

PROPERTIES OF NEPTUNIUM-PLUTONIUM MIXED NITRIDE SOLID SOLUTIONS

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Properties of neptunium-plutonium mixed nitride solid solutions were investigated. The solid solutions covering the whole range of composition were prepared by heating the mixtures of NpN and PuN in nitrogen-hydrogen mixed gas stream at 2023 K. Formation of high-purity solid solution with a single phase was confirmed by X-ray diffraction and chemical analyses and composition dependence of the lattice parameters was examined. Vaporization behavior over the solid solutions was investigated by Knudsen-mass spectrometry and temperature dependence of the partial pressures of Np(g) and Pu(g) was examined. Furthermore, the thermal conductivities were determined from the thermal diffusivities measured and specific heat capacities estimated. The thermal conductivities of the solid solutions lay between those of NpN and PuN.

1. Introduction

Feasibility studies for transmuting minor actinides in fast reactors have been conducted in many countries from the viewpoint of a better management of the high level nuclear waste [1,2]. One of the incentives to using nitride fuel for transmutation is the probable formation of solid solution among actinide mononitrides with an extensive composition besides the superior thermal and neutronic properties. At present, however, the information on the mononitride solid solutions has been quite scarce except that of uranium-plutonium mixed nitride which has been developed as an advanced fuel for fast reactors. So it is significant to prepare the mononitride solid solutions containing minor actinides and determine their properties for the application of nitride fuel to transmutation. This report concerns the preparation and a few properties of neptunium-plutonium mixed nitride solid solutions including their lattice parameters, vaporization behavior and thermal conductivities estimated from thermal diffusivities.

2. Sample preparation

Neptunium-plutonium mixed nitride solid solutions (Np,Pu)N were prepared by heating the mixtures of NpN and PuN synthesized by carbothermic reduction from their oxides. Powders of NpO₂, PuO₂ and graphite were obtained from Harwell Laboratory, British Nuclear Fuels Ltd. and Graphitwerk Kropfmühl GmbH, respectively, and their characteristics were described in earlier papers [3,4]. The mixing molar ratios of graphite to the dioxides, C/NpO₂ and C/PuO₂, for carbothermic reduction were chosen at 2.2. The reduction was carried out at 1823 K in N₂ gas stream for 43 ks, followed by decarburization at 1723 K in N₂-8%H₂ mixed gas stream for 86 ks. The products, NpN and PuN, were mixed at the molar ratios PuN/(NpN+PuN) of 0, 0.25, 0.50, 0.75 and 1.0 for the measurement of lattice parameter and vapor pressures and at 0.33 and 0.67 for the thermal diffusivity measurement. The mixed powders were pressed into green pellets under a pressure of ~300 MPa and heated again for the formation of solid solution at 2023 K in N₂-8%H₂ mixed gas stream for 90-180 ks. Then the pellets were subjected to X-ray diffraction and chemical analyses for characterizing the products.

The typical results of characterization were summarized in Table 1. According to the X-ray diffraction pattern, the formation of solid solution (Np,Pu)N with a single phase of *fcc* was confirmed for all the composition investigated. Namely, no other phases than NaCl-type mononitride were identified and the separation of the diffraction lines into K α 1 and K α 2 at high angles was fairly good. The results of chemical analysis indicated that both the oxygen and carbon contents in the samples, which are considered as principal impurities in nitride fuel prepared by carbothermic reduction, were lower than 0.05 wt.%. On the other hand, the nitrogen contents almost corresponded to the stoichiometric composition. The manner of the characterization mentioned above was described in detail elsewhere [5]. Although the chemical analyses of neptunium and plutonium were not conducted in this study, it was considered that the nominal composition kept unchanged since no significant loss of actinides by vaporization was observed during the sample preparation stage. In this study, the preparation of samples was carried out in the gloveboxes with high-purity argon gas atmosphere.

3. Results and discussion

3.1 Lattice parameter

Five X-ray diffraction lines of (600/442), (531), (440), (511/333) and (422) were used to calculate the lattice parameter of (Np,Pu)N solid solutions. The composition dependence of the lattice parameter was shown in Fig. 1. Lattice parameters of NpN and PuN were 0.48971 ± 0.00003 and 0.49501 ± 0.00002 nm, respectively, which agreed well with the reported values [6,7]. The lattice parameter increased with PuN content in the solid solution as was anticipated. However, the change in the lattice parameter deviated positively from the Vegard's law between NpN and PuN as shown in the figure.

