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Effect of thorium addition on the thermophysical properties of uranium dioxide: Atomistic simulations

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ABSTRACT

The effect of thorium addition on the thermophysical properties of uranium dioxide has been systematically investigated by molecular dynamics (MD) simulation technique in the whole concentration range of thorium and in the temperature range from 300 K to 2100 K. The Born-Mayer-Huggins (BMH) interatomic potential with the partially ionic model (PIM) was used and the potential parameters of thorium ion are derived from the experimental lattice constants data of thorium dioxide by the three point method. The predicted lattice parameter, thermal expansion coefficient, enthalpy, specific heat capacity, and thermal conductivity for the $U_{1-y}Th_yO_2$ solid solution all agree well with the available experimental data. The results indicate a significant effect of thorium content on the thermophysical properties of the $U_{1-y}Th_yO_2$ solid solution. The lattice parameters are increasing with the thorium content and closely followed Vegard's law, while the thermal expansion coefficient and enthalpy as well as specific heat capacity decrease very clearly with the thorium content. On the other hand, it is found that the $U_{1-y}Th_yO_2$ solid solution exhibits lower thermal conductivity than both the pure UO_2 and ThO_2. Additionally, a series of consistent equations for the thermophysical properties of $U_{1-y}Th_yO_2$ solid solution are recommended based on the MD data.

1. Introduction

Uranium dioxide (UO_2) is a standard nuclear fuel in modern fission nuclear reactors and has been studied extensively for over half a century. To reduce the fuel cost and the amount of spent fuel per unit energy generation as well as improve the physical properties of fuel matrix, the mixed oxide fuel such as $U_{1-y}Th_yO_2$ solid solution has been considered as an alternative to the conventional UO_2 fuel in the past few decades [1–6]. The reasons why the thorium containing fuels are possibly advantageous compared to pure UO_2 are the desirable properties of ThO_2 which include [7–9]: (1) the neutronic performance of ThO_2 is very excellent due to the high conversion ratio of the Th, (2) the thermal conductivity and melting temperature of ThO_2 fuel are higher than that of UO_2 fuel, (3) the amount of long-lived minor actinides and plutonium generated in the fuel cycle is small, and (4) the corrosion resistance of the ThO_2 fuel in the high-temperature water is very excellent.

Knowledge of the thermophysical properties of a nuclear fuel is of importance for the fuel design and understanding of the fuel behavior during irradiation. For example, the theoretical density of a fuel has been obtained from the lattice parameter and it is used to control the quality of the fuel pellets in the fabrication process. The thermal expansion of fuel is an important data to fuel designers for finding the extent of thermal stress the fuel is going to experience during its entire life in the reactor. The thermal conductivity of fuel is one of the most important properties, which determines the fuel temperature. A poor thermal conductivity will leads to a large temperature gradient across the fuel pellet. However, to the best of our knowledge, the available literature data shows that the lattice parameter [10–15], thermal expansion [16–19], enthalpy increments data [20–24], specific heat capacity [22–26] and thermal conductivity [14, 18, 22, 23, 27–32] of $U_{1-y}Th_yO_2$ solid solution exist over a limited composition and temperature ranges.

With the development of computer simulation techniques, molecular dynamics (MD) simulation has become extremely helpful in providing an atomic perspective on various properties of materials in recent years. Especially, due to the high temperature condition and radioactive toxicities, it is somewhat difficult to experimentally evaluate the thermophysical and other properties. Hence, the MD simulation techniques provide a useful means to simulate such extreme conditions. As far as we know, the thermophysical properties of UO_2 [35–39], ThO_2 [30–34], and (U, Pu)O_2 [40–43] have been predicted by MD method over a wide temperature, and the evaluated results are almost in good agreement with the experimental values.

Therefore, the objective of this study is to identify the effect of Th content on the thermophysical properties, such as lattice parameter, thermal expansion, enthalpy increments, specific heat capacity as well as the thermal conductivity of UO_2 fuel, using the MD simulation in the whole concentration range of Th and in the temperature

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range from 300 K to 2100 K. This study will help for studying the thermophysical properties of $U_{1-y}Th_yO_2$ solid solution at the atomic level in detail and supplement the available experimental data.

2. Simulation methodology

2.1. Interatomic potentials

As with any MD simulation, the reliability and accuracy of the results depends ultimately on the quality of the interatomic potential employed. The BMH potential with PIM which proposed by Arima et al. [38] has been chosen in the present study. This potential is given by

$$U(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6} \quad (1)$$

where, z_i and z_j are the effective partial electronic charges of type i and j; r_{ij} is the separation distance between atom i and atom j; f_0 (= 0.04339 eV/Å) is the adjustable parameter. Potential parameters, a_i, b_i and c_i, are given to the ion of types i. The first term of the right side of Eq. (1) represents Coulomb interactions. The second term is the repulsive potential between ionic cores and the third one is the attractive part of the van der Waals interaction. In the PIM, it is assumed that there exist no case of really pure ionic bonding or pure covalent Bonding in the metal oxides, and both UO_2 and ThO_2 are no exception [36]. The ionic bonding of 67.5% is considered for both UO_2 and ThO_2 systems, and namely that the charges of U ionic (same as the Th ionic) and O ionic are +2.7 and −1.35, respectively. The potential parameters of U^{4+} and O^{2-} ions are obtained from the literature [38]. The potential parameters of Th^{4+} ion are determined by fitting the lattice parameter data from experiment with the three point method, which was proposed originally by Basak [44].

