Chapter 8.

Thermal expansion

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Abstract

Thermal expansion of fuel pellet is an important property which limits the lifetime of the fuels in reactors, because it affects both the pellet and cladding mechanical interaction and the gap conductivity. By fitting a number of available measured data, recommended equations have been presented and successfully used to estimate thermal expansion coefficient of the nuclear fuel pellet. However, due to large scatter of the measured data, non-consensus data have been omitted in formulating the equations. Also, the equation is strongly governed by the lack of appropriate experimental data. For those reasons, it is important to develop theoretical methodologies to better describe thermal expansion behaviour of nuclear fuel. In particular, first-principles and molecular dynamics simulations have been certainly contributed to predict reliable thermal expansion without fitting the measured data. Furthermore, the two theoretical techniques have improved on understanding the change of fuel dimension by describing the atomic-scale processes associated with lattice expansion in the fuels.

Introduction

Upon being heated in reactor, nuclear fuels thermally expand with temperature. Uranium dioxide (UO_2), which is a representative nuclear fuel in light water reactors (~95% of all fuel), has a cubic crystal structure, with uranium in a face centred array and the oxide ions occupying the tetrahedral holes. This cubic structure gives the uranium oxide pellet uniform expansion properties. The thermal expansion of fuel pellet contributes to pellet-clad mechanical interaction, which is known to cause fuel rod failure under operation condition. As manufactured, a roughly axisymmetric gap exists between the outer radius of cylindrical UO_2 fuel pellets and the inner surface of the cladding in fuel rods. The gap thickness is decreased during the operation by the thermal expansion of fuel pellet as well as the cladding creep down due to the high coolant pressure, causing the pellet-cladding mechanical interaction (PCMI) at power transient conditions [1]. In addition, due to

relatively low thermal conductivity of oxide fuel materials, such as ThO_2, UO_2, and mixed oxide of $(U,Pu)O_2$, a steep radial temperature gradient appears in the fuel pellet and leads to differential thermal expansion along the radial direction. The thermal expansion results in the liner strain of fuel and takes part in the degradation of thermal conductivity of fuel in a recurrent manner. As a result of the non-uniform thermal expansion by the radial temperature gradient, the circumferential thermal stress is developed in the pellet, causing radial cracking [2]. The cracks strongly influence on both thermal and mechanical performance of the fuel, altering temperature distribution and causing an anisotropic degradation of the fuel thermal conductivity by the pellet relocation [3]. Owing to these characteristics of fuel pellet, the thermal expansion is one of important parameters in determining the fuel performance during reactor operation. Furthermore, it is essential to predict accurately the thermal expansion of fuel pellet to design and prevent the fuel rod failure in operating condition.

In this report, representative modelling methodologies are encapsulated, which have been satisfactorily used to elucidate thermal properties of nuclear fuels. First, measured data fitting is reviewed and equations to estimate thermal expansion of fuels are recommended. Subsequently, the application of first-principles techniques is described to calculate the expansion coefficient of UO_2. Molecular dynamics (MD) methods are also summarised and the results are compared with experiments. Finally, the current status of first-principles and MD simulations is discussed, considering existing limitations such as the application of the approximations for high-temperature behaviour and the determination of parameters in potential functions.

Theoretical methodologies

Empirical correlation

The thermal expansion is typically measured either by a macroscopic length change or by a microscopic change of lattice parameter. A number of measured data, especially for UO_2, have been reported in the literature, and equations of thermal expansion have been recommended by comparing the macroscopic length change with the lattice parameter measurements [4]. Using a weighted least-squares minimisation procedure, D.G. Martin has fit the macroscopic length changes with the lattice parameter measurements and recommended the equations of the thermal expansion for solid UO_2 [5], as written in Equations 1 and 2:

For 273 K ≤ T ≤ 923 K:

$$L = L_{273}\left(9.9734\times10^{-1} + 9.802\times10^{-6}T - 2.705\times10^{-10}T^2 + 4.391\times10^{-13}T^3\right) \qquad (1)$$

