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Multi-scale simulation of Thoria-SiC composites

Barbara Szpunar
Department of Physics and Engineering Physics, University of Saskatchewan

Linu Malakkal, Ravi Kiran Siripurapu & Jerzy A. Szpunar
Department of Mechanical Engineering, University of Saskatchewan

Juan Carlos Zuniga
Information and communications technology, research computing, University of Saskatchewan

ABSTRACT: Multi-scale simulations are used to investigate the thermal conductivity of ThO_2-SiC composites. The predicted, enhanced thermal conductivity of the composities leads to the reduction of centerline temperature and temperature gradients in a fuel pellet. These composite fuels would make nuclear reactor safer as a probability of fuel melting would be reduced. The lower temperature gradients reduce thermal stresses and therefore prevent fuel cracking and longevity of the fuel is increased.

1 INTRODUCTION

Recent nuclear accident in Fukushima clearly illustrates the risks associated with the present design of reactors based on pure uranium oxide fuel and justify the research towards accident tolerant fuel. Failure analysis shows that this accident could have been avoided using nuclear fuels with enhanced thermal conductivity. These fuels with enhanced thermal conductivity can withstand the loss of coolant for a long time by allowing faster dissipation of heat, thus lowering the centerline fuel temperature and preventing the melting of the fuel.

Pioro et al. [1] demonstrate that the traditional urania fuel is not suitable for some designs of new generation reactors due to its low thermal conductivity (e.g. the estimated fuel centerline temperature for SuperCritical Water reactor (SCWR) surpasses the industry accepted limit of 1850°C).

Thoria based fuel is regarded as a safer alternative since it does not oxidize, has higher melting temperature and thermal conductivity than urania. However its thermal conductivity is still too low for some designs and therefore it is worth to explore its composites using materials with high thermal conductivity.

Silicon carbide and Beryllium oxide are considered as candidate materials for making composites because of its excellent properties. It has been already demonstrated that the thermal conductivity of uranium oxides can be improved by the addition of BeO [2]; for example 10 vol.% of continuous phase BeO in UO_2 increases its thermal conductivity by ~ 50%. However thermal conductivity is very sensitive to porosity. It is therefore encouraging that the experimental techniques have been proposed to produce fully dense composities using Spark Plasma Sintering (SPS) [3]. However these experiments are very costly and time consuming, therefore we developed a method, which combines the predictive power of the first principles calculation with multiscale simulation. This approach can be used as an introductory step in evaluating the properties of various possible additives in composite fuels to increase theirs conductivity since enhancing the thermal conductivity is crucial in developing accident tolerant nuclear fuel.

2 MULTI-SCALE SIMULATION

The aim of our multi-scale simulation is first to calculate the thermal conductivities of various composities and next to use it to evaluate the temperature and temperature gradient profiles in operating cylindrical fuel rod. We investigate here 5vol%, 10vol% and 15vol% SiC/ThO_2 composities.

2.1 *Thermal conductivity calculations*

It has been demonstrated previously [4-6] that the phonon contribution to the thermal conductivity of thoria can be well reproduced using a simplified Slack model [7] with the input parameters evaluated from the first principles calculation. The first principles molecular dynamics calculation allows us to predict thermal expansion and to model thermo-mechanical properties of thoria up to a very high

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temperatures (up to 3300 K) [6], but they are computationally very demanding.

Here we use the results obtained by quasi-harmonic approximation as in Refs [4,5]. They have been described in details recently [8]. In the calculation of the thermal conductivity of SiC and ThO_2 [8] we used the Quantum ESPRESSO (QE) code [9].

The calculation for hexagonal SiC structures (2H, 4H) were carried out implementing density functional theory within a Perdew-Zunger (Local Density Approximation) [10] and norm conserved pseudopotential from QE PP library (pz-vbc.UPF). The structural and mechanical properties have been calculated using a kinetic energy cutoff of 70 Ry over a Brillouin zone integration of 8x8x5 mesh. The dynamical matrices were calculated on a mesh of 4x4x2 q-points in the irreducible Brillouin zone. In case of ThO_2, the recently proposed GGA functional for solids, PBEsol [11] was used with the pseudo-potentials generated using opium code [12] for PBE [13] functional. The kinetic energy cut-off of 70 Ryd and Brillouin zone integration was performed on a Monkhorst-Pack k-point mesh 8x8x8. For the Lattice dynamic calculation the dynamical matrices were calculated on a 4x4x4 mesh.

