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Lattice thermal expansions of NpN, PuN and AmN

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Abstract

Lattice parameters of NpN, PuN and AmN were measured by a high temperature X-ray diffraction method from room temperature up to 1478 K. Linear thermal expansions of these TRU nitrides were determined as a function of temperature. The average coefficients of linear thermal expansion from 293 to 1273 K were 8.8, 11.1 and $11.2 \times 10^{-6}\ \mathrm{K}^{-1}$ for NpN, PuN and AmN, respectively. The instantaneous coefficient of thermal expansion either at 293 or at 1273 K against the reciprocal decomposition temperature under 1 atm of nitrogen showed a linear relationship for TiN, ZrN, HfN, UN, NpN and PuN. Based on this relationship, the decomposition temperature of AmN was roughly predicted to be 2700 K.

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1. Introduction

For the advanced nuclear fuel cycle involving the multi recycling of Pu and the transmutation of minor actinides (MAs), many concepts of the fuel form are being studied in conjunction with the reactor types and reprocessing systems. Nitride is expected as a potential fuel material adapted to fast reactors and also the accelerator driven system (ADS) [1,2]. To understand the performance of such an advanced fuel containing MAs, the establishment of the database on material properties has become an important work.

Thermal expansion data are used to evaluate the change in dimensions and density of fuel pellets with temperature. Dilatometer is a device to measure the expansion of a bulk specimen directly. Some data sets on UN, PuN and (U, Pu)N are available in the data book [3]. In case of the transplutonium nitrides, however, it is often difficult to prepare a bulk specimen with the dimensions enough for dilatometer because of the high radiation dose. The sintering or oxidation of a specimen during measurement could influence the data. On the other hand, the thermal expansion of crystal lattice measured by a high temperature X-ray diffraction (XRD) method is rather fundamental one. Since the data can be obtained with the smaller amount of sample, this method is useful for TRU nitrides.

Lattice parameters of UN at elevated temperatures were reported by Benz et al. [4] and Kempter et al. [5]. Hayes et al. [6] reviewed these data and the linear thermal expansion (LTE) was expressed as a function of temperature from 298 to 2523 K. For NpN, only the low-temperature XRD data from 10 to 300 K was reported by Aldred et al. [7]. For PuN, the low-temperature XRD data (50–345 K) by Benedict et al. [8] and the high temperature XRD data up to 1073 K by Carroll [9] are available. However, the latter data for PuN may have been affected by the sample oxidation during measurement, where the reproducibility was not confirmed. No data on AmN and CmN at high temperatures have been reported. Considering the poor situation described above, it is necessary to obtain the precise data on the thermal expansions of TRU nitrides that will make the components of nitride fuels.

In this study, the lattice parameters of NpN, PuN and AmN were measured by a high temperature XRD method.

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The linear thermal expansions of these TRU nitrides were determined as a function of temperature. The correlation between thermal expansion coefficients and decomposition temperatures for some selected nitrides will be discussed.

2. Experimental

2.1. Sample preparation

NpN, PuN and AmN were prepared by carbothermic reduction of the respective dioxides. The powders of NpO_2, PuO_2 and AmO_2 calcined at 1070 K in oxygen gas stream were blended with amorphous carbon (ASTM type N-326 equivalent) at carbon/metal molar ratios of 2.61, 2.68 and 3.99, respectively. Specifications of the dioxides are summarized in Table 1. The mixtures were ground well in an agate mortar and then compacted into tablets at a pressure of 100 MPa.

The tablets loaded into a tungsten crucible were heated in N_2 gas stream or N_2 and 4 vol.%-H_2 mixed gas stream for nitridation. Formation of the nitrides is formally expressed by the reaction,

$$MO_2 + 2C + 1/2N_2 \rightarrow MN + 2CO, \tag{1}$$

where M corresponds to a metal element. The CO gas evolution was monitored by an infrared spectroscopy to judge the progress of reaction. The nitridation was performed at 1723 K for 4.5 h in N_2 gas stream for NpN, and at 1623 K for 2.5 h in $N_2 + 4\%H_2$ gas stream for PuN. On the other hand, for AmN, the temperature was raised gradually from 1573 to 1823 K in 7 h in N_2 gas stream. After the nitridation, the tablets were heated subsequently in $N_2 + 4\%H_2$ gas stream at 1823 K for 5–7 h in order to remove the residual carbon. The obtained nitrides were powdered for the XRD measurements.