For 923 K ≤ T ≤ 3120 K:

$$L = L_{273}\left(9.9672\times10^{-1} + 1.179\times10^{-5}T - 2.429\times10^{-9}T^2 + 1.2119\times10^{-12}T^3\right) \qquad (2)$$

where L and L_{273} are the lengths at temperature T(K) and 273 K, respectively. J.K. Fink has also summarised the measurement of fractional change in length of UO_2 with the recommended uncertainties and the data fit [6]. Although the thermal expansion data from macroscopic and the lattice parameter measurements are overall good agreement with each other, there are non-dispensable problems in assessing the quality of the available data due to the fact that the two principal methods are each subject to

possible errors. For example, it has been known that the lattice parameter measurements obtained from X-ray diffraction can be subject to error at high temperature, because of difficulties in measuring sufficiently the temperature of samples in the high-temperature diffraction camera [5]. Consequently, some of data do not agree with the common consensus and accordingly were excluded in the fitting for formulating Equations 1 and 2. Apart from the difficulties, the contribution of Schottky defects to the macroscopic expansion becomes significant above around 2 700 K and leads to increasing the difference of macroscopically measured data with lattice parameter measurements [7]. Furthermore, the fitting to formulate the recommended equations of thermal expansion is largely governed by appropriate experimental data. Because of those technical difficulties of measurement as well as the lack of appropriate experimental data, it is definitely essential to improve theoretical methods to understand the thermal expansion behaviour of nuclear fuels. Recently, big efforts have been made to develop databases of materials properties by applying atomistic modeling techniques [8,9]. Most of all, assessment of the measurements as well as a step forward in understanding the thermal properties of nuclear fuels can be gained from a better description of atomic-scale processes in nuclear fuels.

First principles modelling

The change of lattice parameter with temperature is directly related to thermodynamics of a system containing particles within molecule or crystals. In thermodynamics, the total free energy of the system at a certain temperature has contributions from the lattice vibrations and the thermal excitation of electrons. To obtain the temperature dependence of the lattice parameter, the Helmholtz free energy, $F(V,T)$, is used at the temperature.

$$F(V,T) = U(V) + F^{phon}(V,T) + F^{el}(V,T) \qquad (3)$$

where $U(V)$ the static lattice energy, $F^{phon}(V,T)$ the phonon contribution to the free energy, and $F^{el}(V,T)$ the free energy of the electronic subsystem. The static lattice energy is the potential energy associated with the static constituent of material and is equal to the total free energy at absolute zero temperature. With increased temperature, the phonon energy due to the lattice vibration as well as the electron contribution becomes significant to the total free energy. First, the static lattice energy can be obtained using various first-principles methods, typically density functional theory (DFT) calculations, at the equilibrium volume at $T = 0K$. Calculating the static lattice energy by the DFT method is explained in Chapter 12 (by M. Freyss) in more detail. The free energy contribution of phonon, $F^{el}(V,T)$, is expressed as follows:

$$F^{phon}(V,T) = \int_0^\infty d\omega\, g(\omega) \left[\frac{\hbar\omega}{2} + k_B T \ln(1 - e^{-\hbar\omega/k_B T}) \right] \qquad (4)$$

The phonon density of states (DOS), $g(\omega)$, the force constant matrix can be extracted from the Hellman-Feynman forces, which are calculated by using either the linear response theory or the direct approach, is used. In the former approach, a perturbation of the atomic positions with the periodicity of the original lattice is treated with standard perturbation theory, and first-order corrections are computed [10,11]. In the direct approach, or so-called supercell method, a finite displacement of several atoms is employed in a supercell to compute atomic force constants and the phonon spectrum [12,13]. The free electron energy has been approximated using the following expression:

$$F^{el}(V,T) = -(\pi k_B)^2 / 6D(E_F)T^2 \tag{5}$$

where $D(E_F)$ is the electron DOS at the Fermi level. When the phonon and electrons DOSs are calculated, the thermal expansion coefficient is obtained very straightforward. First, the phonon and electrons DOSs with static lattice energy is calculated for a number of volumes around the T=0K equilibrium. Then, the total free energies are calculated for the different volumes at constant temperature using Equations 3-5. Once the free energy is calculated, the corresponding equilibrium volume is obtained. By repeating the process for different temperatures, the thermal expansion coefficient, α, defined by:

$$\alpha \equiv \frac{1}{a}\frac{da}{dT} = \frac{1}{3V}\frac{dV}{dT} \tag{6}$$

where a is the lattice constant. Figure 1(a) shows the thermal expansion coefficient of UO$_2$ calculated by Yun et al. [9] using the first-principles DFT method. To obtain the phonon free energy as written in Equation 5, the phonon density of state of UO$_2$ was calculated using a 96-atom supercell based on the direct method. They presented that the electronic contribution was not included in the calculation, because the electronic contribution can be negligible in the temperature range up to 1 000 K, which is the range of interest in the work. In Figure 1(a), the calculated thermal expansion coefficient considering only the phonon contribution is in good agreement with experimental data [20] especially up to 500 K, and the deviation becomes significant at around 1 000 K. This might be due to an increased electronic contribution to the thermal expansion. It is important to note that the phonon calculation from first-principles is based on the harmonic lattice approximation that the atomic deviations are assumed to be so small, and this is generally a good approximation, at least at relatively low temperatures [14].

Molecular dynamics with empirical potentials

Molecular Dynamics (MD) is useful in the study of non-equilibrium dynamic processes at the atomic level. Especially, in extreme conditions of high temperature or high pressures, the MD simulation is often the best way to obtain the necessary information [15]. In recent years, a number of studies on thermophysical and transport properties of nuclear fuels have been published using classical potentials in the MD simulations. The MD results have been overall in good agreement with experimental data. It should be noted that in the MD simulations it is crucial to select well-established interatomic potential function to obtain reliable results, because it requires technically many fitting parameters or coefficients of interatomic potentials. A number of interatomic potentials developed over the past decades are categorised into two kinds of functions [16]: (1) rigid-ion model and (2) shell model. T. Arima et al. calculated the lattice constant of UO$_2$ with temperature applying two different sets of rigid-ion potentials [17]. One is the Born-Mayer-Huggins (BMH) potentials with the fully ionic model (FIM), which assumes that UO$_2$ crystal is fully ionic-bonded with 100% of the ion valence. The BMH potential with FIM is given by:

$$U_{FIM}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + A_{ij}\exp(-\frac{r_{ij}}{\rho_{ij}}) - \frac{C_{ij}}{r_{ij}^6} \tag{7}$$

where r_{ij} is the distance between ions of types i and j, z_i is the charge of type i. A_{ij}, ρ_{ij} and C_{ij} are potential parameters. The other function developed by T. Arima et al. is the BMH potential with the partially ionic model (PIM) and is written by:

$$U_{PIM}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i + b_j)\exp\left\{-(\frac{a_i + a_j - r_{ij}}{b_i + b_j}) \times \left(-\frac{r_{ij}}{\rho_{ij}}\right)\right\} - \frac{c_i c_j}{r_{ij}^6} \tag{8}$$

where f_0 is the adjustable parameter. Potential parameters, a_i, b_i, c_i are given to the ion of types i. In this equation, z_i is the effective charge of type i ion. Following the Pauling's equation, T. Arima et al. assumed the ionic bonding of 67.5% for UO_2.

Figure 1. Lattice constants of UO_2 using the first-principles DFT method [9] and (b) using MD [17] and compared with experimental data: a) [20], b) [21], c) [5]
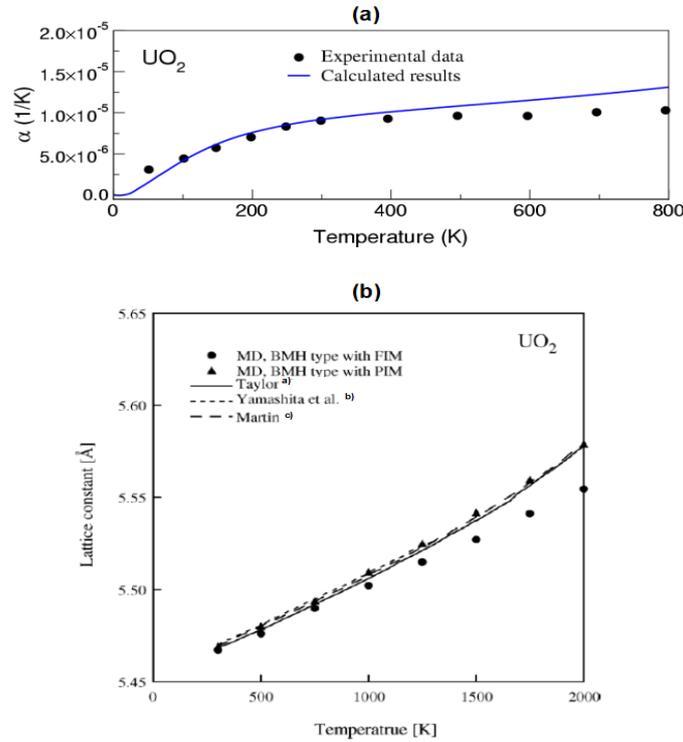

