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Thermal expansion of TRU nitride solid solutions as fuel materials for transmutation of minor actinides

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ABSTRACT

The lattice thermal expansion of the transuranium nitride solid solutions was measured to investigate the composition dependence. The single-phase solid solution samples of $(Np_{0.55}Am_{0.45})N$, $(Pu_{0.59}Am_{0.41})N$, $(Np_{0.21}Pu_{0.52}Am_{0.22}Cm_{0.05})N$ and $(Pu_{0.21}Am_{0.18}Zr_{0.61})N$ were prepared by carbothermic nitridation of the respective transuranium dioxides and nitridation of Zr metal through hydride. The lattice parameters were measured by the high temperature X-ray diffraction method from room temperature up to 1478 K. The linear thermal expansion of each sample was determined as a function of temperature. The average thermal expansion coefficients over the temperature range of 293–1273 K for the solid solution samples were 10.1, 11.5, 10.8 and $8.8 \times 10^{-6}\,K^{-1}$, respectively. Comparison of these values with those for the constituent nitrides showed that the average thermal expansion coefficients of the solid solution samples could be approximated by the linear mixture rule within the error of 2–3%.

1. Introduction

Actinide nitrides are considered as the potential fuel or target materials for the transmutation of minor actinides (MAs) in fast reactors and also in the subcritical core of accelerator driven systems (ADS) [1,2]. In addition to its superior thermal and neutronic properties in comparison with the oxides, the mutual solubility among actinide mononitrides [3] may enable the flexible design in actinide composition and the high concentration of Pu and MAs. To build the material database needed for fuel design and understanding the fuel performance, the authors have been studying on the basic thermal properties like thermal expansion, heat capacity and thermal conductivity of transuranium (TRU) nitrides.

Thermal expansion data are used to evaluate the change in dimensions and density of fuel pellets with temperature. Although a dilatometer is applied to measure the thermal expansion of a bulk specimen directly, the thermal expansion of crystal lattice measured by a high temperature X-ray diffraction (XRD) method is more fundamental data to understand the expansion behavior. Recently we have succeeded in measuring the lattice thermal expansion of NpN, PuN and AmN [4]. Since the MA-bearing nitride fuel will consist of the solid solution among actinide mononitrides, the composition dependence of thermal expansion is the subject to be investigated.

In this study, the lattice parameters of TRU binary nitrides, (Np,Am)N and (Pu,Am)N, quaternary nitride, (Np,Pu,Am,Cm)N, and (Pu,Am)N diluted in ZrN as an inert matrix material were measured by the high temperature XRD method from room temperature up to 1478 K. Their linear thermal expansions were determined as a function of temperature. The average thermal expansion coefficients over the temperature range of 293–1273 K were compared with those for the constituent nitrides to study the composition dependence.

2. Experimental

2.1. Sample preparation

NpN, PuN and AmN were synthesized by carbothermic reduction of the respective dioxides. Details of the method and purity of the oxides were described elsewhere [4]. To prepare the solid solution samples of (Np,Am)N and (Pu,Am)N, the single-component nitrides were mixed at the Np/Am and Pu/Am atomic ratios of unity, and then compacted into tablets at a pressure of 200 MPa. The tablet of NpN–AmN mixture was heat treated at 1870 K in $N_2 + 4\%H_2$ mixed gas flow for 7 h. Totally three runs of compaction, heat treatment, pulverization and phase identification by XRD yielded the single-phase solid solution with the sharp diffraction peaks. Similarly the tablet of PuN–AmN mixture was heat treated at 1830 K and two runs yielded the single-phase solid solution.

Some decrease in the sample weights was observed during the heat treatments. Since the equilibrium vapor pressure of Am over AmN was estimated to be much higher than those of either Np over NpN or Pu over PuN [5–7], the most part of the weight loss was

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considered due to the evaporation of AmN. Therefore, the compositions of the products were determined to be $(Np_{0.55}Am_{0.45})N$ and $(Pu_{0.59}Am_{0.41})N$ based on the material balance.