The methodology used to calculate the thermal conductivity using the thermo-mechanical properties derived from first principle calculations are very well explained in our recent paper [8] on interface to Quantum ESPRESSO. We have also developed a Fortran code for Slack model [7], that accepts the inputs in comma format and generates the lattice contribution to thermal conductivity as a function of temperature in the same format. The Slack equation for lattice thermal conductivity is as shown in Eq. 1:

$$\kappa_L = \frac{C\theta(T)^3 M_M V(T)^{1/3}}{(n\gamma(T))^2 T} \quad (1)$$

where it is assumed that "C" is constant and equal to 3.04×10^4 $Wm^{-2}K^{-1}$ g^{-1} mol for both SiC and ThO_2. "M_M" is molar mass per primitive cell (e.g. 264 g mol^{-1} for ThO_2) and "V(T)" is the volume of the primitive cell in cubic m. "θ" is the Debye temperature (in K) evaluated within the isotropic approximation [14]. In the denominator "n" is the number of atoms per primitive cell (e.g. 3 for ThO_2), "γ(T)" is the Grũneisen parameter evaluated as described previously [6,8] for the temperature "T".

2.2 *Temperature profile calculations*

In order to determine the temperature distribution, the thermal conductivity of the fuel must be known. In our previous simulations [15] we investigated fuel behavior up to the very high temperatures, therefore electronic and radiative contribution to the thermal conductivity had to be taken into account. Here we perform simulation at lower temperatures (up to 1600 K) where thermal conductivity is dominated by lattice contribution and can be expressed in an analytical form as a function of temperature as:

$$k_L = \frac{1}{a + bT} \quad W\ m^{-1}\ K^{-1} \quad (2)$$

where "a" and "b" parameters are independent on the temperature T. Using the predicted thermal conductivity as a function of temperature from Eq. 1, as described in 2.1, we can find the respective "a" and "b" parameters by fitting the analytical formula to the data calculated by Eq. 1. Next the thermal conductivities of the composites can be approximated as an average over volume concentrations of the thermal conductivities of the constituents of composites (e.g. for ThO_2-SiC):

$$k_L^{SiC/ThO_2} = (C_{vol\%}^{SiC} k_L^{SiC} + C_{vol\%}^{ThO_2} k_L^{ThO_2})/100 \quad (3)$$

The temperature of cylindrical fuel rod is calculated for various composites using the thermal conductivity evaluated by Eq. 3 and by solving the steady state heat conduction equation for cylindrical symmetry:

$$\frac{1}{r}\frac{d}{dr}\left(r k_L^{SiC/ThO_2} \frac{dT}{dr}\right) + H = 0 \quad (4)$$

where "r" is radial coordinate of cylinder and "H" is volumetric heat generation rate from fission as described previously [15]. Eq. 4 is subject to the boundary conditions:

$$\frac{dT}{dr} = 0, \quad r = 0$$
$$T = T_S, \quad r = a \quad (5)$$

Where it is assumed that the temperature on the fuel surface is constant and equals to "T_S" and "a" is the radius of the fuel pellet. Eq. 4 is solved using the code developed in MAPLE [15] and both the temperature and the temperature gradients (dT/dr) are printed as a function of radial (r) coordinate of the cylindrical shape fuel pellet.

3 RESULTS

3.1 *Ground State Properties*

Thoria has a cubic structure as shown in figure 1a, while SiC forms many polytypes.

We evaluated properties of cubic SiC in our previous work [8] while here we investigate lower

thermal conductivity phase: hexagonal 8H SiC, as shown in figure 1b. The predicted ground state properties of both 8H hexagonal SiC and Thoria in cubic structure by Quantum Espresso code shows good agreement with experiment and is shown in Table 1.

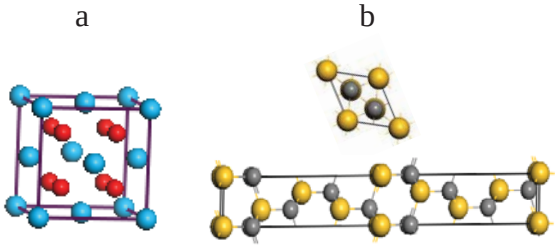

Figure 1. The crystal structure: a) ThO_2 (larger spheres indicate Th atoms), b) 8H SiC, where larger spheres indicate Si atoms.

