and to some extent scattered. The previously reported values for the heat capacity of UN show almost a linear increase with temperature except those of Conway et al. [26] who indicated a strong upward trend at temperatures over 1500 K for $Cp - T$ curves. This behavior shows an analogy with that of actinide carbides as pointed by Blank [3]. The assessment by Hayes et al. adopts the results of Conway et al.

The heat capacities of PuN and (U,Pu)N are plotted in Fig. 3. Information on them is very scare and limited to low temperatures. Furthermore, the two data sets on PuN given by Alexander et al. [23] and Spear et al. [27] are not consistent. The heat capacity of PuN reported by Spear et al. is lower than that of UN, but the data of Alexander et al. are larger and very close to those of UN. The values for the UN–PuN solid solution by Alexander et al. [24] are intermediate between those of PuN by Spear et al. and UN. The data reported by Alexander et al. for PuN and (U,Pu)N seem to be in conflict with each other. In addition, the temperature dependence of the heat capacities of PuN and its solid solution are almost linear, although it is suggested that they may shift toward higher values at elevated temperatures as that of UN.

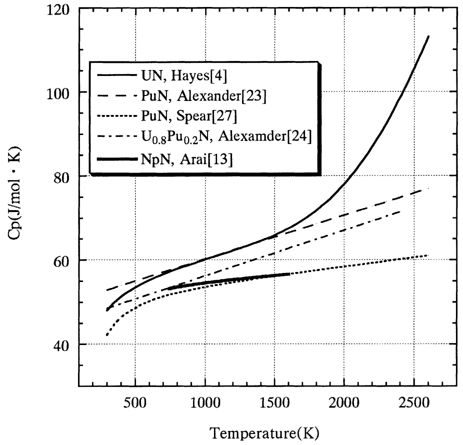

Fig. 3. Heat capacity of actinide mononitrides

No experimental result is reported on the heat capacities of NpN and its solid solutions. Therefore, the heat capacity of NpN was estimated by Arai et al. [13] by using the equations given by Kubaschewski et al. [28]. The result is also plotted in Fig. 3. It is suggested from the estimation that the heat capacity of NpN might be between those of UN and PuN. Furthermore, the estimated values of UN and PuN by this procedure are relatively close to the data by Hayes et al. [4] and Spear et al. [27], respectively. In the texts of Matzke [1] and Blank [3], the data of Spear et al. have been also quoted for that of PuN. At present, the data by Spear et al. may be preferable for PuN, but should be confirmed experimentally, because they were derived from theroretical considerations.

In case of the estimation of the heat capacities of the solid solutions, the Kopp's law has been applied for the calculations of thermal conductivity [8], because no experimental result is available. It is requested to determine the heat capacities of transuranium mononitrides and their solid solutions because of the insufficient information.

3.3. Thermal conductivity

Before the comparison of the data of thermal conductivity, porosity correction should be necessary to estimate the thermal conductivity with 100% of the theoretical density (K_{TD}) from measured values (K_P). For the correction, the following Maxwell–Eucken equation is used:

$$K_P/K_{TD} = (1-P)/(1+\beta P) \quad (\beta = 1,2,3),$$

where P is porosity and the constant β is related to the characteristics of pores in the matrix. For β, unity is popular and used in our case where samples were fabricated by a conventional powder–metallurgical route as mentioned above. However, it is noted that β might be about 3 when samples have large and closed pores, as pointed out by Arai et al. [8].

