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Perturbation Molecular Dynamics Simulation of Thermal Conductivity of Zirconia

Zhang Feng[a], Fan Qun-Bo[b], Wang Fu-Chi and Zhang Hui-Ling

School of Material Science and Engineering, Beijing Institute of Technology, Beijing 100081, China

[a]zhangfeng@bit.edu.cn, [b]fanqunbo@bit.edu.cn

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Abstract. Thermal conductivity of zirconia and yttrium stabilized zirconia (YSZ) is calculated with perturbation molecular dynamics method (PMD). The results showed that thermal conductivity of YSZ is lower than that of pure zirconia and PMD is a very effective way in thermal conductivity calculation for ceramics. In higher temperature region, the calculated values show a different tendency with the experiment ones, which is because that photon conduction is not considered in PMD method. By taking photon effects into account, the calculated thermal conductivity curve is found fairly well coherent with measurements. In addition, the thermal expansion of zirconia is also presented by calculating the volumes at different temperatures. The results and methods in this paper have been proved to be very helpful in further design of new ceramic materials in the field of thermal barrier coatings (TBCs).

Background

The operating temperature of the new generation engine is getting higher and higher. To meet the requirement of elevated operating temperature, TBCs are usually used to insulate heat so that alloys can work at a temperature below their soften-temperature. Under the high temperature and high pressure in a gas turbine, it's necessary that TBC materials possess relatively lower thermal conductivity and higher thermal expansion coefficient (TEC) than traditional materials. Instead of trial and error experiments, computer aided materials design is playing a more and more important role in recent years. Powerful computing ability of present computers makes it possible to simulate a system with theories like molecular dynamics to predict both the thermal conductivity and thermal expansion coefficient. As is well known, thermal conductivity based on phonon conduction theory have been discussed by using equilibrium molecular dynamics, non-equilibrium molecular dynamics, and perturbation molecular dynamics in a lot of literatures [1-5]. However, it might be noted that photon contribution to thermal conductivity, especially in high temperature is usually ignored due to its complex nature. Hence for the very first time, with respect ZrO_2 and Y_2O_3-doped ZrO_2 (YSZ), the photon conductivity is introduced into the perturbation molecular dynamics in the present work. In addition, thermal expansion coefficient is also simulated by employing classical molecular dynamics.

Computation Procedures

Calculations of thermal conductivity by MD can be done using one of these three methods: a) the equilibrium method (EMD) [1, 2], b) the direct method (NEMD) [3, 4] and c) the perturbation method (PMD) [5]. In EMD, thermal conductivity is calculated without any artificial effects. Because of this, thermal noise in the energy flux is too excessive, which makes the curve of energy flux autocorrelation function need a long time to converge [2]. In addition, it's generally known that the integral of a Coulombic system exhibits long timescale oscillations due to the long-range nature of Coulombic interactions, especially in the case of ionic crystals. NEMD simulates the real experiment situation, under which there is a temperature gradient in the cell [4]. So a quite large cell is necessary to simulate the temperature gradient, causing the calculation take a long time too.

To reduce the computation time and get more reliable results, perturbation molecular dynamics method (PMD) is adopted, in which an external perturbation (F_{ext}) is applied to the system. Hence, relatively smaller supercells are also acceptable for the calculation. Thermal conductivity is calculated from heat flux during the equilibrium process as follows.

$$k = \frac{V}{F_{ext}\, T} \lim_{t\to\infty} \langle J \rangle_t \qquad (1)$$

where V and T are volume and temperature, and J is a component of heat flux vector. F_{ext} is the perturbation, which refers to the external force applied to the system.

Photon conductivity is calculated with Eq.1 [6]

$$K_r = 4\sigma T^3 n^2 L = 2.27\times10^{-7} T^3 n^2 L (Wm^{-1}k^{-1}) \qquad (2)$$

where σ is Stefan-Boltzmann constant, T is temperature. L and n are thickness and refractivity of a TBC, respectively. Thermal expansion coefficient is defined as follow [7].

$$\alpha = \frac{1}{L_0}\left[\frac{\Delta L}{\Delta T}\right]_P \qquad (3)$$

where ΔL is length increment and L_0 is the initial length at a fixed temperature.

During the calculation, Buckingham potential function is chosen to describe short-range interatomic energy and force. The reported potential parameters [8] are used. The calculation for thermal conductivity is carried out under NTV ensemble, 100000 total simulation steps and 0.5 fs for each step. The calculation for thermal expansion coefficient is carried out under NTP ensemble, 20000 total simulation steps, 10000 for relaxing and 10000 for temperature changing, with each time step of 0.5 fs. A 6 × 6 × 6 ZrO_2 super cell is used in the simulation. The model of YSZ cell has been built by substituting Zr atoms with Y randomly, which contains 398 Zr^{4+}, 34 Y^{3+} cations, 847 O^{2-} anions and consequently, 17 O vacancies. So, mol percentage of YSZ in this model is 4.09%.

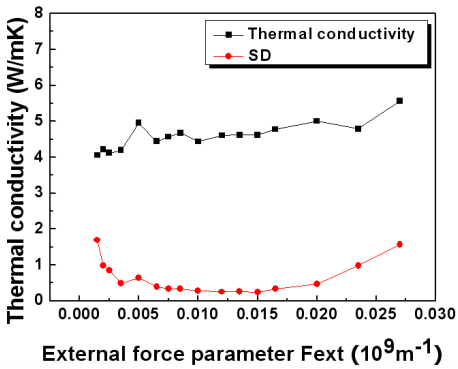

Fig.1. Average thermal conductivity of ZrO_2 and corresponding standard deviation of instantaneous thermal conductivity as a function of magnitude of the external force at 1800K.