(Np,Pu,Am,Cm)N was synthesized by the simultaneous carbothermic reduction of $^{237}NpO_2$, PuO_2, $^{243}AmO_2$ and $(^{240}Pu,^{244}Cm)O_2$ mixture at the Np/Pu/Am/Cm atomic ratio of 0.20/0.50/0.25/0.05. The mixture was blended with amorphous carbon at the carbon/metal atomic ratio of 3.90. The compacted mixture was then heat treated in nitrogen gas flow for nitridation, at which the temperature was raised gradually from 1570 to 1673 K in 3 h. Progress of the reaction was monitored by measuring the CO gas content in the nitrogen flow by an infrared spectroscopic method. Subsequently to the nitridation, the sample was heat treated at 1800 K in $N_2 + 4\%H_2$ mixed gas flow for 7 h to remove the residual carbon as HCN gas. The product was compacted again and heat treated at 1910 K for 4 h for homogenization. From the weight loss of AmN during the heat treatment, the composition was determined to be $(Np_{0.21}Pu_{0.52}Am_{0.22}Cm_{0.05})N$.

A part of (Pu,Am)N powder was mixed with ZrN synthesized from metal through hydride at the (Pu + Am)/Zr ratio of 0.40/0.60. Two runs of compaction and heat treatment at 1870 K in $N_2 + 4\%H_2$ mixed gas flow for 7 h yielded the single-phase solid solution. The composition was determined to be $(Pu_{0.21}Am_{0.18}Zr_{0.61})N$ taking the weight loss of AmN into account.

Further, compacted ZrN was heat treated at 1773 K for 5 h in N_2 gas flow prior to the high temperature XRD measurement. Composition of light elements in the pulverized ZrN was determined to be $Zr(N_{0.993}O_{0.006}C_{0.001})_{0.97}$ from the results of quantitative analyses on the content of nitrogen, oxygen and carbon.

2.2. High temperature X-ray diffraction

The lattice parameters of the nitride solid solution samples and ZrN were measured from room temperature up to 1478 K by the high temperature XRD method. The goniometer installed in a glove box with purified argon atmosphere was employed to avoid the hydrolysis and oxidation of samples during handling and measurements. Details of the technique were described elsewhere [4]. The atmosphere of the sample chamber was kept with the $N_2 + 4\%H_2$ mixed gas flow of 500 ml/min purified by passing through the columns of moisture and oxygen absorber. Diffraction profiles were recorded at every 100 K in most cases with Mo-Kα radiation. The lattice parameters calculated from $K\alpha_1$ peak positions were extrapolated to $2\theta = 180°$ using the Nelson–Riley function for refinement. To reduce the effect of lattice expansion induced by the self-irradiation damage, the XRD measurements were started immediately after the heat treatment, especially in case of the sample containing ^{244}Cm.

3. Results and discussion

Partial XRD profiles of the solid solution samples at room temperature are shown in Fig. 1. Each product was identified as the single phase with NaCl-type structure. Any oxide phases other than the nitrides and the sample holder were not detected. Split of the $K\alpha_1$ and $K\alpha_2$ peaks was enough to determine the $K\alpha_1$ peak positions precisely.