The temperature dependence of the thermal conductivities of actinide mononitrides is shown in Fig. 4, where the data on UN assessed by Hayes et al. [4] and experimental data by Arai et al. [8] are plotted. These data agree well with each other below 1300 K, but there seems

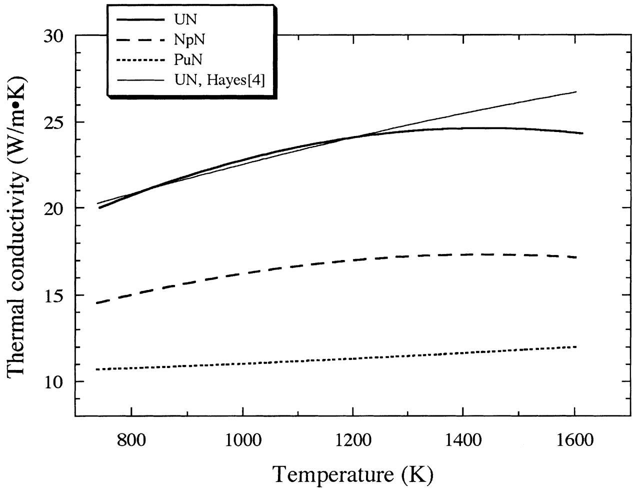

Fig. 4. Thermal conductivity of actinide mononitrides

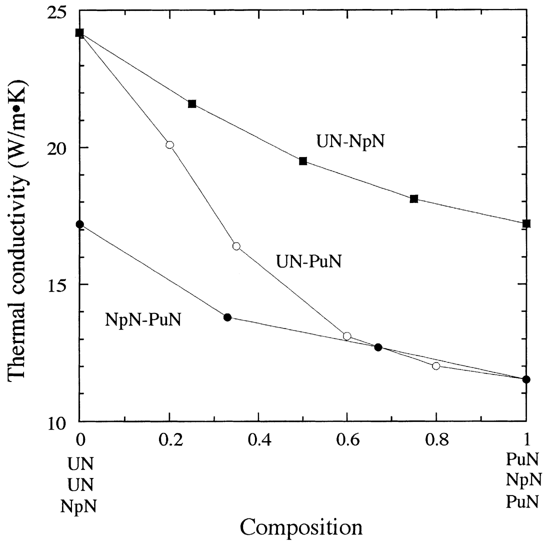

Fig. 5. Thermal conductivity of solid solutions of actinide mononitrides at 1273 K

some discrepancy between the two data sets at high temperatures. It should be noted that the data points at the temperature range are scare and scattered. The thermal conductivity of PuN, which is much lower than that of UN, was reported by Arai et al. [8], Alexander et al. [23], and Keller [25]. These literature data are consistent with each other. The thermal conductivity of NpN was obtained from the diffusivity and found to have intermediate values between those of UN and PuN. The temperature dependence is also similar to them [13]. As a result, the data set reported by Arai et al. are considered to be a reference for the thermal conductivities of actinide mononitrides at present. However it should be noted that the literature values for actinide mononitrides contains some uncertainty caused from the inaccuracy of the data on the heat capacity.

Comparing the data, it is clear that the thermal conductivity of actinide mononitrides decreases with the atomic number of actinide elements. Although the phonon and electronic contribution could be considered for the thermal conductivity of actinides mononitrides, the electronic contribution might be predominant at higher temperatures. The electrical resistivity of actinide mononitrides increases with the atomic number, so the tendency of the decrease of the thermal conductivity with the atomic number would correspond to the lowering of electronic contribution [11].

The thermal conductivities of the solid solutions of the actinide mononitrides were reported by Arai et al. [8], Gangury et al. [17], Alexander et al. [24] and Keller [25] for the UN–PuN system and by Arai et al. for the NpN–PuN and UN–NpN systems [10,11]. The data presented by the authors are plotted in Fig. 5. The data by Arai et al. for the UN–PuN system agree with the data by the other investigations. The thermal conductivity of UN–PuN solid solutions shows intermediate values between those of UN and PuN and the temperature dependence is similar to those of the respective mononitride, but it decreases rapidly with the addition of PuN. It means that a simple average method might not be proper for the evaluation of the thermal conductivity of the solid solutions of actinide mononitrides. In the case of UN–NpN and NpN–PuN solid solutions, the behavior was found to be similar to that of (U,Pu)N [11].

