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Thermal conductivity of actinide mononitride solid solutions

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Abstract

The thermal conductivities of actinide mononitride solid solutions, (U,Np)N and (Np,Pu)N, were determined from thermal diffusivities measured using the laser flash method from 740 to 1630 K. It was found that the thermal conductivities of the solid solutions have a similar temperature dependence to that of the respective mononitride and decreased from the UN-side to the PuN-side in order, especially in the UN-rich region for (U,Np)N and the NpN-rich region for (Np,Pu)N over the temperature range investigated. © 1998 Elsevier Science S.A.

Keywords: Neptunium nitride; Nitride fuel; Plutonium nitride; Thermal conductivity; Thermal diffusivity; Uranium nitride

1. Introduction

The solid solution of actinide mononitride is considered to be an advanced fuel for fast reactors [1] and actinide burning reactors [2]. One of the characteristics of nitride fuel is that it has both high thermal conductivity and high melting temperature, which leads to the design of reactor cores with wide safety margins. Being analogous to other NaCl-type AnX (An, actinide; X, metalloid) compounds, the heat conduction of nitride fuel is dominated by electron transfer at the reactor-operating temperature. Several results have so far been reported for the thermal conductivity of uranium mononitride, UN [3,4], plutonium mononitride, PuN [5,6], and their solid solution, (U,Pu)N [7,8]. Further, the thermal conductivity of neptunium mononitride, NpN, has recently been measured by the present authors [9]. In this study, solid solutions of (U,Np)N and (Np,Pu)N were prepared and their thermal conductivity was examined from 740 to 1630 K.

2. Experimental

2.1. Samples

Solid solutions of (U,Np)N and (Np,Pu)N were prepared by heating a green pellet of mixtures of UN, NpN and PuN in a nitrogen–hydrogen mixed gas stream at 2023 K for up to 180 ks. Carbothermic reduction of the dioxide in nitrogen and nitrogen–hydrogen mixed gas streams was adopted for synthesizing the respective mononitride. Details of the carbothermic reduction and characteristics of the starting materials have been described in earlier papers [10,11]. The Np/(U+Np) mixing atomic ratio was chosen as 0.25, 0.50 and 0.75 for (U,Np)N, and Pu/(Np+Pu) as 0.33 and 0.67 for (Np,Pu)N solid solutions for the investigation of thermal conductivity.

The formation of a solid solution with a single phase was confirmed from X-ray diffraction patterns. No other phase other than a NaCl-type structure was identified and the separation of the diffraction line into Kα1 and Kα2 was satisfactory at high angles. Nitrogen, oxygen and carbon contents were determined by chemical analyses. Characteristics of the (U,Np)N and (Np,Pu)N solid solutions used in the measurement are summarized in Table 1. It can be seen that the samples have an almost stoichiometric mononitride composition and the oxygen and carbon impurity levels could be maintained at $<$500 ppm. Preparation of the above samples was carried out in gloveboxes with purified argon gas.

2.2. Measurement of thermal diffusivity

Solid solution pellets were sliced into discs of about 8 mm diameter and 1.4 mm thickness using a diamond wheel cutter for thermal diffusivity measurements. Thermal diffusivities were measured from 740 to 1630 K in vacuum by the laser flash method. The apparatus and measurement method were described in detail in an earlier paper [12]. To avoid any influence of self-radiation

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Table 1
Characteristics of (U,Np)N and (Np,Pu)N solid solutions used for the thermal diffusivity measurements

Composition:	$(U_{0.75}Np_{0.25})N$	$(U_{0.50}Np_{0.50})N$	$(U_{0.25}Np_{0.75})N$	$(Np_{0.67}Pu_{0.33})N$	$(Np_{0.33}Pu_{0.67})N$
Nitrogen content (wt.%)	5.62	5.74	5.62	5.64	5.60
Oxygen content (wt.%)	0.03	0.01	0.02	0.04	0.03
Carbon content (wt.%)	0.03	0.02	0.01	0.02	0.03
Phase	fcc	fcc	fcc	fcc	fcc
Lattice parameter (nm)	0.48901	0.48914	0.48943	0.49002	0.49033

damage on the thermal diffusivity, the sample was preheated at 1473 K on the preceding day of the measurement. Thermal diffusivities were measured in both heating and cooling processes and the sample was weighed before and after measurement to examine the actinide loss.

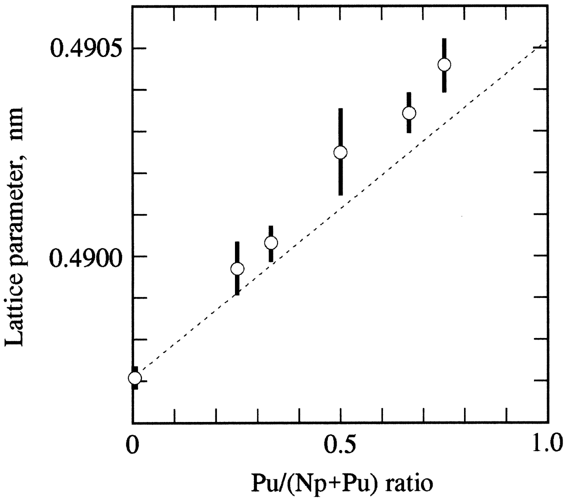

Fig. 2. Lattice parameters of (Np,Pu)N solid solutions.