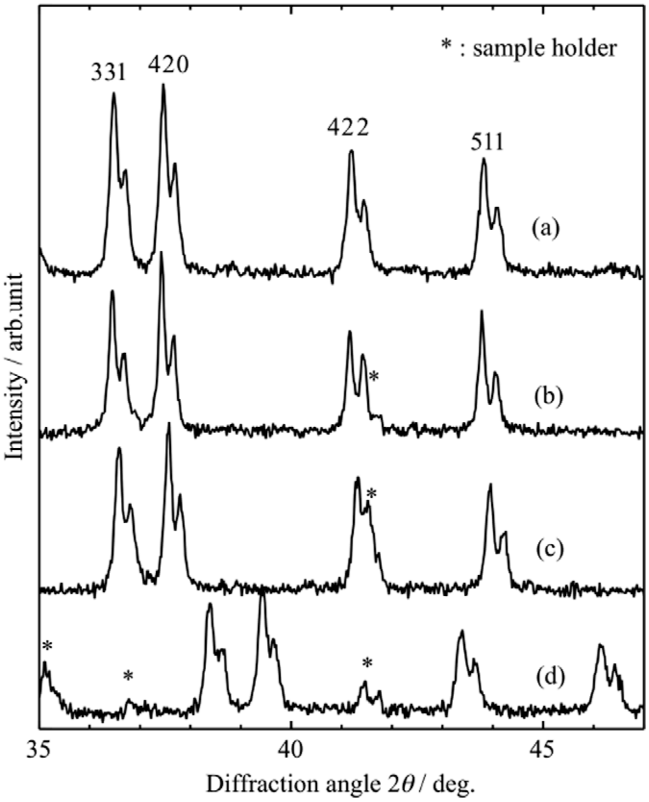

Fig. 1. Partial XRD profiles of the solid solution samples at room temperature: (a) $(Np_{0.55}Am_{0.45})N$, (b) $(Pu_{0.59}Am_{0.41})N$, (c) $(Np_{0.21}Pu_{0.52}Am_{0.22}Cm_{0.05})N$, and (d) $(Pu_{0.21}Am_{0.18}Zr_{0.61})N$.

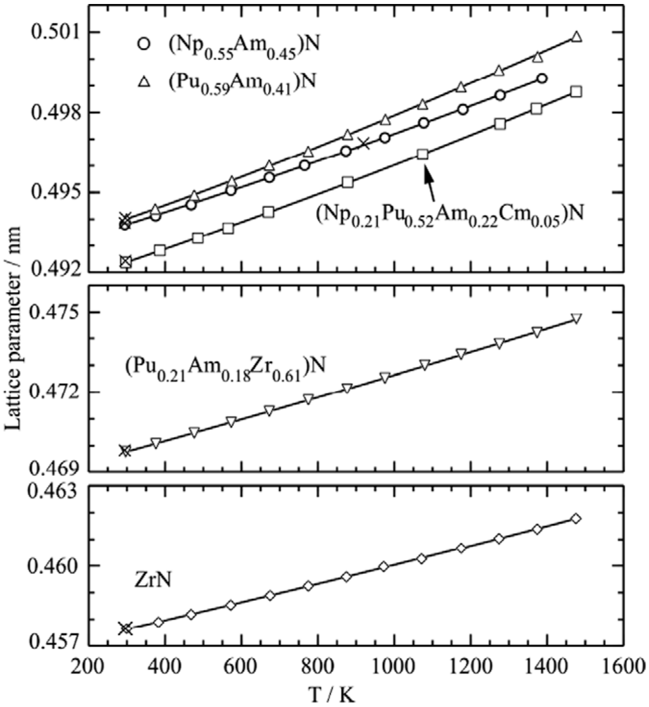

Fig. 2. Lattice parameters of the solid solution samples and ZrN as a function of temperature. Symbol '×' represents the results obtained after the high temperature measurements to confirm the reproducibility.

The lattice parameters of the solid solution samples and ZrN are shown in Fig. 2 as a function of temperature. The values at room temperature before and after the high temperature measurements agreed within the difference of 0.00003 nm for each sample. Judging from the excellent reproducibility, increase in the dissolved oxygen content or change in the actinide composition was negligible during the high temperature measurements. The solid lines in the figure represent the least square fitting to the following third order polynomial:

$$a_T\ (\mathrm{nm}) = a_0 + a_1 T + a_2 T^2 + a_3 T^3, \qquad (1)$$

where a_T is the lattice parameter at temperature T (K) and a_0–a_3 are the fitting constants. Regression results are listed in Table 1,

Table 1
Regression data for a_T (nm) = $a_o + a_1T + a_2T^2 + a_3T^3$, a_{293} values and the upper limit of temperature, T_{max}.

