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Understanding the effect of porosity on thermal properties of yttria-stabilized zirconia using molecular dynamics simulation

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ABSTRACT

Thermal properties of yttria stabilized zirconia (YSZ) were investigated using molecular dynamics (MD) simulation. Several YSZ samples were designed to elucidate the effect of porosity on thermal conductivity of the designed YSZ systems. Mean square displacement (MSD), vibrational density of state (VDOS) and atomic movement in designed YSZ and other samples were also investigated. Results of MD simulation indicated the key role of pores in preventing thermal transport behavior. For same volume of a single pore, samples with larger pore volume showed smaller thermal conductivity (κ), while for same amount of total porosity, samples with small-sized pores displayed a smaller thermal conductivity. The latter was due to the presence of relatively larger number of smaller-sized pores as compared to larger-sized ones. Samples with smaller-sized pores in greater numbers also exhibited lower vibration frequency and lower amplitude of single atoms, suggesting smaller thermal conductivity (κ) values. For constant pore volume, YSZ samples were observed to have a decrease in thermal conductivity with increasing number of pores. Among YSZ samples with same levels of porosity, those with smaller pores displayed smaller thermal conductivity. Similar levels of thermal conductivity could be acquired in samples with smaller pore amounts and/or smaller porosity as compared to those with larger pores.

1. Introduction

During the past few years, yttria-stabilized zirconia (YSZ) has been used as an advanced ceramic topcoat in thermal barrier coatings (TBCs) on parts of gas turbine and aero engines, since YSZ has a high coefficient of thermal expansion, low thermal conductivity, high melting point and high thermal shock resistance [1–3]. Several properties of YSZ have been researched experimentally, such as phase transition, oxidation behavior, oxygen ion diffusion and thermal behavior [4–8]. Since conducting experiments at high temperatures is a challenging task for researchers, molecular dynamics (MD) simulation is an excellent alternative tool for studying high-temperature properties. MD simulation has been employed previously to investigate various properties of YSZ, such as oxygen ion diffusion, phase transition, microstructure characterization, grain boundary structure and thermal transport at high temperatures [9–11].

Thermal transport is caused by vibration of phonons and electrons. For ceramic materials, vibration of electrons is negligible and can be ignored in comparison with vibration of phonons. Hence, thermal transport in YSZ samples focuses mainly on non-harmonic interactions among scattered phonons [1]. Although porosity in YSZ samples helps to reduce its thermal conductivity, such porosity harms its structural stability, leading to a reduction in its intensity. Since YSZ has a limitation temperature of 1200 °C [12,13], its thermal properties at high temperatures remain a matter of great importance for research. However, thermal properties and thermal transport behavior of YSZ have not been clearly elucidated till date. This paper is an attempt at addressing this gap.

In this paper, thermal conductivity and thermal transport behavior of tetragonal YSZ samples were investigated. MD simulation was used to calculate thermal behavior and thermal properties of YSZ system with different porosity levels.

2. Simulation details

Thermal conductivity of YSZ samples was studied by molecular dynamics (MD) simulation using LAMMPS code [14]. Periodic boundary conditions were adopted in the simulation process, with two vacuums set on top and bottom of the model. The initial velocities of atoms were observed to conform to the Maxwell-Boltzmann distribution. Temperature and volume of the design system were controlled by applying the Nose-Hoover method. Equations of motion were solved by applying the Velocity-Verlet algorithm. Coulomb's Law and Ewald Term were considered while describing the electrostatic interactions –

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Table 1
The interatomic potential values taken (from Refs. [15–17]) for simulation[a].

Interatomic interactions	kJ/mol
O-O	22,764.00
Zr-O	985.602
Y-O	1325.60

[a] All interacting ions have charges as: O^{2-}, Zr^{4+}, Y^{3+} and La^{3+}.

while these explain long-range interactions, short-range interactions are given by Born-Meyer-Buckingham pair potential as follows [15]:

$$V(r_{ij}) = -\frac{A_{ij}}{r_{ij}^6} + B_{ij}\exp(-C_{ij}r_{ij})$$

where r_{ij} is the distance between ions i and j, while A_{ij}, B_{ij} and C_{ij} parameters represent the interatomic interaction potentials. Values of interatomic potentials are listed in Table 1 below.

Non-equilibrium molecular dynamics simulation (NEMD) was used in MD simulation, with all MD simulations carried out using NVE ensemble. Müller-Plathe approach [18] was adapted to MD simulation to calculate thermal conductivities of various YSZ systems [19]. In this approach, a constant heat flux flows from the hot area to the cold area every 1 ps, as illustrated in Fig. 1. The coldest atom in the hot area and the hottest one in the cold area were chosen to exchange their velocities, with a temperature formed during the exchange process. Heat flux J between the two areas is defined using the following equation [20]:

$$J = \frac{\sum N_{ex}\left(\frac{1}{2}\right)\left(m{v_h}^2 - m{v_c}^2\right)}{N_{ex}t_{ex}}$$

where m is mass of a single atom, N_{ex} is the exchange interval, t_{ex} is the exchange interval number, while v_h and v_c are velocities of the hottest and coldest atoms respectively. After attaining a stable state, temperature gradient of the system was obtained. Thermal conductivity (κ) is calculated as follows [21]:

$$\kappa = \frac{J}{A\Delta T}$$

where J is the heat flux, A is the cross-section area of the model, and ΔT is slope of the temperature gradient curve. Fourier transformation of the velocity auto-correlation function was used to calculate the vibrational density of state (VDOS) [22]:

$$G(\omega) = \frac{1}{\sqrt{2\pi}}\int e^{i\omega t}\left(\sum_{j=1}^{N} v_j(t)v_j(0)dt\right)$$

where $G(\omega)$ denotes velocity at time t, while ω is the vibration wave number. In MD simulation, YSZ samples were allowed to relax for 100 ps, while each step ran for 0.0025 fs. The simulation ran a total of 40,000 steps, or a total of 1000 ps.