It is well known that the dissolution of carbon and oxygen in actinide mononitride lattice results in the increase of the lattice parameter [8,9]. However, the present carbon and oxygen contents, lower than

500 ppm, were considered to be too low to influence the lattice parameter significantly. It was also considered from the experimental results that the incompleteness of the formation of solid solution or the heterogeneity of the sample could not affect the lattice parameter measured. On the other hand, the self irradiation damage had been almost recovered since the X-ray diffraction analysis was conducted on the next day of the heat treatment at 2023 K. From the speculation mentioned above, we now consider that the deviation of the lattice parameter from the Vegard's law has some relation with the bonding characteristics of (Np,Pu)N solid solutions.

Furthermore, we have observed the similar results for (U,Pu)N solid solutions, where the lattice parameter deviated positively from the Vegard's law especially in PuN rich region as shown in Fig. 2 [7,10]. The present lattice parameter of NpN just corresponded to halfway between those of UN and PuN. As the atomic number of the elements in the compound increases, the total number of electrons increases with the change of composition. In actinide mononitrides including their solid solutions, part of the electrons outside Rn shell are thought to be localized to the atom, and part of them itinerant and participating in bonding. Since the change in the lattice parameter reflects the nature of electron population in the solid solutions, we consider that the present and previous results may be related with occupancy states in the unfilled 5f-6d hybridized band near the Fermi level.

3.2 Vaporization behavior

Vaporization behavior of (Np,Pu)N solid solutions was investigated by use of Knudsen-effusion mass spectrometry with a tungsten cell having an orifice of 1 mm in diameter. Three kind of solid solutions, (Np_{0.75}Pu_{0.25})N, (Np_{0.5}Pu_{0.5})N and (Np_{0.25}Pu_{0.75})N, were subjected to the measurements. The apparatus used was described in detail elsewhere [11] and an ionization potential was chosen at 10 eV throughout this study. The actinide bearing species observed in gaseous phase were Np(g), NpO(g), Pu(g) and PuO(g). Among them the pressures of NpO(g) and PuO(g) were much smaller than those of Np(g) and Pu(g) except in the initial heating stage. The absolute pressure was calculated from the ion intensity by use of a modified integral method.

Temperature dependence of the pressures of Np(g) and Pu(g) over the solid solutions was shown in Fig. 3. The pressures of Np(g) over the solid solutions showed the similar temperature dependence with that over Np(l) as in the case of NpN [12], which strongly suggested the precipitation of liquid neptunium during the measurements. On the other hand, temperature dependence of Pu(g) over the solid solutions was rather complicated. At temperatures higher than 1773 K, the slope of the logarithmic pressures of Pu(g) versus the reciprocal temperature was similar with the pressure over PuN [13] and there found a composition dependence of the solid solutions. At temperatures lower than 1473 K, however, the temperature dependence approached that over Pu(l) and the composition dependence became indefinite. At intermediate temperatures between 1443 and 1773 K, the transition stage was observed as shown in the figure. It was considered that the pressures of Pu(g) observed at high temperatures reflected the vapor pressure of Pu(g) over (Np,Pu)N being influenced by the Pu/(Np+Pu) ratio in solid phase, while the pressures of Pu(g) observed at lower temperatures the pressure over Pu(l) precipitated during the measurement.

It is well known that UN(s) vaporizes incongruently precipitating liquid uranium on account of the lower pressure of U(g), while PuN(s) vaporizes congruently into Pu(g)+0.5N₂(g) [14,15]. Recent study on the vaporization behavior of NpN(s) revealed that the precipitation of liquid neptunium occurred during the measurement [12]. Although further study is needed hereafter, the vaporization behavior of (Np,Pu)N solid solutions seems to have both characteristics of those of NpN and PuN. Qualitative and quantitative thermodynamic analyses are under way in this respect.

