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Effect of fission generated defects and porosity on thermo-mechanical properties of thorium dioxide

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ABSTRACT

The effect of fission product (FP) defects and porosity on thermo-mechanical properties of ThO_2 within 300–1500 K has been investigated using molecular dynamics (MD) simulations. We consider two typical FPs: Xe and Kr (0–2% defect). Our results indicate that these FPs reduce the thermal expansion (α) at low temperature; however, α of the defected system is similar to that of pure ThO_2 at the elevated temperature. For porous ThO_2 (0–5% porosity), α is within 5% of that of pure system at all studied temperature. The elastic modulus at finite temperature decreases linearly with the increase in the concentration of Xe, Kr and porosity. The degree of reduction (R) in elastic modulus follows the trend $R_{Xe} > R_{Kr} > R_{Porosity}$ for all the studied concentration of defects. The MD derived changes in the elastic modulus by FPs and porosities can be well described by the affine functions. We report that the porous ThO_2 shows higher reduction in elastic properties than porous UO_2. A detail calculation of 0 K properties as a function of defect concentration is presented.

1. Introduction

Higher abundance of thoria (ThO_2) in the earth crust, 3–4 times higher than traditional urania (UO_2), makes it a potential candidate for alternative fuel. ThO_2 is energy efficient and highly economical as nuclear fuel because of its greater burn-ups and higher concentration of thorium (2–10%) [1]. In addition, ThO_2 does not oxidize to higher oxidation states as Urania fuel and inhibits oxidation of mixed oxide (MOX) fuel when combined with urania [2]. Thoria is also of significant interest as a fuel for safer reactors due to its high thermal conductivity and high melting point [3]. However, in contrast to UO_2, thermo-mechanical properties of thoria have been reported only in a limited number of studies [4–11].

In general, due to irradiation impact, nuclear fuel undergoes severe degradation of physical, thermal and mechanical properties. The irradiation generated fission products and porosities are of significant importance, as these defects can produce bubbles or voids that lead to fuel swelling or fragmentation and that deteriorate fuel performance [12,13]. For example, studies have shown that the released inert gases trapped in the fuel-cladding gap reduce the thermal conductivity of the fuel channel [14]. The reduction in conductivity causes overheating of the fuel element and increases the pressure on the cladding tube [14]. Therefore, in order to better characterize irradiated fuel, a comprehensive understanding of how fission product and porosity affect fuel behavior is essential.

Urania (UO_2), being a traditional component of nuclear fuel assembly, is examined in few studies to understand the effect of porosity on thermal and elastic properties [15–17]. In an experimental study of porous UO_2 with 0–10% (volume fraction) porosity and pore size < 2 μm, Roque et al. showed a linear reduction in elastic properties at room temperature [16]. Additionally, using atomistic modelling, Jelea et al. investigated the effect of porosity (0–12 at%) on thermal expansion and elastic properties of UO_2 as a function of temperature [17]. The authors reported lower thermal expansion coefficient for porous systems in low temperature range, and also concluded that existence of porosity results in a decrease in the elastic modulus at all temperatures. The reduction in elastic properties of UO_2 is described by the affine functions, similar as in the previous studies [15,16]. However, to our best knowledge, no investigation is focused on the effect of fission product defects and porosity on the thermo-mechanical properties in ThO_2. In this work, we will examine the influence of typical fission products Xe, Kr and fuel porosity on thermal expansion and elastic modulus of

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ThO_2 using molecular dynamics (MD) simulation. This study will contribute to the better understanding of changes of structure and properties of ThO_2 fuel after irradiation.

The reliability of MD simulation strongly depends on the accurate description of atomic interactions in nuclear fuel systems. In the past, Cooper, Rushton and Grimes (CRG) [18] developed a many-body interatomic potential for pure and mixed actinide oxides, which was used to predict a wide range of thermo-physical properties of these systems at temperatures between 300 and 3000 K [6,7,11,19]. Later on, Cooper et al. developed a complementary potential set for modelling Xe and Kr incorporations in a number actinide oxides including ThO_2 [20]. Therefore, this potential set is adopted for the present study.

In this work, MD simulations have been used to investigate the effect of fission product (FP) and porosity on the thermal expansion and elastic properties in ThO_2. We consider xenon (Xe) and krypton (Kr) as FPs in a range of temperature from 300 to 1500 K. Thermal expansion of pure and defected ThO_2 is evaluated from the changes in corresponding lattice parameters. Three independent elastic constants are calculated for each system, which are then used to estimate the elastic modulus. The reduction of elastic properties resulting from Xe, Kr and porosity is calculated for different concentration of the defects. A comparison is made between the effect of FPs and porosities. The elastic modulus of porous ThO_2 is also compared with that of conventional UO_2. Particular attention has been paid to the fitting of the elastic modulus to the affine functions. Elastic properties at 0 K as a function of defect concentration is also calculated.

