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Image-based multi-scale simulation and experimental validation of thermal conductivity of lanthanum zirconate

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ABSTRACT

Lanthanum zirconate ($La_2Zr_2O_7$) is a promising candidate material for thermal barrier coating (TBC) applications due to its low thermal conductivity and high-temperature phase stability. In this work, a novel image-based multi-scale simulation framework combining molecular dynamics (MD) and finite element (FE) calculations is proposed to study the thermal conductivity of $La_2Zr_2O_7$ coatings. Since there is no experimental data of single crystal $La_2Zr_2O_7$ thermal conductivity, a reverse non-equilibrium molecular dynamics (reverse NEMD) approach is first employed to compute the temperature-dependent thermal conductivity of single crystal $La_2Zr_2O_7$. The single crystal data is then passed to a FE model which takes into account of realistic thermal barrier coating microstructures. The predicted thermal conductivities from the FE model are in good agreement with experimental validations using both flash laser technique and pulsed thermal imaging-multilayer analysis. The framework proposed in this work provides a powerful tool for future design of advanced coating systems.

1. Introduction

Thermal barrier coatings (TBCs) are multi-layered ceramic coating systems deposited on turbine and combustor parts, which provide thermal insulation to the metallic substrate and improve the durability and energy efficiency of gas turbines [1,2]. Typically, TBCs are deposited by using air plasma spray (APS) or by electron beam physical vapor deposition (EB-PVD) process. The primary requirements of TBCs for the turbine designer are low thermal conductivity and low density to minimize centrifugal loads [3,4]. Other basic requirements include high-temperature phase stability, high thermal expansion coefficient, and low sintering activity [5,6]. Recently, lanthanum zirconate has become a very promising candidate for thermal barrier coating applications, because it has low thermal conductivity and high-temperature phase stability. A transmission electron microscopy (TEM) image of $La_2Zr_2O_7$ coating powder is shown in Fig. 1.

For thermal barrier coating materials, one of the most important material properties is thermal conductivity. There are several experimental methods to measure thermal conductivity. The most common one is flash method, which was first proposed by Parker et al. [7]. Three thermal properties – thermal diffusivity, specific heat capacity and thermal conductivity – can be deduced simultaneously using one sample [7]. The flash method is designated as the standard thermal diffusivity method specified in ASTM E1461-11. The measurement error of the standard flash method is less than 5% [8]. Using flash method, Vassen et al. measured the thermal conductivity of hot pressed fully dense $La_2Zr_2O_7$ disk samples to be 1.5–2.0 W/m/K in a temperature range of 200–1500 °C [5]. Zhu et al. did similar studies for hot pressed disk samples using $La_2Zr_2O_7$ spray-dried $La_2Zr_2O_7$ powders [9,10]. The measured thermal conductivities were 1.9–3.0 W/m/K in a temperature range of 200–1600 °C. We measured thermal conductivities for porous 8 wt% yttria stabilized zirconia (8YSZ) coating and porous $La_2Zr_2O_7$ coating using flash method in our previous work [11]. The measured average thermal conductivity of $La_2Zr_2O_7$ (porosity 11.54%) was about 0.59–0.68 W/m/K at the temperature range of

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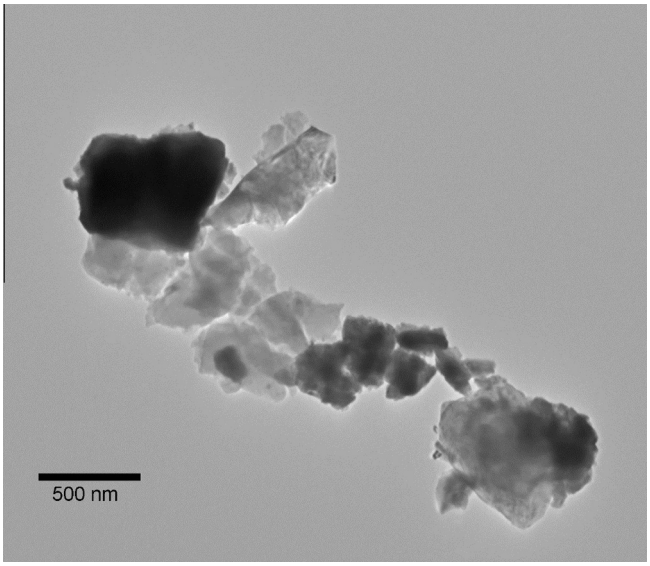

Fig. 1. TEM image of $La_2Zr_2O_7$ coating powder.