Table 1 The calculated versus measured lattice constants (a, c; in Å) and bulk moduli (B; in GPa) of 8H hexagonal SiC and ThO_2.

Property	Calculated	Experiment
a_{Thoria}	5.528	5.598 [16]
a_{SiC}	3.067	3.079 [17]
c_{SiC}	20.065	20.147 [17]
B_{Thoria}	202.8	223[18], 193[19]
B_{SiC}	224.7	

We noted that, the "a" values of lattice constants for SiC hexagonal polymorphs do not change much when performing geometry optimization for 4H and 8H hexagonal SiC (3.063 Å versus 3.067 Å). Interestingly it was also found experimentally [20] that the principal axial thermal expansion coefficients of SiC polytypes (3C, 4H, 6H) are identical, including that of <111> direction of cubic SiC. This experimental observation together with our studies of the structure of 4H and 8H SiC lead us to the conclusion that we can restrict our calculation of lattice dynamics to only 4H SiC. The bulk modulus of hexagonal 4H and 8H SiC polytypes has been found to be the same and equal 224.7 GPa, which is close to the experimental value of 230.2 (4) for 6H SiC and 223 GPa for 2H SiC [21]. We could not find experimental data on the mechanical properties of 8H SiC.

3.2 *Thermal conductivity*

In the temperature range (up to 1600 K) considered here the thermal conductivity is satisfactory described by phonon contribution only. In figure 2a we compared the phonon contribution to the thermal conductivity (Eq. 1) of thoria with experiment [22], corrected by factor $(1\text{-}0.05)^{1.5}$ for 5% porosity and agreement with experiment is good. The figure 2a also shows that the theoretical κ_L results for 6H & 8H SiC are very close to the experimental [23] (6H SiC, corrected for 2% porosity by factor $(1\text{-}0.02)^{1.5}$). As discussed in Section 3.1 we used here for 8H SiC the thermal expansion calculated for 4H SiC.

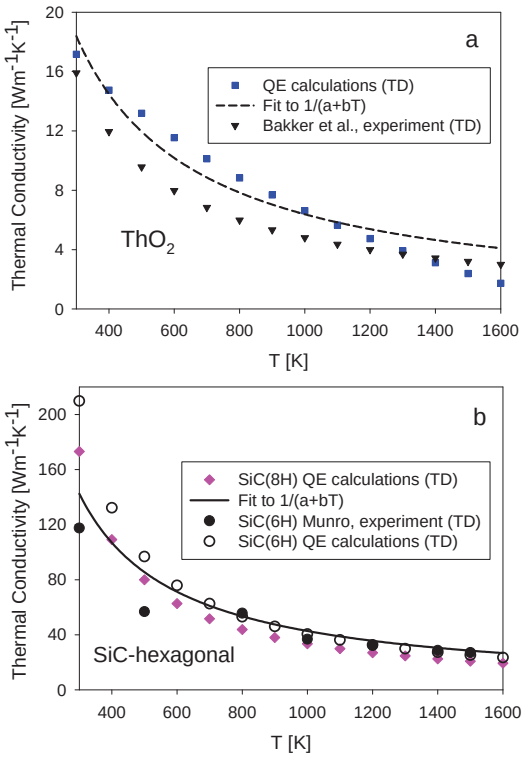

Figure 2. Thermal Conductivity of ThO_2 (a) and SiC (b). The fitted parameters of Eq. 2 are for ThO_2 :a= 0.00042, b = 0.000146, for SiC: a= 8.66×10^{-19}, b = 2.34×10^{-5}, in $W^{-1}m$ and $W^{-1}mK^{-1}$ units, respectively.

The fitted analytical functions (Eq. 2) to the lattice contribution to the thermal conductivity are also in good agreement with the respective experimental results. Note that the parameters "a" and "b" are assumed here to be constant, which is in contrast when urania fuel is used, which forms also higher oxidation states and therefore these parameters are dependent on the oxidation state. Thoria has advantage over urania fuel that it does not oxidizes, therefore the observed in urania deterioration of the thermal conductivity due to oxidation does not take place.