2.2. High temperature X-ray diffraction

Lattice parameters of the nitride samples were measured by a high temperature XRD system (RIGAKU, RINT Ultima+). The goniometer installed in a glove box with a purified argon atmosphere was employed to prevent the samples from hydrolysis and/or oxidation during handling and measurements. About 20 mg of the powder sample was loaded on a platinum or tungsten holder (2 mm thick and 0.1 mm deep). The holder was then mounted horizontally on the sample stage attached with a Pt–Rh heater. The inside of the leak-tight sample chamber was kept with $N_2 + 4\%H_2$ gas stream of 500 ml/min during the high temperature measurements.

Table 1
Specifications of the TRU dioxides used for nitride preparation

Formula	Purity (%)
$^{237}NpO_2$	Total Np > 99.5
$^{239}PuO_2$	Total Pu > 99.8 ^{239}Pu in Pu: 97
$^{243}AmO_2$	Total Am > 99.7 ^{241}Am in Am: 0.72 ^{244}Cm < 0.05

XRD profiles were obtained with Mo Kα radiation from room temperature up to 1478 K at every 100 K. Prior to the measurement at each temperature, the alignment of the system, i.e. the sample stage height and diffraction angle θ, was adjusted after keeping the sample isothermally for 30–60 min to eliminate the influence of geometrical deviation. The sample temperature was monitored by a Pt/Pt–13Rh thermocouple inserted into a hole of the sample holder, and was controlled within ±1 K of fluctuation. To correct the monitored temperature to the actual sample temperature, the thermal expansion of MgO powder (99.99% purity) was measured by the same method. The results were compared with the reported value [3].

Lattice parameters calculated from at least 8 reflections up to 78° in 2θ were plotted against the Nelson–Riley function and extrapolated to $\theta = 90°$ for refinement. Wavelength of 0.070926 nm for Mo $K\alpha_1$ radiation was used for the calculation. Errors in the lattice parameter determination increased from 0.00003 nm at low temperatures to 0.00007 nm at 1478 K.

3. Results and discussion

XRD profiles of the nitrides at room temperature are shown in Fig. 1. Each sample was a single phase with NaCl-type structure. The diffraction peaks were well split enough to determine the $K\alpha_1$ peak positions precisely. The lattice parameters were 0.48960 nm at 300 K, 0.49053

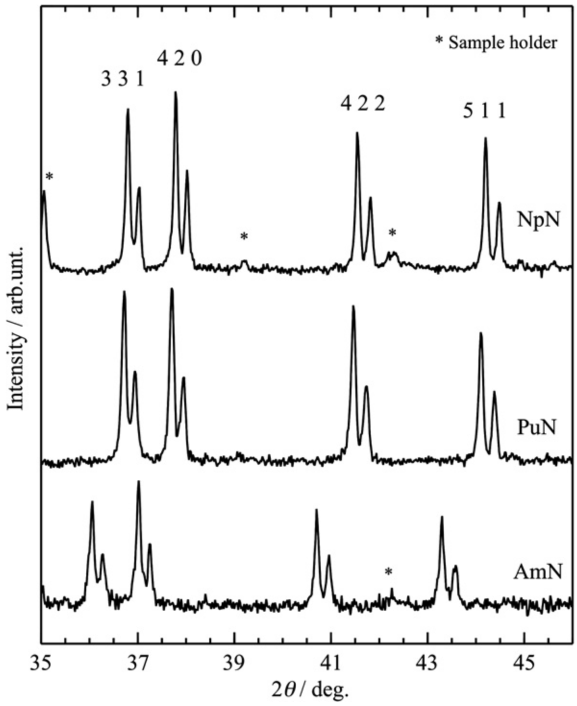

Fig. 1. Partial XRD profiles of the prepared nitrides at room temperature (Mo Kα radiation).

and 0.49915 nm at 296 K for NpN, PuN and AmN, respectively. That of NpN prepared by Suzuki et al. [10] is 0.48968 nm with the oxygen and carbon contents of 0.03 and 0.09 wt%. Muromura [11] estimated that of ‘pure’ PuN to be 0.49049 nm from the data on PuN samples with various oxygen and carbon contents. Another AmN sample prepared by the present authors with the oxygen and carbon contents of 0.05 and 0.02 wt%, respectively, had 0.49911 nm. Comparing with these values, the impurity levels of the prepared nitrides were considered to be fairly low.

