

A non-equilibrium molecular dynamics study of the thermal conductivity of uranium dioxide

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Abstract The thermal conductivity of uranium dioxide in the temperature range of 300–2400 K was estimated by non-equilibrium molecular dynamics calculation using Fourier law. The Kawamura function was adopted as the interatomic potential function. The calculated thermal conductivities are found to be strongly dependent on the temperature of the simulation cube. The thermal conductivity simulation results are compared with the experiment results and agreed well with the experimental results when the temperature is above 600 K. The thermal conductivities scale effects are found to be existed in uranium dioxide nanometer thin film. The approximate mean free paths of phonons in different temperatures can be examined.

Key words Uranium dioxide, Thermal conductivity, Non-equilibrium molecular dynamics

1 Introduction

Thermal conductivity of nuclear fuel is very important for designing a nuclear power facility. Temperature of the fuel elements in a PWR (Pressurized Water Reactor) is 550–1800 K, a temperature range in which the lattice vibration is a major factor affecting the thermal properties. Therefore, lattice dynamics (molecular dynamics) can provide useful information to undertake microscopic consideration of thermal properties of the nuclear fuel materials. In recent years, with the advance of computer simulation techniques, there have been many atomic level simulations of the thermal transport properties of different materials^[1–5].

Watanabe T *et al*^[6] studied the UO₂ thermal transport parameter and found obvious scale effect in the thermal conductivity by two different potential models. Philippe P *et al*^[7] studied the UN viscosity, diffusion coefficients and thermal conductivity, using the local density function considering influence of the electron gas to analyze the thermodynamic parameter in quantum electrodynamics level. Chandra C B^[8] simulated the UC thermal properties. The calculated lattice parameters, bulk modulus and coefficient of

thermal expansion of UC, using the potential parameters, are in good agreement with experimental data. Yamada K *et al*^[9] used molecular dynamics to study the specific heat and thermal conductivity that vary with temperature. Variations of the thermal conductivity, obtained by the Green–Kubo approach, agreed well with the experimental data. In these studies, however, information in a limited temperature range was reported using equilibrium molecular dynamics, in which there are not temperature-different and non-equilibrium heat transport. So, one cannot use this method to analyze influence of thin film's direction, which shows the same thermal conductivity in normal and tangential direction.

In this work, uranium dioxide in temperatures ranging from 300 K to 2400 K was studied by the non-equilibrium molecular dynamics to evaluate the thermal properties of UO₂.

2 Molecular dynamics simulation

In molecular dynamics simulation, the movement track and velocity of the atom or ion can be acquired according to the Newton equations of the motion of atomic system in the cube. In order to build the

non-equilibrium molecular dynamics simulation condition, two constant temperature reservoirs in opposite direction are set up. The reservoir temperature decides the velocities of reflecting atoms, which is a random sampling function of Maxwell velocity distribution.

$$\Phi(v) = 4\pi n [m/(2\pi k_B T_w)]^{3/2} v^2 \exp[-mv^2/(2k_B T_w)] \quad (1)$$

where, T_w is the reservoir temperature, v is the atom velocity, k_B is the Boltzmann constant number. The Kawamura potential model is employed to describe the interaction among different ions in the cube, which shows the Kawamura potential model is reliable to describe the potential properties^[9]. The potential includes a covalent contribution between the nearest anion–cation pair as follows,

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

where, f_0 is a constant for unit conversion; Z_i and Z_j are the effective partial electronic charges on the i and j ion, respectively; r is the atom distance, which is the bond length of anion–cation pair in vacuum; D_{ij} and β_{ij} denote the depth and the shape of this potential; and a_i , a_j , b_i and b_j are characteristic parameters depending on the ion species. The first term describes the Coulomb interactions, the second term denotes core repulsions, the third term is the van der Waals term, and the fourth is the Morse-type potential that applies only to cation–anion pairs. The values of the inter-atomic potential function parameters used in the present study are given in Table 1.

Table 1 Potential model parameters used in the present calculation.