3.3 Thermal conductivity

Thermal diffusivities of two kind of solid solutions, (Np_{0.67}Pu_{0.33})N and (Np_{0.33}Pu_{0.67})N, were measured from 750 to 1630 K by laser flash method. The apparatus used was described in detail elsewhere [16]. The samples for the measurement, discs of ~8mm in diameter and ~1.4mm thickness, were obtained by slicing the sintered solid solution pellets by a diamond wheel cutter. The results of the thermal diffusivity measurements are shown in Fig. 4. It was seen that the thermal diffusivities gradually increased with temperature and decreased with PuN content in the solid solution over the temperature range investigated, although the exact comparison was difficult on account of

the difference of density between the two samples. The origin of the difference in sintered density is not clear for the moment.

Thermal conductivity could be calculated by the product of thermal diffusivity, specific heat capacity and bulk density of the sample. The specific heat capacities of the (Np,Pu)N solid solutions were unknown unfortunately, and they were evaluated by the Kopp's law as a first approximation. The specific heat capacity of PuN was quoted from the report of Spear and Leitnaker [17] and the value for NpN was estimated from an empirical equation by the authors [18]. The thermal conductivities of two kind of the solid solutions obtained are shown in Fig. 5, in which they are corrected for porosity to the theoretical density by Maxwell-Eucken equation and the results for NpN [18] and PuN [19] are included for comparison.

It was seen from the figure that the thermal conductivities of the present solid solutions lay between those of NpN and PuN and showed almost the similar temperature dependence with them. The thermal conductivities also decreased with PuN content in the solid solutions, especially in NpN rich region. However, we must bear in mind that the results mentioned above have several uncertainties derived from the estimation of specific heat capacity and the correction for porosity besides the experimental error itself. The measurement of the specific heat capacity is planned in near future by use of differential scanning calorimeter.

4. Summary

The solid solutions of neptunium-plutonium mixed nitride (Np,Pu)N were prepared and some properties were examined in this study. The results are summarized as follows.

- (1) Formation of the (Np,Pu)N solid solutions with a single phase of *fcc* was confirmed over the whole range of composition.
- (2) Change in the lattice parameter of the solid solutions deviated positively from the Vegard's law as was reported in the case of (U,Pu)N solid solutions.
- (3) Vapor pressures of Np(g) over the solid solutions suggested the precipitation of liquid neptunium during the measurements, while that of Pu(g) showed a rather complicated temperature dependence.
- (4) Thermal conductivities of the solid solution, which were determined from thermal diffusivities measured and specific heat capacities estimated, lay between those of NpN and PuN and decreased with PuN over the temperature range investigated.

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Table 1 Typical characteristics of the samples after the heat treatment in N₂-8%H₂ mixed gas stream

Composition	NpN	75NpN-25PuN	67NpN-33PuN	50NpN-50PuN	33NpN-67PuN	25NpN-75PuN	PuN
Heat-treatment period (ks)	43	43	86	43	86	43	43
Phases	fcc	fcc	fcc	fcc	fcc	fcc	fcc
N content (wt.%)	5.65	n.d.	5.64	n.d.	5.60	n.d.	5.57
O content (wt.%)	0.03	n.d.	0.04	n.d.	0.04	n.d.	0.04
C content (wt.%)	0.05	n.d.	0.02	n.d.	0.03	n.d.	0.03