3.4. Vaporization behavior

The major vapor species observed over UN are nitrogen gas, N_2(g), and mono-atomic uranium gas, U(g). UN(g) is also detected in addition to U(g) and N_2(g) [17], but the pressure is three order lower than that of U(g) so that the contribution of UN(g) can be ignored in practice. Some data on the pressures of N_2(g) and U(g) over UN are shown in Fig. 6. Hayes et al. [4] recommended equations

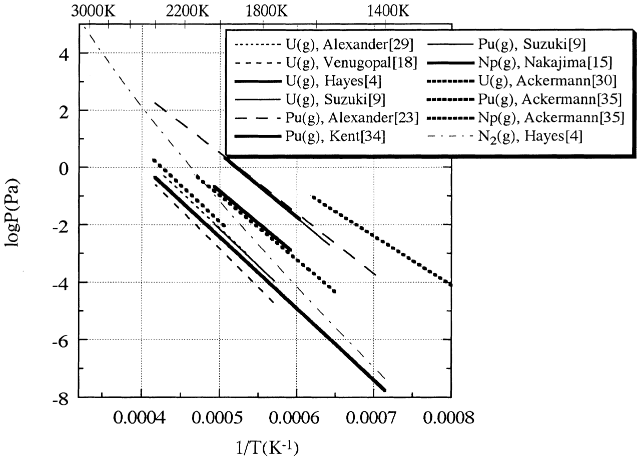

Fig. 6. Partial pressures of nitrogen and actinide mono-atomic gases over actinide mononitrides

for the pressures of N_2(g) and U(g) by fitting eight experimental investigations. According to their paper, the reported data on N_2(g) agree with each other, but those of U(g) over UN is a little scattered. The U(g) pressure obtained by us [7] is a little larger than the equation given by Hayes et al., but in agreement with those by Alexander et al. [29]. It is considered that UN may form a liquid phase under a low N_2 pressure; i.e., UN(s) = U(1) + $1/2N_2$(g) and U(1) = U(g). The vapor pressure U(g) over UN is close to or a little lower than that over metal [30]. It is suggested that the dissolution of nitrogen and/or impurity metal from crucibles into the liquid phase could affect the partial pressure. After Hayes et al., Venugopal et al. [17] reported U(g) over UN at high temperatures, but their data are significantly lower than the other data. They applied a Knudsen cell made of tantalum instead of tungsten. There is some possibility that dissolved tantalum may reduce the activity of uranium. Some scattering of the previously reported data on U(g) over UN may be also caused from the reaction of the liquid phase in UN with crucible materials. From this point, it is suggested that the partial pressure of U(g) over UN should be a little higher than the recommendation by Hayes et al.

The vapor species over PuN are Pu(g) and N_2(g). The N_2 pressure over PuN was reported by Alexander et al. [23], Olson et al. [31], Pardue et al. [32] and Campbell et al. [33]. These data seem to agree with each other and are not so different from N_2(g) over UN. The vapor pressure Pu(g) over PuN was determined by Alexander et al. [23], Kent et al. [34] and the authors [9]. Some of the data are plotted in Fig. 6. The Pu(g) pressure is larger than that of N_2(g), but still much smaller than that of Pu(g) over Pu metal [35]. According to Alexander et al. [23], the ratio of Pu(g)/N_2(g) is 5.8 in the investigated temperature range of 1400 to 2400 K and PuN may evaporate congruently; i.e., PuN(s) = Pu(g) + $1/2N_2$(g). However, recently our data indicate that Pu(g) over PuN at temperatures lower than 1600 K is higher than the values extrapolated from the high temperature data and approaches that over Pu metal with the decrease of temperature. There is some possibility that a microscopic liquid phase might form at the surface of the sample during cooling stages of mass spectrometric measurements because PuN has a nonstoichiometric composition range at elevated temperatures, while it is a line compound at low temperatures. By reheating, Pu(g) approaches the high temperature data again. This might be caused from the rapid evaporation of Pu. However, the increase of Pu(g) at low temperatures denies the congruent evaporation of PuN at the temperature range when the stoichiometric composition is kept.