Ions	z	a	b	c	D_{ij}	β_{ij}	r_{ij}^*
O^-	-1.2	1.926	0.160	20	—	—	—
U^+	2.4	1.659	0.160	0	18.0	1.25	2.369
(for U-O pairs)							

Different cell layer temperature can be computed since the Boltzmann distribution function allows the straightforward derivation of the kinetic energy in the following way:

$$T_{j,MD} = (\sum m v_i^2) / (3N_j k_B) \quad (i=1-N_j) \quad (3)$$

where, m is the mass of the atom in the j cell layer, and N_j is the atom number of the j layer.

3 Non-equilibrium molecular dynamics simulation results and discussion

3.1 Temperature dependence of thermal conductivity of uranium dioxide

First, the simulation was done with a cube containing $3 \times 3 \times 3$ UO_2 cells, i.e. a system of 324 ions including 108 cations and 216 anions (Fig.1), with the UO_2 being arranged in the face-centered cubic type crystal structure. The atoms are assumed to move periodically throughout the cube in every direction, hence no boundary effect. In the simulation, any atom entering the periodic boundary will become a mirror atom in another side of the cube.

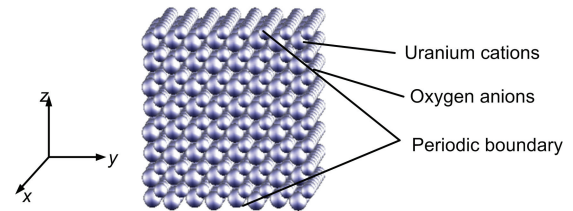


Fig.1 First temperature dependence cube used in the present calculation.

The thermal conductivity can be calculated according to statistic thermodynamics method. The thermal conductivity can be computed according to Fourier law.

$$K = (\Delta E_{j,in} + \Delta E_{k,out}) / (2tA|\nabla T|) \quad (4)$$

where, $\Delta E_{k,in}$ and $\Delta E_{k,out}$ are heat transfer from the high temperature and low temperature heat walls, respectively; ∇T is the temperature gradient along heat conduction direction; t is a time step; and A is the heat transfer area.

The thermal conductivity variations of thin UO_2 film at 300–2400 K are showed in Fig.2, together with the data, measured or simulated, in Refs.[10–12]. Our results agree well with experiment data at temperatures above 600 K. At low temperatures, our simulation results differ greatly from the measured thermal conductivities. This indicates that the molecular dynamics is suitable for thermal conductivity simulation at middle and high temperatures.

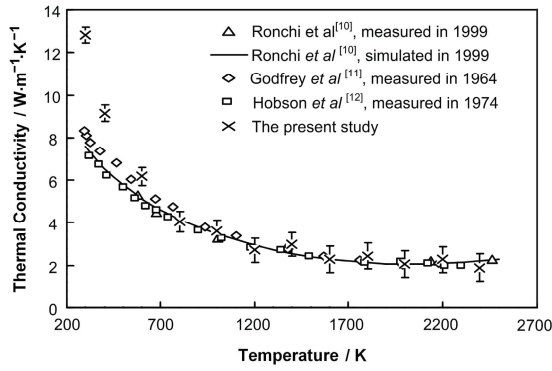


Fig.2 Thermal conductivity of UO_2 as a function of temperature.

Theoretically, the UO_2 thermal conductivity consists of k_{ph} , k_e and k_{rad} , which are thermal conductivities of phonon, electron and photon radiation, respectively, i.e. the total thermal conductivity $K = k_{\text{ph}} + k_e + k_{\text{rad}}$. The phonon thermal conductivity of UO_2 is

$$k_{\text{ph}} = (a + bT)^{-1} \quad (5)$$

At high temperatures, thermal conductivity of the UO_2 is affected by the photon radiation and electron diffusion. The photon radiation thermal conductivity is

$$k_{\text{rad}} = 5.33 \kappa n^2 T^3 \alpha^{-1} \quad (6)$$

where κ is the Stefan-Boltzmann constant, n is the refractive index, and α is the absorption coefficient. Thermal conductivity of the electron diffusion, k_e , obeys the Widman-Fulanz law,

$$k_e = 2T\kappa^2 e^{-2} \sigma [1 + 2\sigma^{-2} (2 + 0.5E_a \kappa^{-1} T^{-1})]^2 \quad (7)$$

where, σ is the total electrical conductivity; σ_1 and σ_2 are the electron and hole conductivities, respectively; and E_a is the activation energy. From Eqs.(5) and (7), k_e is bigger than k_{ph} at low temperatures, and has a major contribution of the thermal conductivity of UO_2 . As the temperature increases, k_{ph} would rise to approximately the same as k_e .