The lattice parameters at elevated temperatures are shown in Fig. 2. The solid lines represent the least square fitting to the following third order polynomial:

$$a_T(\text{nm}) = a_0 + a_1T + a_2T^2 + a_3T^3 \tag{2}$$

where a_T is the lattice parameter at temperature T (K) and a_0–a_3 are constants. The maximum deviation from the fitted curves was 0.00004 nm. The regression data are listed in Table 2, together with the calculated lattice parameters at the reference temperature 293 K and the upper limits of temperature range where the data were obtained.

The symbol × in Fig. 2 represents the data obtained again after the high temperature measurements. The excellent reproducibility at room temperature was confirmed for all the samples; namely the changes in lattice parameters were within 0.00003 nm. If the content of oxygen dissolved into the nitride phase increased during the high temperature measurements, the lattice parameter would be affected. Although the XRD profiles at room temperature after the high temperature measurements contained some faint peaks of the oxides, the reproducibility showed that the increase in dissolved oxygen content was negligible.

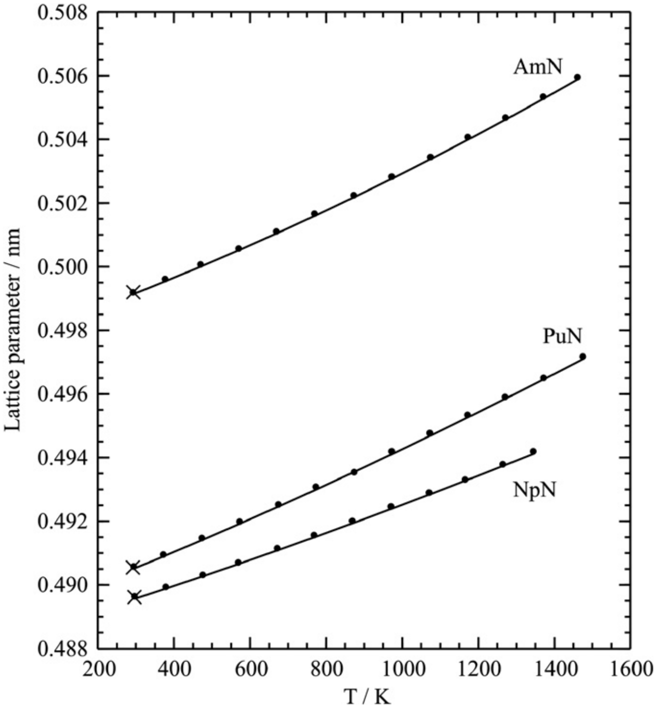

Fig. 2. Lattice parameters of NpN, PuN and AmN as a function of temperature.

Linear thermal expansions, LTE (%), defined by $(a_T - a_{293})/a_{293} \times 100$ for the nitrides are plotted against temperature in Fig. 3. The curves represent the least square fitting to the following equation:

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

where b_1, b_2 and b_3 are constants. The regression data and LTE values at 1273 K are listed in Table 3. The average thermal expansion coefficients over the temperature range of 293–1273 K are also shown in the table. The LTE values at 1273 K for PuN and AmN are very close to each other, and they are approximately 1.28 times greater than those for UN and NpN. If the linear mixture rule is valid for LTE values for the nitride solid solutions, the LTE for (Pu, Am)N is expected to be almost independent of the composition. Addition of NpN to (Pu, Am)N would lower the LTE. The actual composition dependence of LTE for the TRU nitride solid solutions is a subject to be investigated.