The information on the evaporation behavior of NpN is very scare. The N_2 pressure over NpN was determined only by Olson et al. at high temperatures [36]. They reported that NpN evaporates congruently at the melting temperature under 10 atm N_2 pressure. The partial pressure of Np(g) over NpN was determined by Nakajima et al. [15]. The pressure of Np(g) over NpN is shown in Fig. 6. The N_2 pressure is close to that over UN and the Np(g) pressure is between those of U(g) over UN and Pu(g) over PuN. The pressure of Np(g) was found to be almost consistent with that over Np metal [35]. These results suggest that NpN may form a liquid phase as UN. From the present experimental data on Np(g) over NpN and the literature data on N_2 partial pressure [36] and the free energy of formation of Np(g) [35], the free energy of formation of NpN has been derived as follows;

$$\Delta Gf(\mathrm{J/mol}) = 427\,000 - 98.99T \ (1700 - 2100\ \mathrm{K}).$$

The data are just located between the free energies of formation of UN and PuN [37,38].

The vapor pressures of actinide metal gases over the solid solutions of the UN–PuN system were determined by Suzuki et al. [9] and Alexander et al. [24]. The partial pressures of U(g) and Pu(g) depend on the compositions; namely, U(g) decreases and Pu(g) increases with the concentration of Pu. According to Alexander et al. [24], the PuN component in $(U_{0.8}Pu_{0.2})N$ evaporates congruently at least below 2000 K. The estimation of the activity reveals that the activity coefficients of UN and PuN considerably differ from unity especially in the Pu-rich composition [9]. As understood from the deviation of the lattice parameters of UN–PuN solid solutions from the Vegard's law, it is also suggested that the system cannot be treated as an ideal solution.

The vaporization behavior of NpN–PuN solid solutions seems to be relatively complicated [14]. The partial pressures of Np(g) slightly depend on the PuN concentration and the temperature dependence is close to that of Np(g) over NpN. On the other hand, the pressures of Pu(g) decrease remarkably with the decrease of PuN concentration and have a similar temperature dependence as PuN at high temperatures. It is noted, however, that at low temperatures the partial pressure of Pu(g) increases and becomes close to that of Pu(g) over Pu metal with decreasing temperature. This result suggests that the PuN component in the solid solutions evaporates congruently at high temperature, while evaporation behavior may change at lower temperatures [14]. In other words, the Pu content in the liquid at high temperatures is supposed to be relatively low because of high evaporation of Pu and the partial pressure of Np(g) becomes close to that over Np metal despite the composition. At lower temperatures, the composition of the liquid phase may be affected by the change of the single phase region of mononitride with temperature and the Pu content in the liquid phase may increase although there is no information on the composition. It should be necessary to determine the Np–Pu binary system to confirm the behavior. The vaporization behavior of UN–NpN is under investigation.

The vapor pressure of Am(g) from AmN was estimated from the mass spectrometric measurements of PuN samples containing Am–241 as a daughter isotope [16]. The enthalpy of formation of AmN has been estimated to be −294 kJ/mol at 1600 K, which is close to those of UN and PuN [35]; −296 and −299 kJ/mol, respectively.

4. Conclusion

The thermophysical and thermodynamic properties of actinide mononitrides and their solid solutions, which are candidate materials for advanced fuels for burning/breeding transuranium elements, are summarized focusing on the recent investigations. Actinide mononitrides form the solid solutions in the whole composition range, but the lattice parameters deviate largely from the Vegard's law, which suggests that the system cannot be treated as an ideal solution. The formation of the solid solution with a variety of composition is an advantage of nitride fuel compared with oxide fuel. It is confirmed that the thermal conductivity of actinide mononitrides is much higher than that of actinide oxides. The thermal conductivities of actinide mononitrides increase gradually with temperature and decrease with the atomic number of actinide elements. The solid solutions show intermediate behavior of the respective mononitride. From Knudsen mass spectrometric measurements, it is shown that NpN form a liquid phase as UN does, while PuN evaporates congruently. The evaporation behavior of the solid solutions is also described. It is also pointed out that the data on heat capacity and thermal expansion of transuranium mononitrides are not enough and additional information should be necessary.

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