3.2 Scale dependence of UO_2 thermal conductivity

The second thin film system is located between two constant temperature reservoirs in UO_2 nanometer film in order to study the scale dependence of the thermal conductivity of UO_2 . A heated wall boundary is adopted in direction z normal to the film. An atom moving near the heated wall boundary will collide with heated wall, which will reflect the atom back into the system. The periodic boundary is adopted in x and

y directions of the film (Fig.3). The average temperature of the thin film is from 400 K to 1200 K. Thickness of the UO_2 film ranges from 2.19 nm to 16.4 nm. The cube contains from $3 \times 3 \times 2$ to $3 \times 3 \times 30$ unit cells (216 ions to 3240 ions).

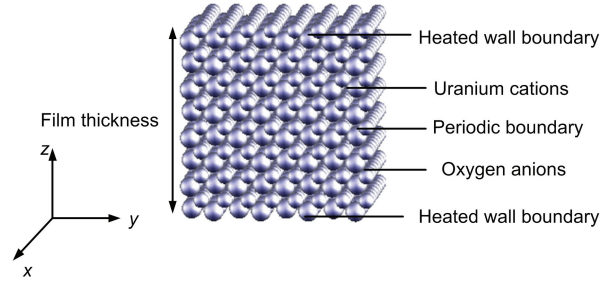


Fig.3 Second size dependence study cube used in the present calculation.

The thermal conductivity can be computed according to Fourier law. As shown in Fig.4, the simulated scale dependence of UO_2 thermal conductivity can be compared with the thermal conductivity results in Fig.2. The thermal conductivity increases gradually with the film thickness and becomes a steady value approximately equal to the periodic boundary simulation results in Fig.2. This shows the scale effect of thermal conductivity in the UO_2 film.

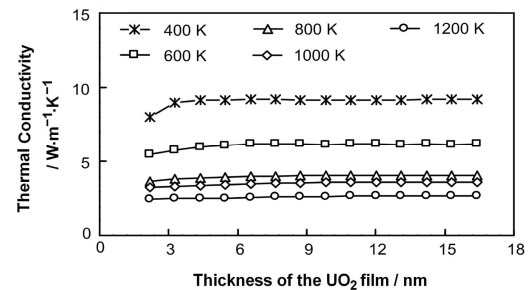


Fig.4 Thermal conductivity of UO_2 films in different thicknesses at different temperatures.

From Fig.4, the UO_2 thermal conductivity does not vary linearly with the film thickness. A thin film restricts the phonon mean free path and the phonon relaxation time, so that the motion of phonon mainly represents the interface thermal resistance of the thin UO_2 film. When the film thickness is less than the phonon mean free path, the scale of film thickness is near to the phonon mean free path. With increasing film thickness, influenced by boundary scattering process, the phonon mean free path increases non-linearly.

Using the phonon gas elementary kinetic theory, it can be shown that,

$$k = C_v v_s l_{\text{eff}} / 3 \quad (8)$$

where, C_v is the volumetric specific heat, v_s is the mean sound velocity, and l_{eff} is the effective mean free path of phonons. When the film thickness is greater than phonon mean free path l_{∞} , $l_{\text{eff}} = l_{\infty}$. The phonon mean free path includes the defect scattering, boundary scattering and phonon-phonon scattering. In a thin film, according to Matthiessen Rule^[13], valid phonon mean free path will be

$$1/l_{\text{eff}} = 1/l_{\text{defect}} + 1/l_{\text{boundary}} + 1/l_{\text{phonon}} \quad (9)$$

Then, one can get the valid thin film thermal conductivity equation,

$$1/k_{\text{eff}} = 1/k_{\text{defect}} + 1/k_{\text{boundary}} + 1/k_{\text{phonon}} \quad (10)$$

The $1/k_{\text{boundary}}$, affected by boundary scattering, is not a constant value. Ignoring k_{defect} , k_{eff} is adopted in the scale dependence simulation in Fig.4 and k_{phonon} is adopted in the bulk crystal Ronchi equation thermal conductivity^[10]. The k_{boundary} can be obtained from Eq.(10). Fig.5 showed $1/k_{\text{boundary}}$ variation with the thickness of UO_2 film. Approaching to the zero with the $1/k_{\text{boundary}}$, the boundary scattering influence vanishes and thermal conductivity will equal to the bulk crystal thermal conductivity in larger film thickness.