n.d. = Not determined

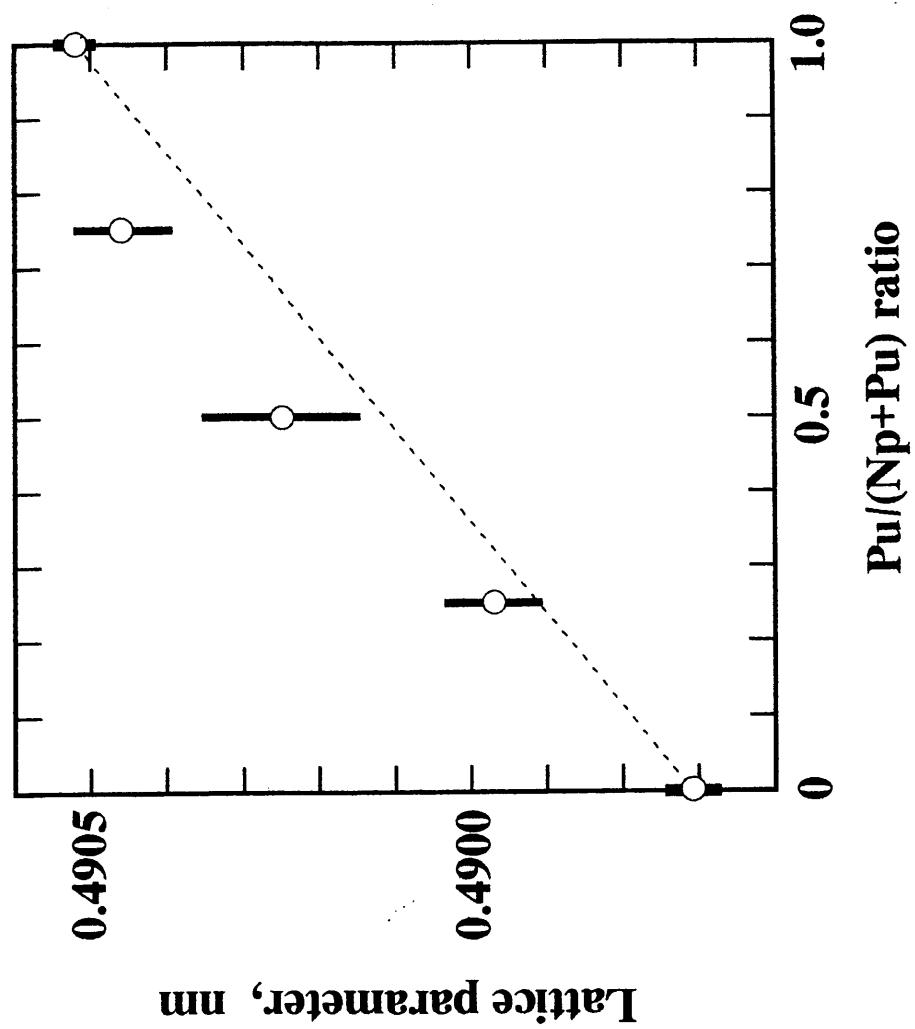


Fig. 1 Lattice parameter of (Np,Pu)N solid solutions