Composition	a_o	a_1 (10^{-6})	a_2 (10^{-10})	a_3 (10^{-14})	a_{293} (nm)	T_{max} (K)
$(Np_{0.55}Am_{0.45})N$	0.49250	4.184	5.365	−2.993	0.49377	1387
$(Pu_{0.59}Am_{0.41})N$	0.49262	4.328	11.49	−21.64	0.49398	1478
(Np,Pu,Am,Cm)N[a]	0.49097	4.566	4.954	−0.9481	0.49235	1476
$(Pu_{0.21}Am_{0.18}Zr_{0.61})N$	0.46862	3.809	2.233	−0.9285	0.46975	1477
$ZrN_{0.97}$	0.45674	2.919	4.800	−9.786	0.45763	1476

[a] Np/Pu/Am/Cm = 0.21/0.52/0.22/0.05.

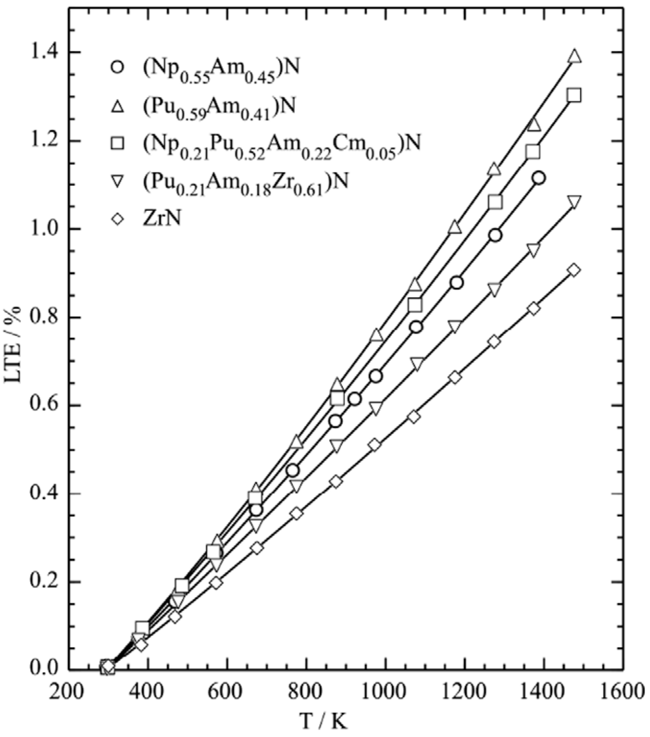

Fig. 3. Linear thermal expansions of the solid solution samples and ZrN from 293 K as a function of temperature.

together with the lattice parameters a_{293} at the reference temperature 293 K, and the upper limit of temperature range, T_{max}. The maximum deviation from the fitted curve was 0.00008 nm for $(Pu_{0.59}Am_{0.41})N$ at 1375 K, and within 0.00004 nm for the other data points.

The values of a_{293} for the solid solution samples were compared with those calculated by the Vegard's law using the lattice parameters of the constituent nitrides: namely 0.48956, 0.49050, 0.49915 nm for NpN, PuN, AmN, respectively [4], 0.5027 nm for CmN [8], and 0.45763 nm for ZrN obtained in this work. The a_{293} values for $(Np_{0.55}Am_{0.45})N$, $(Pu_{0.59}Am_{0.41})N$ and $(Np_{0.21}Pu_{0.52}Am_{0.22}Cm_{0.05})N$ agreed reasonably with the calculated values of 0.4939, 0.4940 and 0.4928 nm, respectively. For $(Pu_{0.21}Am_{0.18}Zr_{0.61})N$ the a_{293} value was somewhat smaller (−0.0022 nm) than the calculated value of 0.4720 nm.