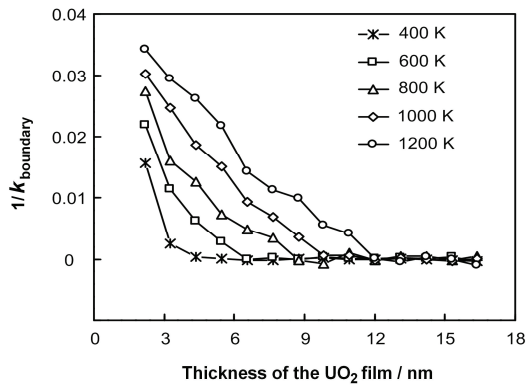


Fig.5 Simulation results of $1/k_{\text{boundary}}$ for UO_2 films in different thicknesses at different temperatures.

The thermal conductivity can be written as a function of system length as^[6]

$$1/k_{\text{eff}} = \{6/[k_B(v_l + 2v_t)n]\} / (1/l_{\text{eff}} + 4/l_{\text{boundary}}) \quad (11)$$

where k_B is the Boltzmann constant, n is the number density of the ions, v_l and v_t are the longitudinal and transverse sound velocities. This means that the

infinite size bulk thermal conductivity is obtained from molecular dynamics simulations by the extrapolation of the conductivity values to $1/l_{\text{boundary}}=0$ or $1/k_{\text{boundary}}=0$.

When the film thickness is less than the phonon mean free path, the scale of thin film thickness is near to phonon mean free path. From Fig.5, $1/k_{\text{boundary}}$ will approach to the zero and thermal conductivity will be a constant value in larger film thickness, *i.e.* the phonon mean free path approximately equal to the film thickness in the pivotal point of the thermal conductivity, and the film thickness of pivotal point would be the approximate phonon mean free path of $\lambda=4.05, 5.70, 8.02, 9.29$ and 11.45 nm for $T = 400, 600, 800, 1000$, and 1200 , respectively.

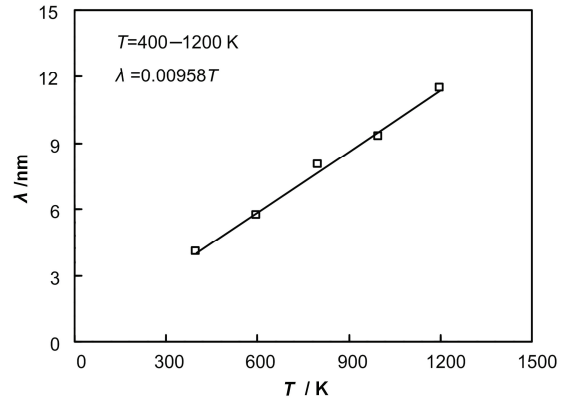


Fig.6 Simulated phonon approximate mean free path in UO_2 .

We can get the UO_2 phonon approximate mean free path variation tendency at different temperatures (Fig.6), and an approximate linear relation between the phonon mean free path and temperature. At high temperatures, disturbance of the phonon increases, and so does the phonon mean free path.

4 Conclusion

In this paper, the temperature dependence and scale dependence of thermal conductivities of uranium dioxide are studied using the non-equilibrium molecular dynamics method.

It is found that the thermal conductivity results agree well with the experiment data when the temperature is above 600 K. The results indicate that the non-equilibrium molecular dynamics simulation

supplies creditable support on the research of middle and high temperature thermal conductivity using the Kawamura function.

Scale dependence thermal conductivities of uranium dioxide thin films are studied in the present paper. Obvious scale effect of thermal conductivity exists in the film because of the impact of the boundary scattering and phonon mean free path decreases.

Uranium dioxide phonon approximate mean free path in different temperature can be gotten when thermal conductivity becomes a steady value. We can find out a linear relation between the phonon approximate mean free path and the temperature.

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