DETERMINATION OF THERMO-PHYSICAL PROPERTIES OF (Th,Ce)O₂ MOX USING CLASSICAL MOLECULAR DYNAMICS SIMULATIONS

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INTRODUCTION

In the recent past, considerable attention is being devoted to develop U₁₋xThₓO₂ and Puₓ₁₋xThₓO₂ mixed oxide (MOX) fuel for conventional pressurized water reactors and advanced heavy water reactors (AHWR) due to its superior performance in reducing the large plutonium stockpile while maintaining acceptable safety and control characteristics of the reactor system [1,2]. Moreover, Puₓ₁₋xUₓO₂ MOX have been used as fuels for fast reactors in many countries and MOX with higher amounts of PuO₂ are being considered as potential fuels for the plutonium burner reactors [1,2]. In order to understand the behavior of the thorium based fuel during irradiation and to predict its performance under accidental conditions, the thermophysical properties such as thermal expansion and thermal conductivities need to be evaluated first at ambient conditions. Moreover, determination of thermophysical properties of ThO₂-PuO₂ by experimental means is very difficult because of radioactivity and toxicity of PuO₂ based systems which require extensive and expensive safety precautions. One way to overcome this problem is to use CeO₂ as a surrogate material for PuO₂ as they both have very similar physio-chemical properties. Under this scenario, classical molecular dynamics (MD) simulation technique is a powerful tool to evaluate thermal properties of MOX in the desired composition range as well as in the high temperature regime not accessible to experimental techniques.

In the present study, we adopted classical MD simulation methodology to predict lattice thermal expansion (LTE) and thermal conductivity (TC) of pure ThO₂, CeO₂ and (Th,Ce)O₂ MOX using an interatomic potential consisting of Coulomb-Buckingham form.

THEORETICAL MODEL

The pair interaction potential of two particles in the ThO₂ system consists of Coulomb, short range repulsive and covalent bonding contributions:

\[ \phi_{\alpha\beta}(r) = \phi_{\alpha\beta}^{(C)}(r) + \phi_{\alpha\beta}^{(S)}(r). \]

The electrostatic interaction of two ions of type \( \alpha \) and \( \beta \) is given by Coulomb law:

\[ \phi_{\alpha\beta}^{(C)}(r) = \frac{q_{\alpha}q_{\beta}}{4\pi \varepsilon_0 r}, \]

where \( q_{\alpha} \) and \( q_{\beta} \) are partial charges of Th and O, respectively.

The short-range interaction is described by Buckingham-type potential (\( \alpha, \beta = \text{Th, O} \)):

\[ \phi_{\alpha\beta}^{(S)}(r) = A_{\alpha\beta} \exp\left(-\frac{r}{b_{\alpha\beta}}\right) - C_{\alpha\beta} r^6. \]

In our parameterization, \( A_{\alpha\beta} \) and \( C_{\alpha\beta} \) were assumed to be zero for Th-Th interactions and its contribution is incorporated through Th-O and O-O interactions. Similar potential model was adopted for CeO₂ and potential parameters were determined by fitting experimentally available lattice thermal expansion data for pure ThO₂ and CeO₂ in the 300-1500K range.

CMD simulations were carried out using the LAMMPS MD Simulator [3] and NPT ensemble with Nose–Hooke thermostat and barostat relaxation times of 0.1 ps and 0.5 ps respectively. Each simulation was carried out for 10 ps over a range of temperatures from 300 to 3000 K with the volume sampled every time step before being averaged over the last 2 ps, thereby ensuring enough time for the system to reach equilibrium.

RESULTS

This study determines lattice thermal expansion (LTE) and thermal conductivity (TC) of ThO₂ and (Th,Ce)O₂ MOX using classical molecular dynamic simulations considering an interatomic potential consisting of Coulomb-Buckingham potential form. The potential parameters of Coulomb-Buckingham function for Th-O, Ce-O and O-O were determined by fitting experimentally available LTE data for pure ThO₂ and CeO₂. The calculated linear
thermal expansion coefficients in the temperature range 300-1500K for ThO$_2$, CeO$_2$, Th$_{0.9375}$Ce$_{0.0625}$O$_2$ and Th$_{0.875}$Ce$_{0.125}$O$_2$ are 10.61, 13.08, 10.78 and 10.93x10$^{-6}$ K$^{-1}$, respectively (shown in Fig. 1). The MD calculated LTE values of ThO$_2$ and (Th,Ce)O$_2$ MOX are slightly higher than the experimentally determined values by Mathews et al. [4]. As MD calculations are performed on a model system with no incorporation of porosity, impurity effects, etc. In contrast, the experimental samples are not devoid of these effects where some part of the lattice thermal expansion may be accommodated in the porosity of the samples. Moreover, this interatomic potential of ThO$_2$ predicts $\alpha$ values which are close to previous HT-XRD measurements.

The MD calculated TC values, especially, in the high temperature range from 600 to 1200 K, our results accords very well with the our experimental measurements [2] and previous results reported by Cozzo et al. [5] (shown in Fig. 2). At the low temperature range around the Debye temperature of 402 K, our results are slightly different from some experimental results as the difference comes from our presumption that the dominant mechanism for phonon scattering is the Umklapp process.

Fig. 1: Variation of unit cell dimension of pure ThO$_2$, Th$_{0.9375}$Ce$_{0.0625}$O$_2$ and Th$_{0.875}$Ce$_{0.125}$O$_2$ in the 300-3000 K temperature range along with HT-XRD data.

Fig. 2: TC calculated by MD simulations as a function of temperature for ThO$_2$, Th$_{0.9275}$Ce$_{0.0625}$O$_2$ and Th$_{0.875}$Ce$_{0.125}$O$_2$ compared with our experimental values. Solid lines are only for visual guide.

REFERENCES