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Molecular dynamics studies of actinide nitrides

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Abstract

Molecular dynamics (MD) calculations were performed for the actinide nitrides (ThN, UN, NpN, and PuN) in the temperature range 300–2800 K in order to evaluate the following physical properties; the lattice parameter, thermal expansion coefficient, compressibility, and heat capacity. A Morse-type potential function was added to the Busing–Ida type potential to describe the ionic interactions. The interatomic potential parameters were determined by fitting to the experimental lattice parameters. The usefulness and applicability of the MD method to evaluate physical properties of actinide nitrides were established.

1. Introduction

Actinide nitrides are candidate advanced fuels for fast breeder reactors (FBR) and targets for accelerate driven system (ADS). This is due to their superior thermophysical properties, for example high melting point, high metal density, high thermal conductivity, and chemical compatibility with the Na coolant [1,2]. In order to develop the technologies of a nuclear fuel cycle based on nitride fuel, it is very important to understand the thermophysical properties of actinide nitrides.

In our previous studies, we carried out molecular dynamics (MD) simulations to evaluate the properties of oxide fuels, such as UO_2, PuO_2, and MOX [3–5]. We have succeeded in evaluating the linear thermal expansion coefficient, compressibility, heat capacity, and thermal conductivity of these oxides. However, there are few MD studies of actinide nitrides. In the present study, therefore, MD calculations are performed for actinide nitrides (ThN, UN, NpN, and PuN), and their thermophysical properties are evaluated.

2. Calculation procedure

The MD calculations for AnN (An: Th, U, Np, Pu) were performed for a system of 512 ions (cation: 256, anion: 256) initially arranged in the NaCl crystal structure. In the present study, the calculations were performed using a molecular dynamics program based on MXDORTO [6]. Both standard constant pressure–temperature (NPT) and constant volume–temperature (NVT) MD calculations were performed at the thermodynamic equilibrium. A quantum effect was taken into account in the present calculations [7]. The lattice, containing a fixed number of atoms, was assumed to repeat periodically throughout the material, and there was no

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edge or surface effect. The long-range coulomb interaction was treated using Ewald's summation [8]. The equations of motion were integrated using Verlet's algorithm [9] with an integration time step of 2.0×10^{-15} s. At the start of the calculation, the initial velocity of each atom was assumed to take random velocities.

The calculations were carried out in the temperature range 300–2500 K, and in the pressure range 0.1MPa–1.5 GPa. The temperature and pressure of the system were controlled independently through a combination of the methods proposed by Andersen [10] and Nose [11]. An initial 10000-step equilibrium run was made at the desired temperature and pressure.

We employed the semi-empirical two-body potential function proposed by Ida [12] for cation–anion interactions. The potential is a partially ionic model including a covalent contribution [13]:

$$\phi_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6} + D_{ij}[\exp\{-2\beta_{ij}(r_{ij} - r_{ij}^*)\} - 2\exp\{-\beta_{ij}(r_{ij} - r_{ij}^*)\}], \quad (1)$$

where f_0 equals 4.186, z_i and z_j are the effective partial electronic charges on the ith and jth ions, r_{ij} is the interatomic distance, r_{ij}^* is the bond length of the cation–anion pair in vacuum, and a, b, and c are the characteristic parameters depending on the ion species. In this potential function, D_{ij} and β_{ij} describe the depth and shape of this potential, respectively.

Table 1
Values of the interatomic potential function parameters for ThN, UN, NpN, and PuN

Ions	z	a	b	c	D_{ij}	β_{ij}	r_{ij}^*
N	−1.450	1.797	0.080	20			
					(For Th–N pairs)		
Th	1.450	1.358	0.080	2.5	9.10	2.50	2.500
					(For U–N pairs)		
U	1.450	1.228	0.080	0	7.00	1.25	2.364
					(For Np–N pairs)		
Np	1.450	1.248	0.080	1.0	9.56	1.25	2.364
					(For Pu–N pairs)		
Pu	1.450	1.196	0.080	0	0.10	0.80	2.453