Thermodynamic stability at very high temperatures represented by the melting point is an important factor for nuclear fuels, especially in case of a severe accident. The general correlation between melting points and thermal expansion coefficients for solids has been pointed out [12]. For the actinide dioxides from ThO_2 to PuO_2, Yamashita et al. [13] plotted the instantaneous coefficients of thermal expansion against the reciprocal melting points, and they confirmed the reasonable linear relationship among them except for UO_2 at room temperature. The melting behavior of mononitrides, however, depends on nitrogen partial pressure of the system. The congruent melt is observed under pressurized nitrogen atmosphere. Under lower nitrogen partial pressures, the nitrides decompose into nitrogen gas and the liquid metals saturated with nitrogen. Olson and Mulford measured the decomposition temperatures of UN [14], NpN [15] and PuN [16] as a function of nitrogen partial pressure. For transition metal nitrides, Eron’yan et al. performed the similar measurements

Table 2
Regression data for a_T (nm) $= a_0 + a_1T + a_2T^2 + a_3T^3$

Nitride	a_0	$a_1 \times 10^6$	$a_2 \times 10^{10}$	$a_3 \times 10^{14}$	a_{293} (nm)	Max. temp. (K)
UN [6]	0.48790	3.264	6.889	–	0.48892	2523
NpN	0.48848	3.483	6.274	−7.601	0.48956	1348
PuN	0.48913	4.501	6.817	−4.939	0.49050	1478
AmN	0.49786	4.110	9.936	−3.169	0.49915	1464

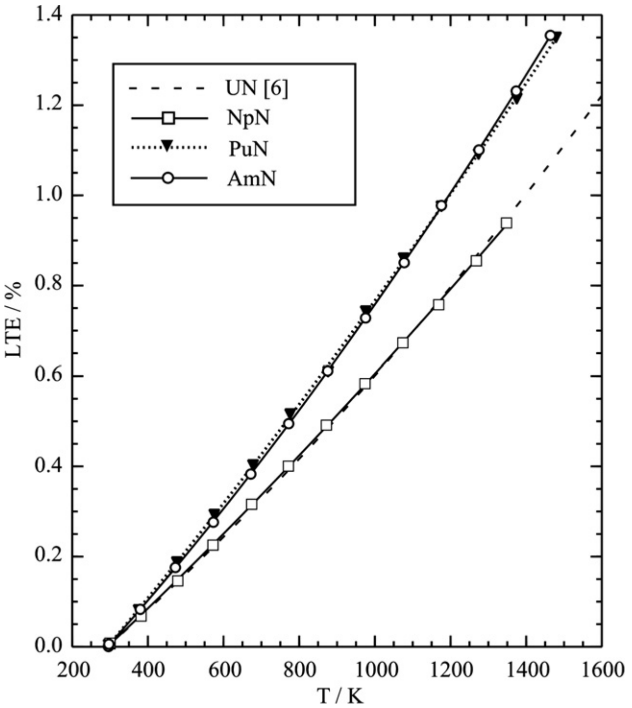

Fig. 3. Linear thermal expansions for NpN, PuN and AmN together with UN [6] as a function of temperature.

Table 3
Regression data for LTE (%) = $b_1(T-293)+b_2(T-293)^2+b_3(T-293)^3$

Nitride	$b_1 \times 10^4$	$b_2 \times 10^7$	$b_3 \times 10^{12}$	LTE_{1273} (%)	$\alpha_{\mathrm{av},1273}$ (10^{-6} K^{-1})
UN [6]	7.505	1.407	–	0.87	8.88
NpN	7.827	1.142	−15.34	0.86	8.80
PuN	9.973	1.288	−9.445	1.09	11.1
AmN	9.387	1.928	−6.052	1.10	11.2

on ZrN [17], TiN and HfN [18], which are considered as the candidate materials of inert matrix for the uranium-free nitride fuels [19,20].

To examine the correlation for these nitrides, the decomposition temperatures, T_d, under 1 atm of nitrogen were applied here. The instantaneous coefficients of thermal expansion, α, defined by $(\mathrm{d}a_T/\mathrm{d}T)/a_{293}$ were calculated using the parameters in Table 2. Those for the nitrides in literatures were estimated from the temperature dependence of lattice parameters or LTE curves. The data used are summarized in Table 4 with references. The LTE data in Thermophysical Properties Research Center, Purdue University (TPRC) data series [3] are provisional or recommended ones based on various data sets of the different compositions (impurity levels and hypostoichiometry) and methods (XRD and dilatometer).

Fig. 4 shows the plots of α values at 293 and 1273 K against the reciprocal values of T_d. The approximately linear relationship between α and $1/T_d$ values is recognized as shown by the broken lines with some exceptions. At 293 K, α value for PuN is obviously greater than that predicted from the line. Although a reason for the deviation is not clear, the α value reported by Benedict et al. [8] (low-temperature XRD) supports our result. At 1273 K, α value for NpN is slightly smaller than that for UN. The similar tendency is observed on the comparison of α values for UO_2 and NpO_2 [13,26] in spite of the higher melting point of UO_2.