Temperature profiles and temperature gradients

Once the thermal conductivity is known one can calculate the temperature distribution in a cylindrical urania (as in examples discussed in Refs.[24,15]) for a specified volumetric heat generation rate from fission (H):

$$H = \frac{P}{\pi a^2}\left[\frac{(aL^{-1})}{2I_1(aL^{-1})}\right]I_0(rL^{-1}) \qquad (6)$$

where "P" is linear power (P = 48 kWm^{-1}), "a" is the radius of the fuel rod (a=0.006 m). The thermal neutron diffusion length (L) equal to 1.1 cm as estimated for natural urania with the burnup of 8000 MWd/t in our previous work [24] is also used here. The neutron diffusion length for pure thoria is longer but it will be shorter when doped with Pu or U, therefore for simplicity we assume the same profile for the neutron flux depression (Eq. 6) where "I_0" and "I_1" are the modified Bessel functions of the first kind. "T_S", fuel surface temperature is assumed the same as in our previous examples [15,24] and equals to 870 K.

In figure 3 we present the calculated by Maple code [15,24] temperature profile in fuel pellet operating for one day with linear power 48 kWm^{-1}. It is assumed that fuel is fully dense and performance of pure thoria is compared with 5vol%, 10vol% and 15vol% SiC/ThO_2 composities.

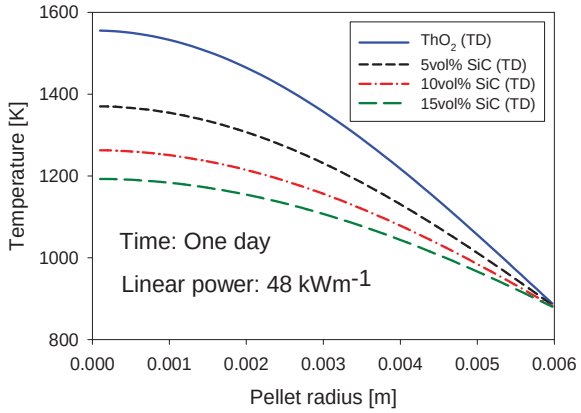

Figure 3. Predicted fuel temperature profile for thoria and 5vol%, 10vol% and 15vol% SiC/ThO_2 composities.

Our calculations demonstrate that by adding just 5vol% of SiC the centerline temperature can be reduced by ~200 K.

The use of a composite has also additional benefit since the thermal gradients are reduced as shown in figure 4. The predicted temperature gradients create local stress gradients, which for cylindrical symmetry can be evaluated from the following relation:

$$\frac{d\sigma}{dr} = Y\alpha_L \frac{dT}{dr} \qquad (7)$$

where "Y" is Young's modulus, "α_L" linear thermal expansion coefficient.

Using calculated by us previously [6] Young's modulus at 1500 K (Y~200 GPa) and the thermal expansion coefficient for thoria (α_L~6×10^{-6} K^{-1}) one can evaluate the thermal stress gradient at the distance of 4 mm from the center of the thoria fuel pellet using the presented in figure 4 temperature gradient (dT/dr ~1.5×10^{-5} Km^{-1}) from Eq. 7 ($d\sigma/dr \sim dT/dr$ ~ 1.8×10^{-3} $GPam^{-1}$). This stress is reduced in thoria by 30% when 5vol% SiC is added.

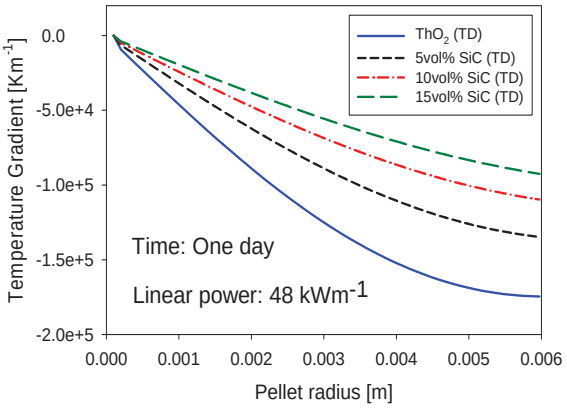

Figure 4. Predicted fuel temperature gradients profiles for thoria and 5vol%, 10vol% and 15vol% SiC/ThO_2 composities.