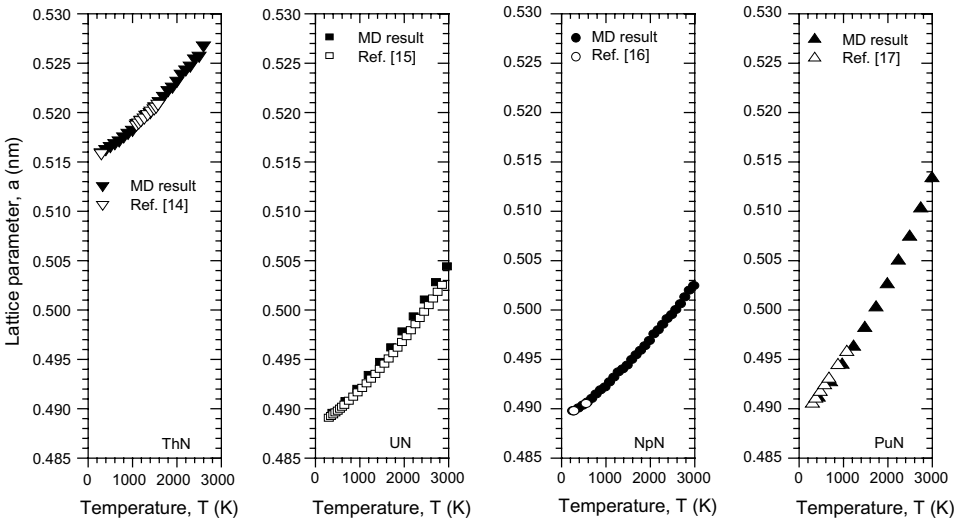

Fig. 1. Calculated results of lattice parameters for ThN, UN, NpN, and PuN as a function of temperature, together with literature data [14–17].

The potential parameters were determined by trial and error using the experimental values of the lattice parameters. Using the parameters so obtained, the linear thermal expansion coefficient (α_{lin}), compressibility (β), and heat capacity (C_P) were evaluated. The values of the interatomic potential parameters used in the present study are summarized in Table 1. A gradual charge to a more ionic character should be expected along the actinide series. In the present study, however, the effective partial electronic charge on actinide ion is assumed to take the same value for all nitrides.

3. Results and discussion

The temperature dependence of the lattice parameters of ThN, UN, NpN, and PuN obtained by the MD calculation controlled at 0.1 MPa is shown in Fig. 1,

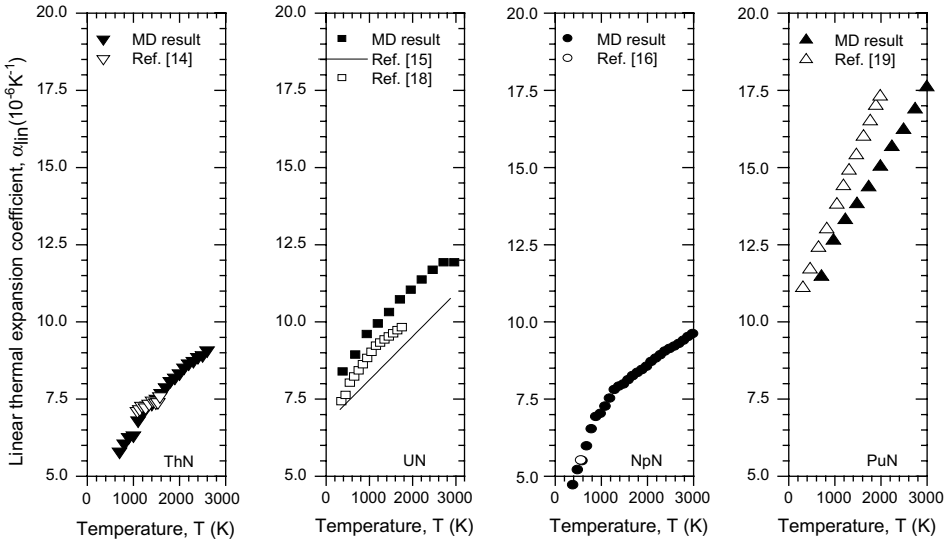

Fig. 2. Calculated results of linear thermal expansion coefficients for ThN, UN, NpN, and PuN as a function of temperature, together with literature data [14–16,18,19].

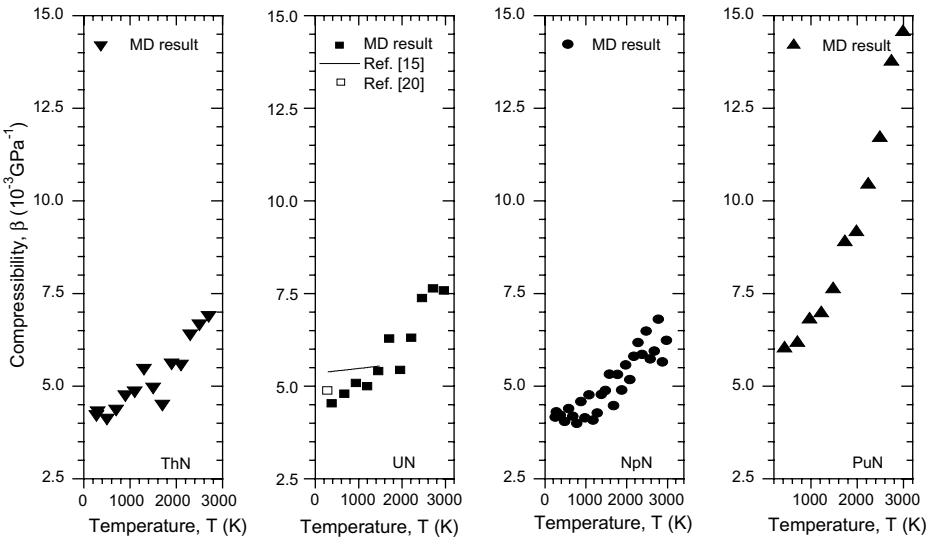

Fig. 3. Calculated results of compressibilities for ThN, UN, NpN, and PuN as a function of temperature, together with literature data [15,20].

