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A molecular dynamics study of zirconium nitride

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Abstract

A molecular dynamics (MD) calculation was performed for zirconium nitride (ZrN) in the temperature range from 300 to 2800 K to evaluate the thermophysical properties, viz., the lattice parameter (a), linear thermal expansion coefficient (α_{lin}), compressibility (β), heat capacity (C_P), and thermal conductivity (λ). A Morse-type potential function added to the Busing–Ida type potential was employed as the potential function for interatomic interactions. The interatomic potential parameters were semi-empirically determined by fitting to the experimental values of variations of the lattice parameter with temperature and pressure. In case of the heat capacity, the lattice vibration contribution (C_V) and lattice dilational contributions (C_d) were evaluated, and in case of the thermal conductivity, only the phonon contribution (λ_{lat}) was evaluated by the MD calculation.

Keywords: Molecular dynamics; Zirconium mononitride; Thermal expansion coefficient; Compressibility; Heat capacity; Thermal conductivity

1. Introduction

Actinide nitrides are under consideration as advanced fuels of fast breeder reactors (FBR) [1] because of their superior thermal, neutronic, and chemical properties for a nuclear fuel cycle, for example, high melting temperature, high metal density, high thermal conductivity, low creep rate, and chemical compatibility with SUS 316 and liquid Na [2–4]. In order to develop the technologies for nuclear fuel cycle based on the nitride fuel, it is very important to understand the thermophysical properties of actinide mononitrides.

In our previous studies, we have carried out a molecular dynamics (MD) simulation to evaluate the properties of nuclear fuels, such as UO_2, PuO_2, MOX [5–7], UN [8,9], and PuN [10]. Zirconium mononitride (ZrN) is candidate for the diluents of actinide nitride targets in accelerator driven systems (ADS). In the present study, the MD calculation was performed for ZrN in the temperature range from room temperature to 2800 K and the thermophysical properties of ZrN were evaluated.

2. Calculation procedure

An MD calculation for ZrN was performed for a system of 512 ions (Zr^{3+}: 256, N^{3-}: 256) initially arranged in the NaCl type crystal structure. In the present study, we used a molecular dynamics program based on MXDORTO [11]. The standard constant pressure–temperature (NPT) and constant volume–temperature (NVT) MD calculations at the thermodynamic equilibrium were performed. A quantum effect [12] was taken into account in the present calculation. The lattice, containing a fixed number of atoms, was assumed to repeat periodically throughout the material, and there was no edge or surface effect. The long-range Coulomb interaction was treated with Ewald's summation [13]. The equations of motion were integrated using Verlet's algorithm [14] 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, which were about 0.01 Å fs^{-1}.

The calculations were made in the temperature range from room temperature to 2800 K, and in the pressure range from 0.1 MPa to 1.5 GPa. The pressure and temperature of the system were controlled independently through a combination of the methods proposed by Andersen [15] and

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Table 1
Values of the interatomic potential function parameters for ZrN

Ions	z	a	b	c	D_{ij}	β_{ij}	r^*_{ij}
N	−1.450	1.797	0.080	20			
Zr	1.450	1.019	0.080	2.35	6.50 (for ZrN pairs)	4.510 (for ZrN pairs)	2.27

Nose [16], respectively. A 10,000-step equilibrium run was made at the desired temperature and pressure.

We employed the semi-empirical two-body potential function proposed by Ida [17] for cation–anion interactions. The potential is a partially ionic model including a covalent contribution [18]:

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

Details of the potential function are described in our previous papers [5–10].

The potential parameters were semi-empirically determined by fitting the experimental values of variations of the lattice parameter with temperature and pressure [19,20]. Using these parameters obtained from the method, the linear thermal expansion coefficient ($\alpha_{\rm lin}$), compressibility (β), heat capacity (C_P), and thermal conductivity (λ) were evaluated. The values of the interatomic potential parameters used in the present study are summarized in Table 1.