The fitting procedure demands that there is no phase transformation in the all interesting temperature range. The first step is to fit the lattice parameter of ThO_2 at a low temperature (300 K in this work); after getting a good value, the same set of potential parameters are used to predict the lattice parameter at a high temperature (2100 K in this work); If the predicted lattice parameter at 2100 K matches experimental value, then the same set of potential parameters are used to calculate the lattice parameter at the intermediate temperature (1200 K). If the value at high temperature does not match well with the corresponding experimental value then start afresh the potential parameter immediately. The details of this method have been discussed elsewhere [44]. The potential parameters thus obtained for Th^{4+} ion as well as other ions are listed in Table 1.

For the pure ThO_2, the lattice constants as a function of temperature are shown in Fig. 1, together with the available experimental data [17, 45, 46]. It is shown that the predicted lattice parameters agree well with the experimental values in the temperature range from 300 K to 2100 K. In additionally, the melting point of pure ThO_2 has been predicted in this work with the two-phase simulation (TPS) method which has been used to evaluated the melting point of pure UO_2 successfully [39]. The predicted melting point of pure ThO_2 with the BMH potential in this work is 3625 ± 25 K, which is in very good agreement with the recent experimental value by Ronchi et al. [47] (3651 ± 17 K) and is also close to that recommended by Benz et al. [48] (3663 ± 100 K). The comparison of the lattice parameter and the melting point between theoretical and experimental results of above shows that the potential parameters obtained by the three point method in this work is appropriate for describing of the ThO_2.

Table 1
Potential parameters for the BMH type with PIM.

Ion	z_i	a_i(Å)	b_i(Å)	c_i(eV$^{0.5}$ Å^3)	Reference
U^{4+}	2.7	1.3180	0.0360	0	[38]
O^{2-}	−1.35	1.8470	0.1660	4.166	[38]
Th^{4+}	2.7	1.3546	0.0316	0	This work

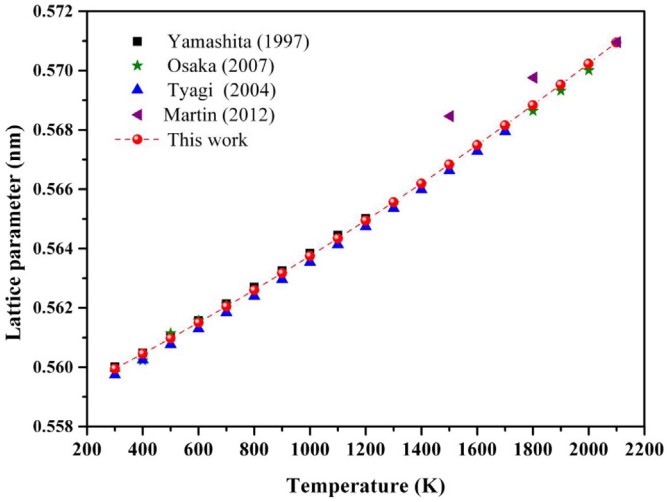

Fig. 1. Lattice parameter of pure ThO_2 dependence on the temperature.

2.2. Simulation techniques and conditions

Pure UO_2 and ThO_2 are identical in crystal structure (FCC CaF_2 type) with close lattice constants of 0.54704 and 0.55975 nm at room temperature, respectively [11]. Uranium or thorium atoms form a face centered cubic network, all tetrahedral sites of which are occupied by oxygen atoms. The mixed $U_{1-y}Th_yO_2$ ($0 < y < 1$) solid solution is assumed have the same structure as the pure UO_2 crystal based on the photomicrographs and X-ray study [11]. The mixed $U_{1-y}Th_yO_2$ ($0 < y < 1$) solid solution is modeled by substituting Th atoms for U atoms at random in the supercell. A cubic box contained 12,000 of atoms (10 lattice parameters a_0 along side) with 4000 cations and 8000 anions were applied to simulate infinite crystallite.

The MD simulation program, Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [49], which was developed at Sandia National Laboratories, is used to perform the simulations in the present work. The periodic boundary conditions (PBC) and the constant number of atoms, constant pressure and constant temperature ensemble (NPT) are used in the MD simulations. The pressure controlled by a Nose-Hoover barostat [50] and the temperature controlled by a Nose-Hoover thermostat [51]. The velocity verlet algorithm is used to calculate the atomic motions and the particle-particle particle-mesh (PPPM) Ewald technique [52] is applied for the calculation of the electrostatic interactions. The calculations were performed in a temperature interval from 300 to 2100 K. The simulation time step is taken to be 1.0×10^{-15} s. An equilibrium state of the system, that set the desired temperature and pressure, was reached during the first 50,000 steps and the thermophysical properties obtained from averages taken over the next 50,000 steps of the simulation.

3. Results and discussion

3.1. Lattice parameters

The changes in the calculated lattice parameter of $U_{1-y}Th_yO_2$ ($0 < y < 1$) solid solution with temperature and the thorium content are shown in Figs. 2 and 3, respectively, together with the available experimental data [6, 13, 17, 19, 24, 53, 54]. As obvious from Fig. 2, the calculated lattice parameters agree well with the experimental data up to 2100 K, although it should be noted that the calculated lattice parameters of pure ThO_2 are slightly overestimated, whereas pure UO_2 are slightly underestimated when the temperature above 1800 K. As