The YSZ sample used for calculation was t-YSZ doped with 4 mol% Y_2O_3. YSZ unit consisted of $10 \times 10 \times 6$ cells, or a total of 7108 ions. Lattice constants of YSZ are $a = 5.17$ Å and $c = 5.30$ Å,[1] while α is the linear thermal expansion coefficient of the system (values in the range ~9.6×10^{-6} K^{-1} to 10.1×10^{-6} K^{-1}).

[1] Lattice constant can be calculated using the formula:
$a(T) = a(T = 300\ K) \times [1 + (\alpha \times (T - 300))]$, where a ($T = 300$ K) is the lattice constant for YSZ at $T = 300$ K. The corresponding values are $a = 5.12$ Å and $c = 5.25$ Å (taken from JCPDS Card No. 17-0923).

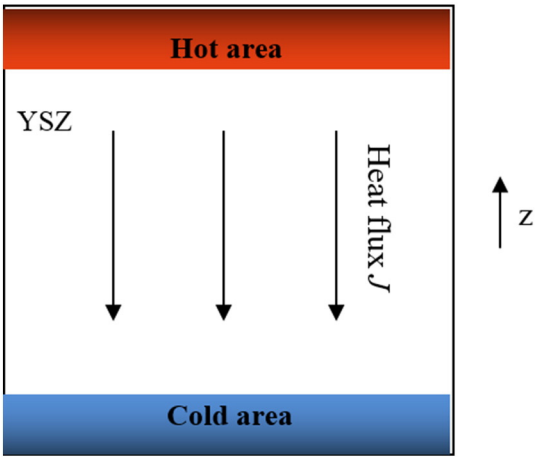

Fig. 1. Illustration of heat flux in YSZ.

3. Results and discussion

Fig. 2 shows the temperature gradient curve of YSZ calculated at 1273 K. Since heat flux was imposed on z-axis direction in the YSZ sample from hot area to cold area (as shown in Fig. 1), temperature gradient was along the z-axis coordinates. For simulation in this paper, heat flux is chosen to be 1 eV/ps.

In order to investigate the effects of porosity density on thermal conductivity of YSZ samples, four groups of samples (14 in number overall) were tested for thermal conductivity measurement at 1273 K. Thermal conductivity of all the samples are listed in Table 2 below.

Displacement of Zr^{4+} ions was investigated to observe the heat flux transport behavior in YSZ and D2 samples. Mean square displacement (MSD) of Zr^{4+} ions in heat flux direction (z direction) for both systems was calculated, as shown in Fig. 3. As can be seen in Fig. 3, MSD curve of Zr^{4+} ions (line a) ranges from 0 to ~0.114 nm^2, with MSD values showing an increase with time. For sample D2, MSD values of Zr^{4+} ions in heat flux direction (line b) ranged from 0 to ~0.095 nm^2, smaller than the range for YSZ sample, with MSD values showing little rise during simulation. Difference in MSD values for both samples indicates a higher displacement of Zr^{4+} ions in YSZ without pores compared to that in YSZ with pores (i.e. in sample D2). The higher value of MSD in YSZ sample is caused by higher heat flux in the model, while in case of sample D2, pores present inside the sample impacted and reduced the heat flux transportation in the YSZ system.

One Zr^{4+} ion was chosen to observe the movement in z-axis direction in YSZ samples – both with and without porosity. Fig. 4a shows

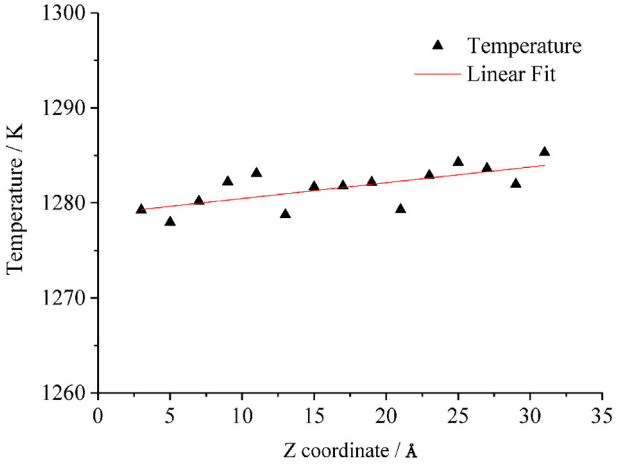

Fig. 2. Temperature gradient curve on z axis of YSZ at 1273 K.