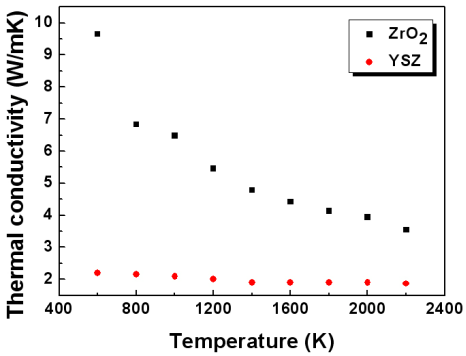

Fig.2 Phonon thermal conductivity of ZrO_2 and YSZ.

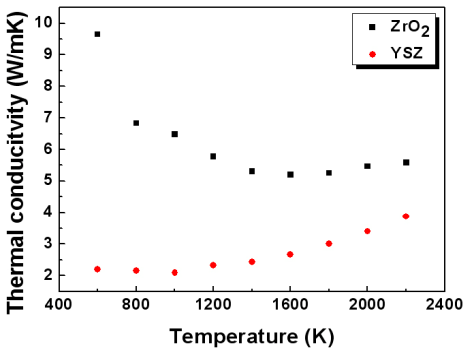

Fig.3 Thermal conductivity of ZrO_2 and YSZ after taking photon conductivity into account

Results and Discussion

Thermal conductivity. It is found in PMD that thermal conductivity values acquired with different external force (F_{ext}) differs a lot. This is because the value of external force must be less than upper limit of the linear response regime of the system. Meanwhile, it cannot make the energy flux autocorrelation function converge quickly and smoothly if F_{ext} is too small. In Fig.1, standard deviation of instantaneous thermal conductivity has been introduced to describe how well the energy flux autocorrelation function converges. It can be seen that standard deviation of instantaneous thermal conductivity has minimum points at the F_{ext} range of $0.0135\times10^{-9}m^{-1}$ ~ $0.015\times10^{-9}m^{-1}$, which means average thermal conductivity calculated within this range is the most reliable value.

Fig.2 shows the calculated thermal conductivity for ZrO_2 and YSZ. It can be seen that the significant decrease in thermal conductivity caused by Y_2O_3 addition. In addition, it's found that with increasing the temperature, the thermal conductivity always decreases both for ZrO_2 and for YSZ. After taking photon conductivity into account, shown in Fig.3, thermal conductivity at temperatures higher than 1200K is found to be rising, instead of always decreasing to a certain value, which successfully reproduces the experimental observations. By contrasting calculated thermal conductivity and experimental ones reported by literatures [9], it can be found that the calculated values are

Table.1 Ratio of experimental and calculated thermal conductivity at 1800K

	Experimental (W/m·K)	Calculated (W/m·K)	Ratio (Cal./Exp.)
ZrO_2	3.4[9]	4.781	1.40
YSZ	2.5-1.6[9]	1.910	1.44

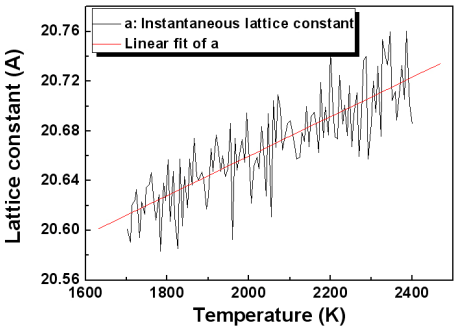

Fig.4 Instantaneous lattice constant of ZrO_2 as a function of temperature

Table.2 Comparison of experimental and calculated TEC ($\times 10^{-6}$) of c-ZrO_2 and YSZ

	Experiment	Calculate
ZrO_2	7-8 [9]	7.6814
YSZ	10-11 [9]	8.2932

relatively higher. But the ratio of calculated thermal conductivity and experimental ones are within a stable range, as is shown in Table 1.

Thermal expansion coefficient. Fig.4 shows instantaneous lattice constant of ZrO_2 as a function of temperature. It can be seen that the instantaneous lattice constant fluctuates around a line which was fit to describe the theoretical relation between lattice constant and temperature. Linear thermal expansion coefficient of a material can be calculated by dividing the slope of the fit line with the initial lattice constant. The ultimate value of linear thermal expansion coefficient is shown in Table 2.

Calculated and experimental values are compared in Table 2. It can be seen that the calculated results are smaller than the experimental ones. But the increment of thermal expansion coefficient caused by Y_2O_3 addition is reproduced well. In spite of possible calculation errors for thermal expansion coefficient, the method proposed in this paper is still acceptable.

Conclusion

The primary conclusions of this study are as follows. 1. For the first time, thermal conductivity is calculated by perturbation molecular dynamics coupled with photon thermal conductivity, and turned out to be more reliable than traditional EMD and NEMD. 2. Results show that thermal conductivity of YSZ is lower than that of pure zirconia, which is in good agreement with experimental observations. 3. Thermal expansion coefficients of ZrO_2 and YSZ are also presented by calculating the volumes at different temperatures. The results and methods in this paper have proved very helpful for further designing new ceramic materials in the field of TBCs.

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