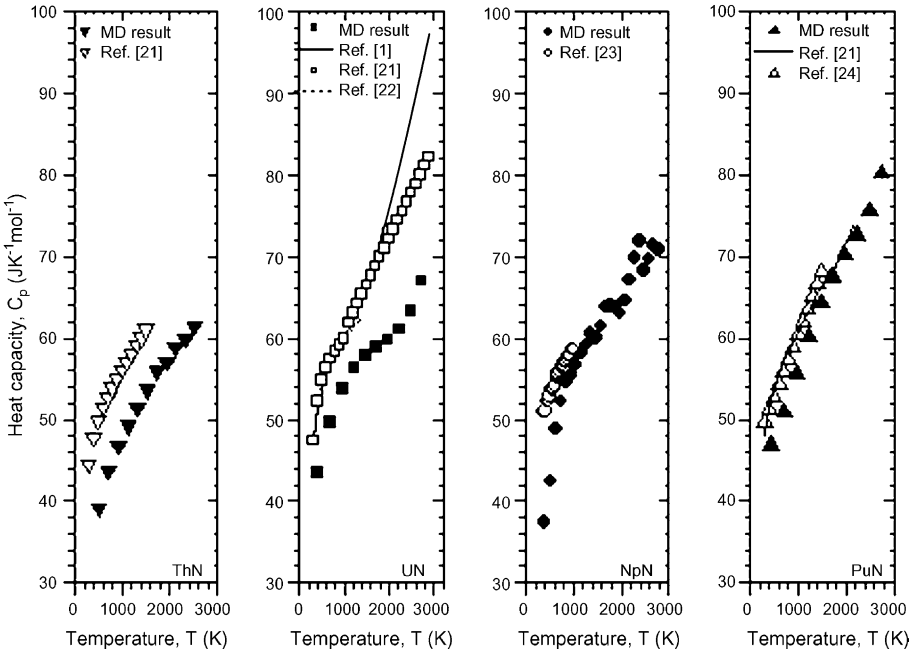

Fig. 4. Calculated results of the heat capacities ($C_V + C_d$) for ThN, UN, NpN, and PuN as a function of temperature, together with literature data (C_P) [1,21–24].

together with literature data [14–17]. Although the temperature range of the experimental data is limited for ThN, NpN, and PuN, the high temperature data are obtained from the MD calculations. The calculated results well agree with literature data.

The linear thermal expansion coefficient (α_{lin}) and compressibility (β) of ThN, UN, NpN, and PuN can be evaluated from the predicted variation of the lattice parameter with temperature and pressure, respectively. In cases of ThN, NpN, and PuN, there is little experimental data for the linear thermal expansion coefficient and compressibility. The calculated results which agree with the literature data [14–16,18–20] are shown in Figs. 2 and 3.

Although there are electronic contributions in actinide nitride system, we can evaluate only the lattice contribution to the heat capacity by the MD simulations. In the temperature range from 300 K to 2800 K, the heat capacity at constant pressure (C_P) was evaluated as the sum of the heat capacity at constant volume (C_V) and lattice dilatation team (C_d). C_V was evaluated from the variation of the internal energy of the system with temperature calculated by the NVT MD simulation. C_d was evaluated from the following relationship:

$$C_d = \frac{(3\alpha_{lin})^2 VT}{\beta}, \quad (2)$$

where V is the molar volume, α_{lin} is the linear thermal expansion coefficient, β is the compressibility, and T is the absolute temperature. C_d was evaluated by using the calculated values of α_{lin}, V, and β obtained from the NPT MD simulation. The temperature dependence of the calculated $C_V + C_d$ of ThN, UN, NpN, and PuN is shown in Fig. 4, together with literature data [1,21–24]. The calculated values of $C_V + C_d$ are slightly lower than the experimental results for all actinide nitrides. This may be caused by the neglect of electronic contributions.

In near future, we will evaluate thermal conductivities through MD simulations. In addition, we will perform MD calculations for not only actinide–nitrogen binary systems but also ternary system such as mixed nitrides. Our final objective is to establish the usefulness and applicability of MD simulations for the evaluation of the thermophysical properties of actinide nitrides.

4. Conclusion

The lattice parameter, linear thermal expansion coefficient, compressibility, and heat capacity of ThN, UN, NpN, and PuN were evaluated through MD simulations. The interatomic potential parameters were determined from the variation of the lattice parameter with temperature. The calculated results agree very well with the experimental data. The present study shows that the MD method can successfully determine the physical properties of actinide nitrides.

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