The linear thermal expansions, LTE (%), of the solid solution samples and ZrN from 293 K are shown in Fig. 3 as a function of temperature. The solid lines represent the least square fitting to the following equation:

$$\mathrm{LTE}\ (\%) = b_1(T-293) + b_2(T-293)^2 + b_3(T-293)^3, \tag{2}$$

where b_1–b_3 are the fitting constants. Regression results are listed in Table 2, together with the LTE values at 1273 K and the average thermal expansion coefficients over the temperature range of 293–1273 K, α_{1273}. The LTE_{1273} values for the TRU nitride solid solutions ranged from 0.99% for $(Np_{0.55}Am_{0.45})N$ to 1.13% for $(Pu_{0.59}Am_{0.41})N$. That of (Pu,Am)N diluted in ZrN was lowered to 0.86% due to the effect of the lower LTE_{1273} value of 0.74% for ZrN.

The correlation between the average thermal expansion coefficients for the solid solution samples and the constituent nitrides is discussed as follows. Fig. 4 shows the plots of α_{1273} values for the solid solution samples against AmN, (Np,Am)N or (Pu,Am)N molar fraction. The bars show the maximum error of ±2% estimated from the uncertainty of ±0.00004 nm in the lattice parameter determination. The α_{1273} values of 8.80, 11.1 and $11.2 \times 10^{-6}\ K^{-1}$ for NpN, PuN and AmN, respectively, were taken from the earlier paper [4] and that for ZrN from this work. The broken lines represent the hypothetical 'linear mixture rule'. The measured α_{1273} values for $(Np_{0.55}Am_{0.45})N$ and $(Pu_{0.59}Am_{0.41})N$ are 2.2% and 3.2% greater than the coefficients at corresponding AmN fractions on the NpN–AmN and PuN–AmN lines, respectively.

For $(Np_{0.21}Pu_{0.52}Am_{0.22}Cm_{0.05})N$, since the Cm content is relatively low and the thermal expansion data for CmN is still missing, the Cm fraction was included in Am and the measured data was plotted as $0.52PuN–0.48(Np_{0.44}Am_{0.56})N$ in Fig. 4 for convenience, where the α_{1273} value for $(Np_{0.44}Am_{0.56})N$ was calculated by the linear mixture rule. The measured value is 1.5% greater than the coefficient on the $PuN–(Np_{0.44}Am_{0.56})N$ line. If the α_{1273} for CmN lies in interval of $10–12 \times 10^{-6}\ K^{-1}$, that for $(Np_{0.21}Pu_{0.52}Am_{0.22}Cm_{0.05})N$ is calculated to be $10.6–10.7 \times 10^{-6}\ K^{-1}$. In this case the deviation of measured α_{1273} value ranges 1.1–2.0%.

A possible reason for the slightly greater α_{1273} values than the calculated ones would be the influence of dissolved oxygen. The dissolved oxygen contents in the solid solution samples were considered to be higher to some extent than those in the NpN, PuN and AmN samples used for the thermal expansion measurements, because of the repeated heat treatment cycles to form the solid solutions.

The solid solution $(Pu_{0.21}Am_{0.18}Zr_{0.61})N$ can be expressed as $0.61ZrN–0.39(Pu_{0.54}Am_{0.46})N$. The measured α_{1273} value for this sample is 1.6% smaller than the coefficient on the $ZrN_{0.97}–(Pu_{0.54}Am_{0.46})N$ line, which shows the opposite tendency to the other solid solution samples. The hypostoichiometric feature of ZrN may possibly affect the thermal expansion coefficient. Another α_{1273} value for the near stoichiometric $Zr(N_{0.994}O_{0.002}C_{0.004})_{0.993}$ obtained by Smirnov et al. [9] is $(7.19 \pm 0.28) \times 10^{-6}\ K^{-1}$. When using this value for ZrN, the measured α_{1273} value for $(Pu_{0.21}Am_{0.18}Zr_{0.61})N$ is 1.0% greater than the coefficient on the $ZrN_{0.99}–(Pu_{0.54}Am_{0.46})N$ line. The (N + O + C)/(Pu + Am + Zr) ratio for the $(Pu_{0.21}Am_{0.18}Zr_{0.61})N$ sample was then presumed to be around 0.98–0.99, though the chemical analysis was not performed.