The decomposition temperature of AmN is still unknown. The α value for AmN increases more dependently on temperature than that for PuN, and is the greatest in these actinide nitrides above 800 K. If the linear relationship shown in Fig. 4 is applicable to AmN, the decomposition temperature under 1 atm of nitrogen is roughly predicted to be 2700 ± 100 K, which is the lowest in the selected nitrides.

Table 4
Decomposition temperatures and thermal expansion coefficients for the selected nitrides

Nitride	Congruent m.p. (K)	Decomp.[a] temp. (K)	Ref.	α_T (10^{-6} K^{-1})		Ref.	Method or comment
				293 K	1273 K		
TiN	3550	3180	[18]	7.0	10.1	[21]	XRD, $TiN_{0.95}$
				6.3	10.4	[3]	TPRC
ZrN	3970	3520	[17]	6.5	7.9	[22]	XRD, $ZrN_{0.99}$
				5.7	8.9	[3]	TPRC
HfN	–	3620	[18]	5.7	–	[23]	XRD
				–	8.0	[24]	XRD
UN	3120	3050	[14]	7.5	10.3	[6]	XRD
				7.4	11.1	[3]	TPRC
NpN	3100	2960	[15]	7.9	9.9	–	This work
				7.6	–	[7]	XRD
PuN	–	2860	[16]	10.0	12.2	–	This work
				10.3	–	[8]	XRD
				–	11.6	[25]	Dilatometer
AmN	–	–		9.4	13.0		This work

[a] Under 1 atm of nitrogen.

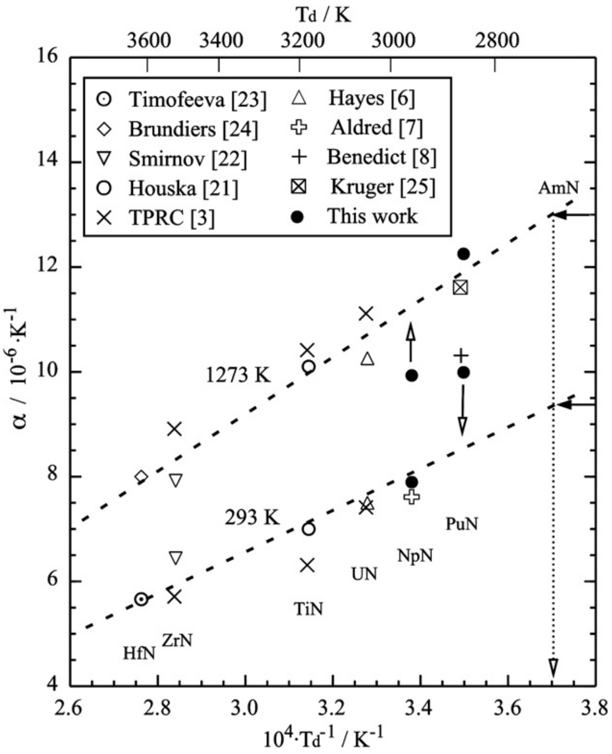

Fig. 4. Plots of the instantaneous coefficients of thermal expansion at 293 and 1273 K against the reciprocal values of decomposition temperature under 1 atm of nitrogen for the selected nitrides.

4. Conclusions

Lattice parameters of NpN, PuN and AmN were measured by the high temperature XRD method from room temperature up to 1478 K. The excellent reproducibility at room temperature showed that the influence of sample oxidation during measurements was negligible. Linear thermal expansions for these nitrides were determined as a function of temperature. The average coefficients of linear thermal expansion over the temperature range of 293–1273 K were 8.8, 11.1 and $11.2 \times 10^{-6}\ \mathrm{K}^{-1}$, respectively. The instantaneous coefficients of thermal expansion against the reciprocal values of decomposition temperature under 1 atm of nitrogen showed the approximately linear relationship for the actinide nitrides and some transition metal nitrides with some exceptions. From this relationship, the decomposition temperature of AmN was predicted to be 2700 ± 100 K.

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