3.3 *Conclusions*

We conclude, that that it is possible to calculate the thermo-mechanical properties of SiC and ThO_2 and its composities by using Quantum ESPRESSO code and the complementary codes that use the properties as predicted by first principles. The calculated thermal conductivities of SiC and ThO_2 using Slack model for up to 1600 K temperatures are also in agreement with experiment. The presented example demonstrates application of Quantum ESPRESSO in predicting the thermo-physical properties of new materials, like composite nuclear fuels. The predictive calculations may complement expensive experiments used in manufacturing development of new accident tolerant fuel materials.

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REFERENCES

[1] I.L. Pioro, M. Khan, V. Hopps, Ch. Jacobs, R. Patkunam, S. Gopaul & K. Bakan, JSME J. of Power and Energy Systems, 2 (2008) 874.

[2] K. H. Sharma, J. Fourcade, S.G. Lee, A.A. Salomon, J. Nucl. Mater. 352 (2006) 324.

[3] S. Yeo, E. Mckenna, R. Baney, G. Subhash, J. Tulenko, J. Nucl. Mater. 433 (2013) 66.

[4] H. Y. Xiao, Y. Zhang & W. J. Weber, Acta Materialia, 61 (2013) 467.

[5] Y. Lu, Y. Yang, P. Zhang, J. Phys. Condens. Matter 24 (2012) 225801.

[6] B. Szpunar, J.A. Szpunar, Solid State Sciences, 28 (2014) 36.

[7] G.A. Slack, Solid State Phys. 34 (1979) 1.

[8] L. Malakkal, B. Szpunar, J. Zuniga, R. Siripurapu, J. Szpunar, 3rd World Congress on Integrated Computational Materials Engineering, TMS, May 31st-June 4th, 2015, Colorado Springs, in press.

[9] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L.Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari & R. M. Wentzcovitch, J. of Physics: Condensed Matter, 21 (2009) 395502.

[10] J. P. Perdew & A. Zunger, Phys. Rev. B 23 (1981) 5048.

[11] Perdew J.P., Ruzsinszky A., Csonka G.I., Vydrov O.A., Scuseria G.E., Constantin L.A., Zhou X., Burke K., 2008, Phys. Rev. Lett. 100 pp. 136406-1 136406-4 (102 (2009) 039902(E)).

[12] I. Grinberg, N.J. Ramer, A.M. Rappe, Phys. Rev. B 62 (2000) 2311e2314. http://opium.sourceforge.net/.

[13] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.

[14] A.A. Blanco, E. Francisco & V. Luana Comput. Phys. Commun. 158 (2004) 57.

[15] B. Szpunar., J.A. Szpunar, Phys. Int. 4 (2013) 110.

[16] J. Staun Olsen, L. Gerward, V. Kanchana & G. Vaitheeswaran, J. of Alloys and Comp., 381 (2004) 37.

[17] Frevel,L.J Peterson,D Saha J.Mater.Sci, Vol 27 page 1913 1992

[18] K.K. Phani, D.Sanyal, J. of Europ. Cer. Soc., 29 (2009), 385.

[19] P.M. Macedo, W. Capps, J.B. Watchman, J. of the Amer. Cer. Soc., 47 (1964) 651.

[20] Z. Li & R.C. Bradt, J. of the Amer. Cer. Soc. 70 (1987) 445.

[21] Landolt-Börnstein - Group III Condensed Matter, 'Group IV Elements, IV-IV and III-V Compounds. Part a - Lattice Properties', Volume 41, Section: Silicon carbide bulk modulus, young's modulus,shear modulus

[22] K. Bakker, E.H.P. Cordfunke, R.J.M. Konings, and R.P.C. Schram, J. of Nucl. Mat. 250 (1997) 1.

[23] R.G.Munro, J. Phys. Chem. Ref. Data, 26 (1997) 1195.

[24] B.J. Lewis, B. Szpunar and F.C. Iglesias, J. Nucl.. Mater., 306 (2002) 30.

[25] M.D. Segall, P.L.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, J.D. Payne, J. Phys. Condens. Matter 14 (2002) 2717e2743.