The thermal conductivity (λ) of the system was calculated using the Green–Kubo relation [21]. Details of the Green–Kubo relations are described in our previous papers [5–10].

3. Results and discussion

The temperature dependence of the lattice parameter of ZrN obtained by the MD calculation controlled at 0.1 MPa is shown in Fig. 1, together with literature data [19,22–24]. The calculation was performed in the temperature range from room temperature and 2800 K. Judging from Fig. 1, the calculated values of lattice parameter well agree with the experimental values. Although the temperature range of the experimental data for ZrN is limited below 2000 K, the high temperature data are obtained from the MD calculation.

The calculated lattice parameter of ZrN as a function of pressure in the range of 0.1 MPa to 1.5 GPa at 300 K are shown in Fig. 2, together with literature data [20]. The lattice parameter linearly decreases with pressure. The calculated values of lattice parameter well agree with the experimental data.

The linear thermal expansion coefficient ($\alpha_{\rm lin}$) and compressibility (β) of ZrN can be evaluated from the variations of

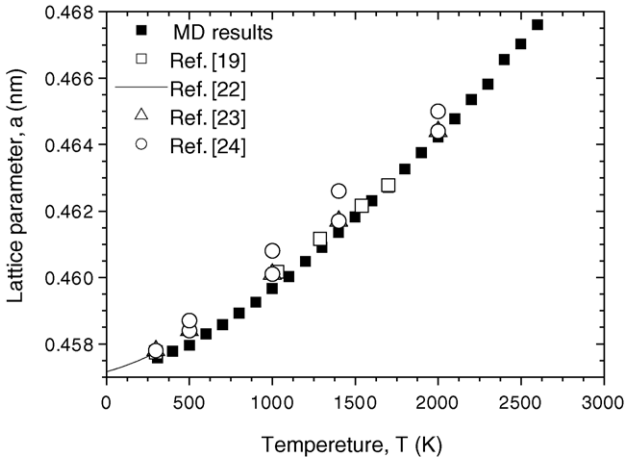

Fig. 1. Calculated results of lattice parameters of ZrN as a function of temperature, together with literature data [19,22–24].

lattice parameter with temperature and pressure as follows:

$$\alpha_{\rm lin} = \frac{1}{a(T_0)}\left(\frac{\partial a(T)}{\partial T}\right)_P, \quad (2)$$

$$\beta = -\frac{3}{a(P_0)}\left(\frac{\partial a(P)}{\partial P}\right)_T, \quad (3)$$

where $a(T_0)$ is the lattice parameter at room temperature, and $a(P_0)$ the lattice parameter under atmospheric pressure.

The calculated results are shown in Figs. 3 and 4, together with literature data [19,20,23,24]. It is shown that the calculated results of linear thermal expansion coefficient of ZrN well agree with most of the literature data [19,24] in the tem-

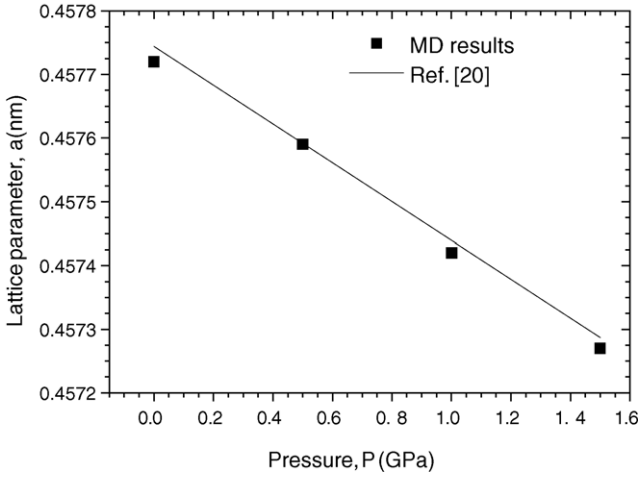

Fig. 2. Pressure dependence of the lattice parameters of ZrN obtained from the MD calculations [20].