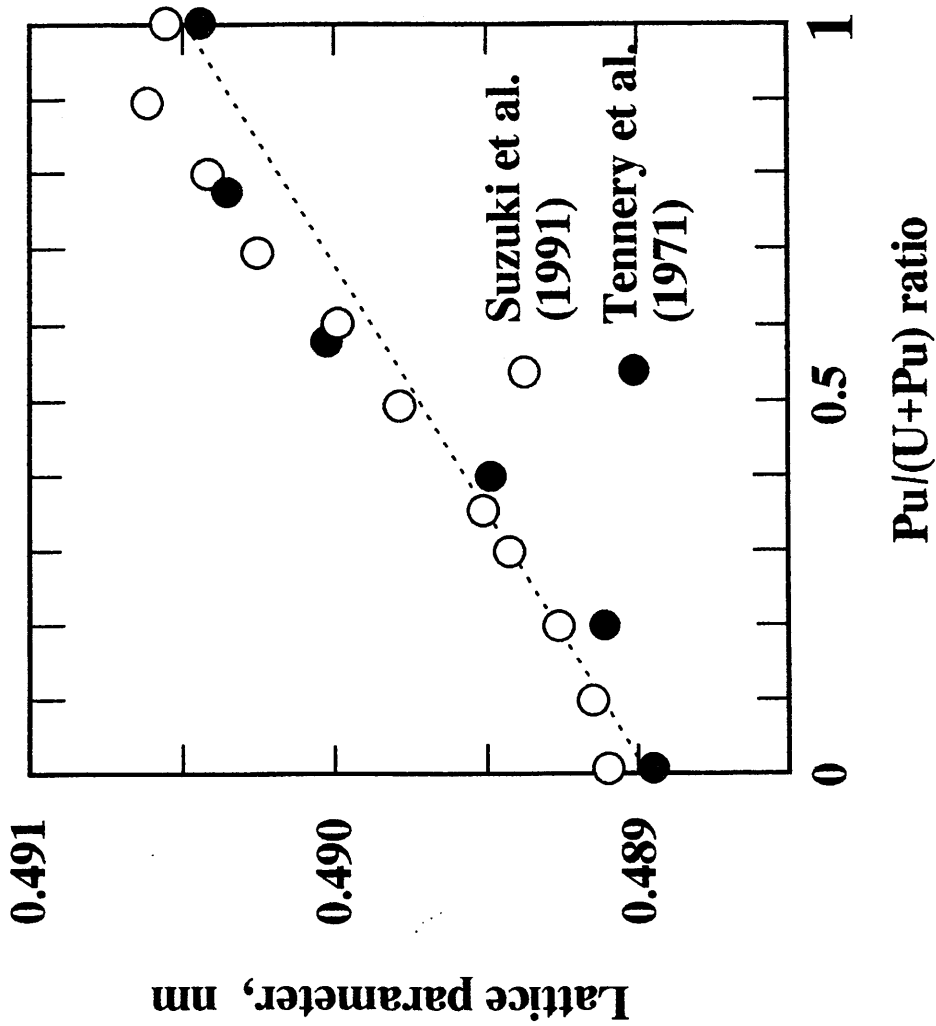


Fig. 2 Lattice parameter of (U,Pu)N solid solutions

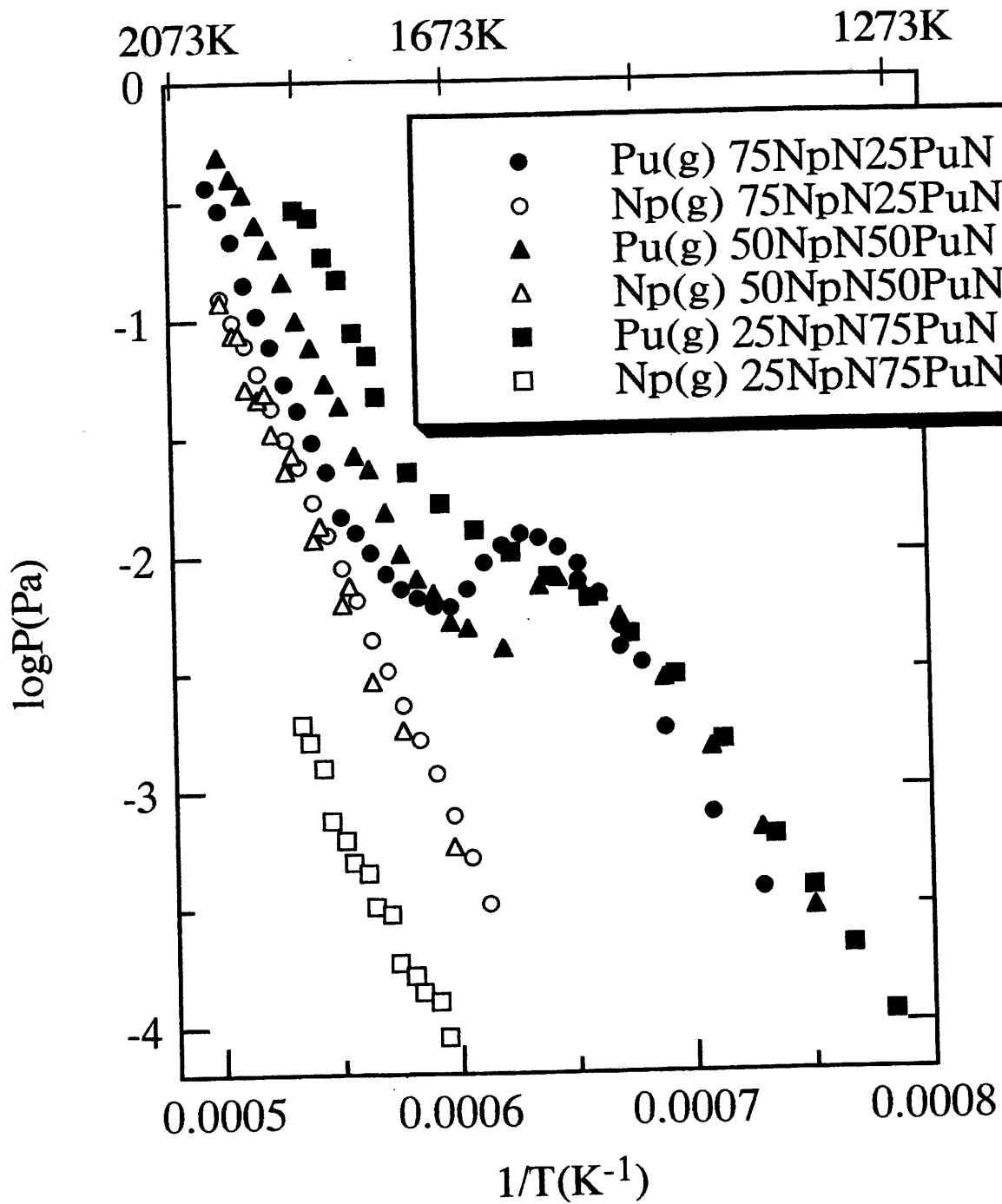


Fig. 3 Vaporization behavior of (Np,Pu)N