From the above discussion, it was confirmed that the average thermal expansion coefficients for the TRU nitride solid solutions over the temperature range of 293–1273 K could be estimated by the linear mixture rule within the error of 2–3%, even in the case for the nitride diluted in ZrN. In order to make more precise

Table 2
Regression data for LTE (%) = $b_1(T-293)+b_2(T-293)^2+b_3(T-293)^3$, LTE_{1273} values and the average thermal expansion coefficients, α_{1273}.

Composition	$b_1(10^{-4})$	$b_2\ (10^{-8})$	$b_3\ (10^{-12})$	LTE_{1273} (%)	$\alpha_{1273}\ (10^{-6}\ \mathrm{K}^{-1})$
$(Np_{0.55}Am_{0.45})N$	9.139	9.866	−5.024	0.99	10.1
$(Pu_{0.59}Am_{0.41})N$	10.04	18.91	−41.41	1.13	11.5
(Np,Pu,Am,Cm)N[a]	9.872	9.671	−0.8295	1.06	10.8
$(Pu_{0.21}Am_{0.18}Zr_{0.61})N$	8.375	4.686	−2.484	0.86	8.82
$ZrN_{0.97}$	6.929	8.741	−22.00	0.74	7.57

[a] Np/Pu/Am/Cm = 0.21/0.52/0.22/0.05.

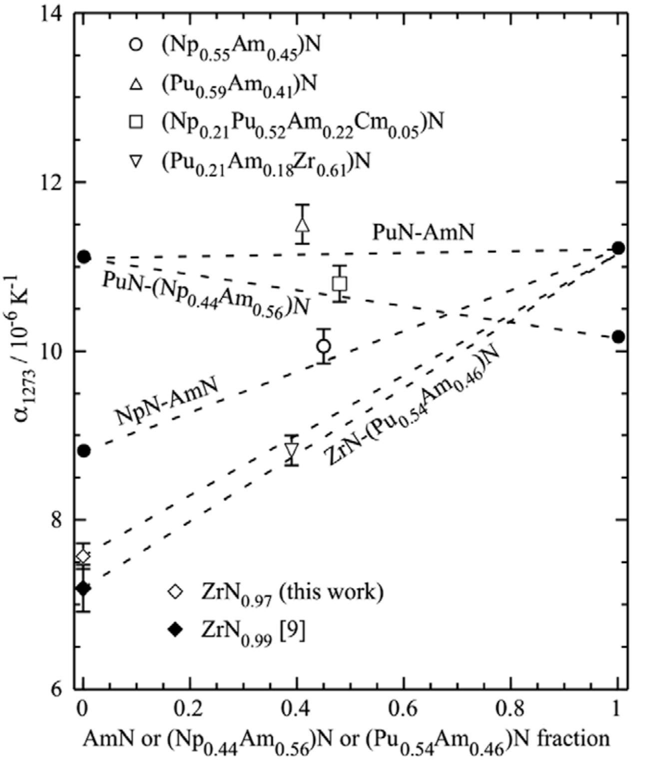

Fig. 4. Plots of the average thermal expansion coefficients (293–1273 K) for the solid solution samples against AmN, (Np,Am)N or (Pu,Am)N fractions. Broken lines represent the hypothetical linear mixture rule.

estimations, the influence of hypostoichiometry and probably the dissolved oxygen content on the thermal expansion, in addition to that of CmN, needs to be investigated quantitatively.

4. Conclusions

The lattice parameters of the TRU nitride solid solution samples, $(Np_{0.55}Am_{0.45})N$, $(Pu_{0.59}Am_{0.41})N$, $(Np_{0.21}Pu_{0.52}Am_{0.22}Cm_{0.05})N$ and $(Pu_{0.21}Am_{0.18}Zr_{0.61})N$, were measured by the high temperature XRD method from room temperature up to 1478 K. Their linear thermal expansions from 293 K were determined as a function of temperature. The average thermal expansion coefficients over the temperature range of 293–1273 K for the solid solution samples were compared with those for the constituent nitrides. It was confirmed that the linear mixture rule could be applicable to estimate the thermal expansion coefficients of these solid solution samples within the error of 2–3%.

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