2. Computational method

In the present study, LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) code [21,22] was used to carry out the MD simulations. The interatomic forces in the actinide oxide are described by the many-body potential developed by Cooper et al. [18]. In order to incorporate the interactions of Xe and Kr with the actinide and oxygen atoms, other sets of complementary parameters have been used [20]. For MD systems, an extension of $10 \times 10 \times 12$ fluorite unit cell has been employed in all cases. The size of the supercells were determined to accommodate different level of defect concentrations. Larger system size ($20 \times 20 \times 20$) was also examined; however, the results obtained were similar. The supercells were created using the equilibrium lattice parameter at each temperature. We investigated a wide range of temperature from 300 to 1500 K at an interval of 300 K.

In order to generate the structures of thorium dioxide with the fission products (FP), Xe and Kr atoms are inserted at different substitutional sites in the system. The FPs replace the actinide and oxygen atoms in a 1:2 proportion such that the fuel material remains charge neutral. Similarly, the fuel porosities are created by removing Th and O_2 atoms and preserving the stoichiometry of ThO_2. As the atoms are removed from different positions, the size of the pores are expected to be one atom diameter. In order to investigate the effect of defect concentration, we generated the ThO_2 structures with 0.25%, 0.5%, 1%, 2% FPs and 1%, 2%, 5% of porosities.

Initially, the system was equilibrated at the temperature of interest for 500–1500 ps using an isobaric-isothermal (NPT) ensemble at zero external pressure. The oxides with higher defect concentration require longer time for the equilibration. Periodic boundary conditions were applied in all directions in these simulations and a time step of 1fs was used throughout.

The lattice parameters were calculated as a function of temperature for all concentrations of defects and porosities. Subsequently, the linear thermal expansion coefficients (α) were determined from the first derivative of the lattice parameter with respect to temperature using the following relation:

$$\alpha = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_P \tag{1}$$

where, L is lattice parameter and $\left(\frac{\partial L}{\partial T}\right)_P$ was extracted from the slope of the plot of lattice parameter as a function of temperature. The slope is calculated by fitting a straight line to the lattice parameter changes at a specific temperature and other data points within 30 K on either side [7].

As thorium dioxide has cubic structure ($Fm\bar{3}m$ symmetry), there are three independent elastic constants to calculate: C_{11}, C_{12} and C_{44}. Once the elastic constants are computed, we measured the isothermal bulk modulus (B) and shear modulus (G) and young's modulus (Y) using Hill's average [23] approach obtained from Voigt [24] and Reuss [25] methods. The compressibility is also estimated as the inverse of the bulk modulus.

The bulk modulus for a cubic system is same for Voigt, Reuss and Hill's average and is calculated using the following relation:

$$B = (C_{11} + 2C_{12})/3 \tag{2}$$

Voigt [24] formulation used to calculate the shear modulus is as follows:

$$G_V = (C_{11} - C_{12} + 3C_{44})/5 \tag{3}$$

On the other hand, according to Reuss [25] method, the shear modulus is:

$$G_R = (5(C_{11} - C_{12})C_{44})/(4C_{44} + 3(C_{11} - C_{12})) \tag{4}$$

The Hill's average [23] of shear modulus is obtained by the arithmetic mean of Voigt (G_V) and Reuss (G_V) approach:

$$G_H = (G_V + G_R)/2 \tag{5}$$

Having derived B and G_H, the young's modulus for an isotropic aggregate was calculated from the following equation [26]:

$$Y = 9BG_H/(3B + G_H) \tag{6}$$

3. Results and discussion

3.1. Lattice parameter

The calculated lattice parameter (L) of pure ThO_2 as a function of temperature is shown in Fig. 1. The fitted line indicates a linear increase in L with the temperature within the studied range. For comparison, experimental data by Mathews et al. [27] and Yamashita et al. [28] are also included. Fig. 1 shows a good agreement between MD derived values and the experimental results.

In Fig. 2, lattice parameter of defected ThO_2 is plotted as a function of fraction (%) of Xe and Kr (Fig. 2a) and porosity (Fig. 2b). The figures show a linear increase in L with the concentration of the fission products and porosities. Because of comparatively bigger atomic radius of Xe, the ThO_2–Xe system has larger lattice parameters than that of ThO_2–Kr and the difference increases with the increase in temperature. In addition, Fig. 2a and b demonstrate that the porosity increases the L to a smaller extent compared to that observed for fission products. For 2% Xe, Kr and porosity, L is increased by 1.09, 0.8 and 0.1% respectively at 300 K and 1.16, 0.86 and 0.11% respectively at 1500 K. Therefore, the rate of increment in L with temperature increases marginally in all cases.