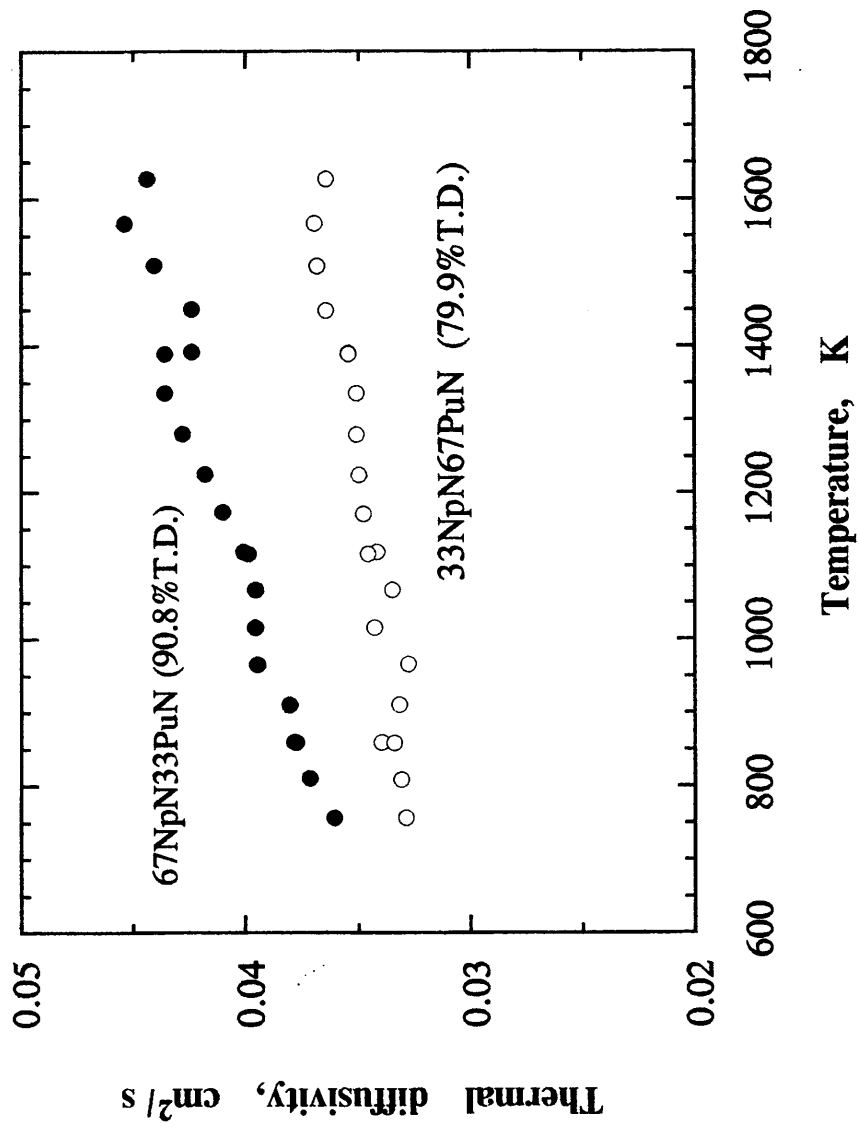


Fig. 4 Thermal diffusivity of (Np,Pu)N solid solutions

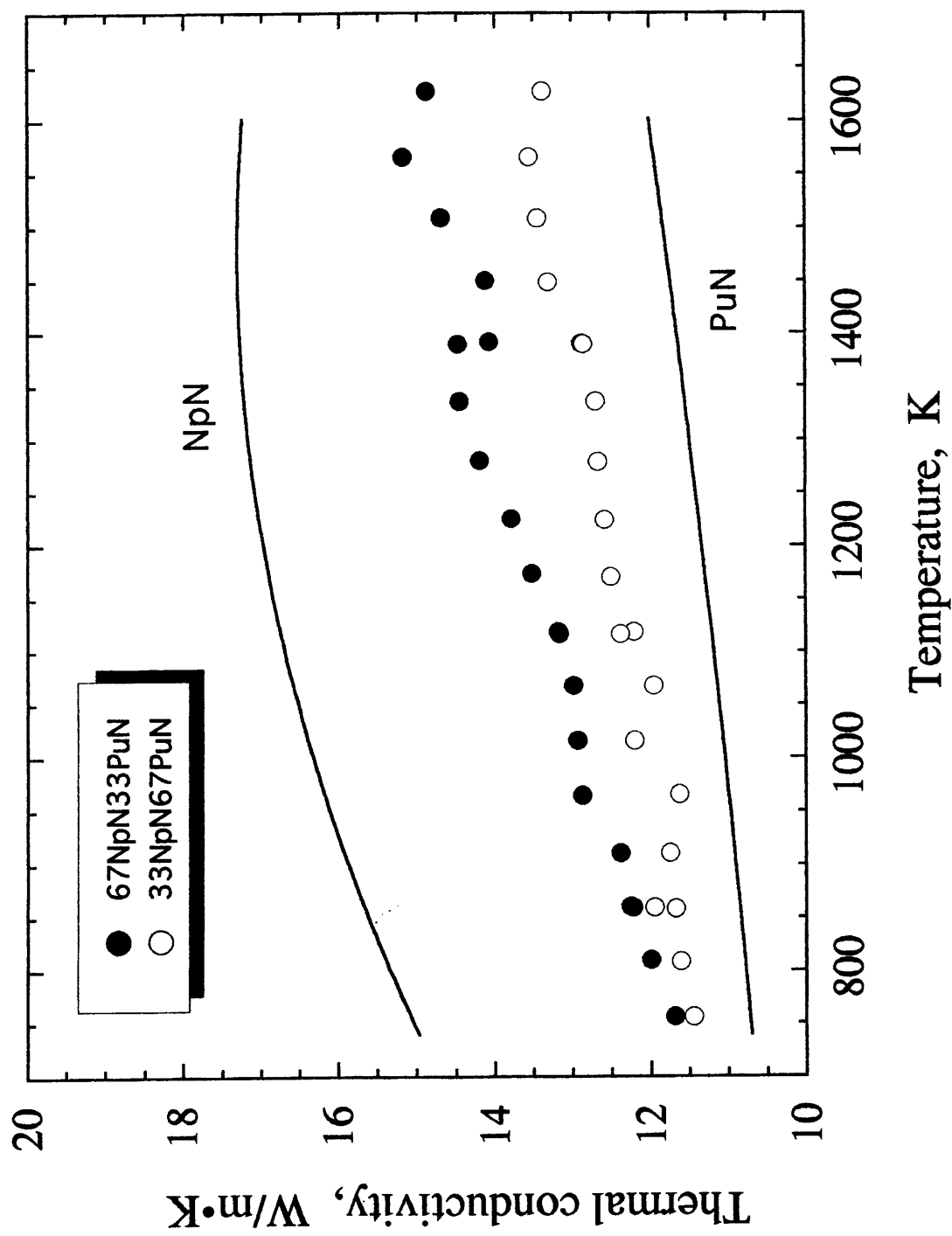


Fig.5 Thermal conductivity of (Np,Pu)N solid solutions corrected to 100%T.D. compared with those of NpN [18] and PuN [19]