Figure 1 shows the lattice constants of UO_2 using both the BMH potential with the FIM and PIM, and compared the results with experimental data. The results obtained for the FIM are comparable with experimental data up to 1 000 K, but above 1 000 K, the PIM better reproduced the experimental data than the FIM. It is because the depressing Coulomb force between uranium and oxygen ions leads to the relatively large thermal expansion at high temperature. On the other hand, the Morse potential successfully explained the temperature dependence of the thermal expansion coefficient, especially for fluorite-type compounds [18], such as ThO_2, UO_2, and PuO_2.

$$V(r) = D[\exp\{-2a(r - r_0)\} - 2\exp\{-a(r - r_0)\}] \tag{9}$$

where D is the depth of the potential, r is the interatomic separation, r_0 is the interatomic separation at the potential minimum, and a is the inverse line width of the potential. H. Inaba presented the thermal expansion coefficients calculated by the morse potential for ThO_2 and UO_2.

The calculated thermal expansion coefficients are overall in good agreement with the experimental data below around 1 300 K for ThO_2 and 1 000 K for UO_2, but the difference is increased above the temperatures both for ThO_2 and UO_2. It is considered that the larger experimental values of the thermal expansion coefficient at high temperature are mainly due to the contribution of vacancies created.

Conclusion and future challenges

Along with the consistent development of interatomic potentials, the description on thermal expansion behaviour of nuclear fuels has also been improved for the past decades. However, the parameters in the potential functions have been fitted on different experimental data, and are normally difficult to apply to other materials. Hence, it is still challenging to establish potentials which can be applied to various nuclear fuel materials at broad temperature ranges. In addition, system size (up to few million atoms) and time (up to a few nanoseconds) is a major limitation required to be improved in the MD simulations[16]. The application of first-principles methods is even more demanding. The first-principles calculation is fundamentally to describe the ground states of materials, and the harmonic lattice approximation is valid at relatively low temperature. Therefore, there are limits to extending the application of the first-principles method at high temperature [8], in particular, over 1 000°C that nuclear fuels are exposed to under reactor operation. For a better description of temperature-dependent properties including thermal expansion, DFT-based MD simulations have been successfully applied over a wide range in temperature, up to about 2 700°C [19]. Despite a significant step forward in development of temperature-dependent DFT in combination with MD simulations, it has not yet been employed to nuclear fuels, especially no application result yet for thermal expansion behaviour of the fuel materials. In order to successfully apply DFT-MD methods for thermodynamic properties of nuclear fuel, both the first-principles and MD methods need further improvement, with the primary need being associated with the ability to scale up to larger numbers of atoms and to develop high-temperature predictions of nuclear fuel behaviour.

With increased temperature, the free energy of electrons became significant. To take into account for the contribution of electrons on the total free energy, a finite temperature DFT functional is needed, such as Mermin functional [22], rather than the ordinary DFT energy functional to treat the thermal excitation of electrons. Beside the thermal expansion of fuel itself, the fuel expansion originates from swelling due to fission products. Therefore, fuel burn-up is also needed to be considered to accurately estimate the fuel expansion during irradiation.

It is challenging to describe the thermal expansion of nuclear fuel during irradiation because of the complex environment in reactor and various parameters affecting to fuel behaviour, such as temperature, burn-up, stoichiometry, fission products, and correlations between the parameters. Therefore, broader consideration is required from the fundamentals of thermal properties of fuel to the macroscopic thermal behaviour in

reactors to accurately estimate the thermal expansion of fuel. To achieve this, it is necessary to improve the theoretical estimation techniques and a multi-length and -time scale approach will be an appropriate method to assess such a complex fuel behaviour.

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