3. Results and discussion

3.1. Lattice parameter

The lattice parameters of the solid solutions listed in Table 1 and that of NpN [9] are shown in Figs. 1 and 2 for (U,Np)N and (Np,Pu)N, respectively; results for the samples prepared for investigating vaporization behavior [13] are also included in Fig. 2. The lattice parameters of (U,Pu)N solid solutions reported by the authors [14] and by Tennery et al. [15] are also shown in Fig. 3 for comparison. The lattice parameter of the present NpN and that of PuN in Fig. 3 agree well with literature values [16,17]. On the other hand, the authors' data for UN in Fig. 3 exhibits a slightly higher lattice parameter than the literature value [18]. This UN contained as much as 2300 ppm of carbon and the larger lattice parameter could be caused by dissolution of carbon in the mononitride lattice [8]. It is seen from Fig. 1 that the composition dependence of the lattice parameter of (U,Np)N deviates negatively from Vegard's law, while Fig. 2 shows that of (Np,Pu)N, in contrast, deviates positively. The lattice parameters of the authors' (U,Pu)N in Fig. 3 showed a positive deviation from Vegard's law in the PuN-rich region, while Tennery et al. reported a composition dependence similar to an S-shape. It should be noted that the authors' (U,Pu)N samples in Fig. 3 are considered to contain a larger amount of carbon than (U,Np)N and (Np,Pu)N [8]. Therefore, if a correction for the dissolution of carbon is made to the lattice parameter of the authors'

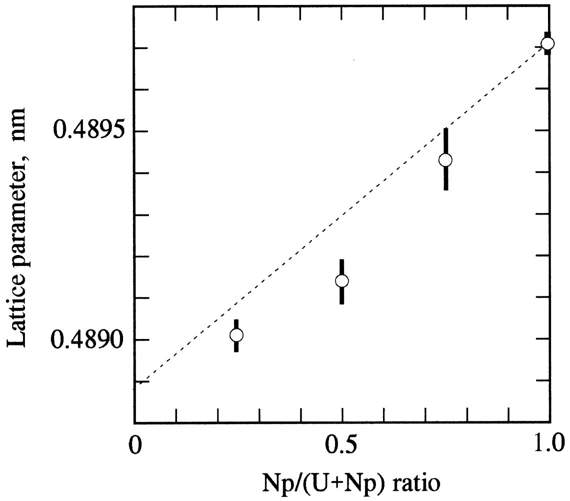

Fig. 1. Lattice parameters of (U,Np)N solid solutions.

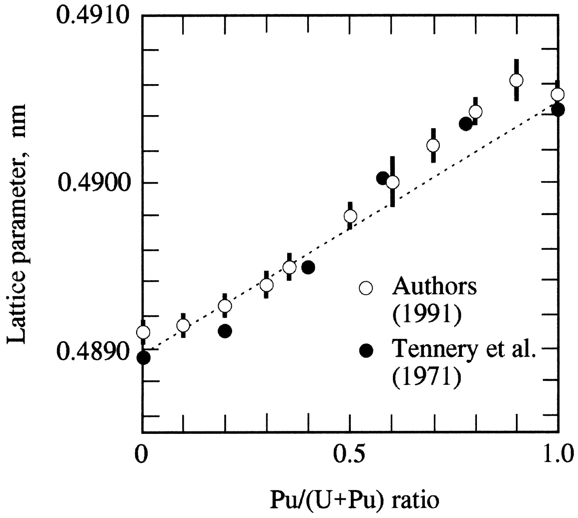

Fig. 3. Lattice parameters of (U,Pu)N solid solutions.

(U,Pu)N, the composition dependence is similar to that of Tennery et al., who used a sample prepared by the metal-hydride–nitride route. In other words, the lattice parameters of (U,Np)N and (Np,Pu)N reflect the left-half and right-half of (U,Pu)N, respectively. The present results suggest that the thermodynamic properties of actinide mononitride solid solutions cannot necessarily be treated using an ideal solution model.

3.2. Thermal conductivity

The thermal conductivity of the solid solutions was calculated using the product of the thermal diffusivity, specific heat capacity and bulk density of the sample. The specific heat capacities of the solid solutions were not available, therefore they were estimated from those of the respective mononitride by assuming Kopp's law as a first approximation. The specific heat capacities of UN and PuN were obtained from the literature [19], while that of NpN was derived by the authors [9] following Kubaschewski's text [20].

The thermal conductivities obtained for (U,Np)N and (Np,Pu)N solid solutions in addition to those for the respective mononitrides are shown in Fig. 4 as a function of temperature, where the values are corrected for porosity to the theoretical density by the Maxwell–Eucken equation. The results for the heating and cooling processes agree with each other and the weight change before and after measurement could be neglected in all cases. The figure shows that the thermal conductivities of mononitrides, including their solid solutions, have a similar temperature dependence, which gradually increases with temperature over the temperature range investigated.

The thermal conductivities were approximated by the quadratic equation and their composition dependence at 773 and 1273 K was obtained, as shown in Fig. 5, where the values for (U,Pu)N solid solutions [8] re-evaluated using the specific heat capacities recommended by Matzke [19] are also included. It can be seen from the figures that the thermal conductivities of the solid solutions decrease from the UN-side to the PuN-side in order at both temperatures, especially in the UN-rich region for (U,Np)N, the NpN-rich region for (Np,Pu)N and the UN-rich region for (U,Pu)N solid solutions.

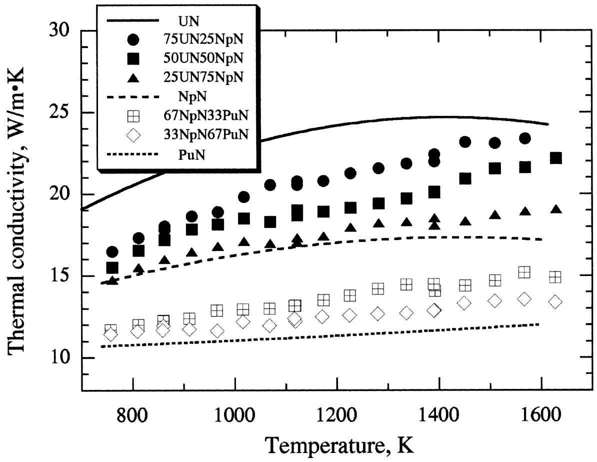

Fig. 4. Thermal conductivity of (U,Np)N and (U,Pu)N solid solutions.

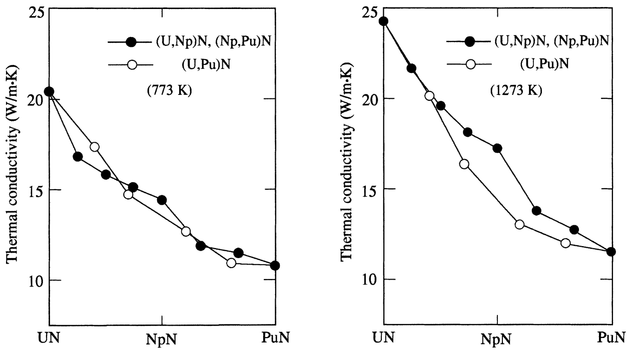

Fig. 5. Composition dependence of the thermal conductivity of actinide mononitride solid solutions at 773 K (left) and 1273 K (right).

These results indicate that the high thermal conductivity of nitride fuel is retained in the present solid solutions, although the decreasing rate of thermal conductivity for UN to PuN is larger than that for UO_2 to PuO_2. The decrease in thermal conductivity from the UN-side to the PuN-side is possibly caused by the decrease of the electronic contribution to the total thermal conductivity since the electrical resistivity of AnN has a tendency to increase with the atomic number of An in the temperature range studied. Indeed, at 773 K the difference in the total thermal conductivity between UN and PuN, ΔK_{tot}(UN−PuN), and that of the electronic contribution, ΔK_{ele}(UN−PuN), have a similar value of 9–10 $\mathrm{W\,m^{-1}\,K^{-1}}$ when the Lorenz number ($L_0=2.45\times10^{-8}\ \mathrm{V^2\,K^{-2}}$) was assumed in calculating the electronic thermal conductivity using the electrical resistivity of UN and PuN from the literature [21,22]. Also at 1273 K, where data for the electrical resistivity of NpN and PuN are missing, the same reasoning can be applied since the calculated electronic contribution predominates over 80–90% in the case of UN.

The mononitrides of U, Np and Pu have similar lattice parameters (Δa(PuN−UN)=1.6 pm) and the results of a magnetic study suggest the same valence state for An in AnN, possibly +3, as in the same manner for AmN and CmN [23]. This bonding character would lead to the formation of a mononitride solid solution with a wide variety of composition. On the other hand, the present mononitrides have the smallest An–An distance in NaCl-type AnX compounds. This leads to strong 5f–5f interactions and the delocalization of 5f electrons at the An site. Accordingly, some 5f electrons will participate in bonding, being strongly hybridized with 6d electrons. Such a complicated electronic state may explain the present results for the lattice parameter and thermal conductivity.

4. Conclusion

Solid solutions of actinide mononitride, (U,Np)N and (Np,Pu)N with a single phase of rock-salt structure were prepared. However, their lattice parameters had a tendency to deviate from Vegard's law, negatively in the UN–NpN region and positively in the NpN–PuN region. The thermal conductivities of the solid solutions derived from thermal diffusivities showed a similar temperature dependence to those of the respective mononitrides. The thermal conductivities decreased from the UN-side to the PuN-side in order, especially in the UN-rich region for (U,Np)N and the NpN-rich region for (Np,Pu)N solid solutions. The decrease is considered mainly to be caused by the decrease of the electronic contribution to the total thermal conductivity.

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