297 to 1172 K (24–899 °C), which was about 25% lower than that of porous 8YSZ at the same temperature range.

In parallel to experimental technique, molecular dynamics (MD) method can also be used to investigate the thermal conductivity. For single crystals, there are two common molecular dynamics methods for thermal conductivity calculations, i.e., direct method [12,13] and Green–Kubo method [14,15]. The direct method is a non-equilibrium molecular dynamics (NEMD) method, which imposes a temperature gradient to the system. The Green–Kubo method is an equilibrium MD (EMD) method, which uses the current fluctuation to calculate the thermal conductivity according to the fluctuation–dissipation theorem [16]. Schelling et al. predicted the thermal conductivities of several dozens of single crystal pyrochlores with composition of $A_2B_2O_7$ (A is a rare element, and B = Ti, Mo, Sn, Zr or Pb) using the NEMD methods with Buckingham potentials [12]. The calculated thermal conductivity of single crystal $La_2Zr_2O_7$ was 1.98 W/m/K at 1200 °C [12]. A more reliable method to compute thermal conductivity is the reverse NEMD (RNEMD) method [17]. In RNEMD method, the Muller-Plathe algorithm [18] is used to exchange kinetic energy between two atoms in different regions of the simulation box every finite steps to induce a temperature gradient in the system. It works by exchanging velocities between two atoms in different parts of the simulation cell. At set intervals, the velocity of the fastest atom in one region is replaced by the velocity of the slowest atom in another region, and vice versa. Consequently, the first region become colder, whereas the second region increases in temperature. The system will react by flowing energy from the hot to the cold region. Eventually a steady state sets in when the energy exchanged offsets the energy flowing back with a temperature gradient over the space between the two regions. This enables the thermal conductivity of a material to be calculated. The usual NEMD approach is to impose a temperature gradient on the system and measure the response as the resulting heat flux. In RNEMD using the Muller-Plathe algorithm, the heat flux is imposed, and the temperature gradient is the system's response. The advantage of NEMD over traditional NEMD is that there are no artificial "temperature walls" in the simulated system, since these cause a fluid structure different from the bulk. Additionally, energy and momentum are conserved, and there are no thermostat issues [17]. We have calculated thermal properties of $La_2Zr_2O_7$ such as specific heat and coefficient of thermal expansion (CTE) in our previous work [19,20]. In this work, we will compute temperature-dependent thermal conductivity of $La_2Zr_2O_7$ single crystal using RNEMD method to provide data in later finite element model in order to compare against experimental data. As shown in the TEM image in Fig. 1, there are very few defects in the crystal, therefore $La_2Zr_2O_7$ single crystal can be described by using molecular dynamics model.

Finite element (FE) method can be used to simulate the heat conduction process of coating structures with cracks and pores [21]. In addition, quantitative imaging analysis method has been used to investigate the non-uniformity properties of the porous coating with polycrystalline microstructure [22,23]. Pore and crack morphology of thermal barrier coating are important parameters affecting the mechanical and thermal properties [24,25]. The thermal properties of non-uniform porous polycrystalline coatings can be calculated using image based FE method. Image based FE method uses scanning electron microscope (SEM) images to generate microstructures and import into a FE model [26]. Arai et al. studied the thermal conductivities of TBCs with different porosities using SEM image based FE modeling [25]. They found that the presence of the pores disturbed heat flow in materials. In addition, the thermal conductivity of plasma sprayed porous yttria-stabilized zirconia (YSZ) was investigated by several researchers using FE method [27,28]. The calculated effective thermal conductivities were in good agreement with experimental results.

In this paper, we propose a novel image-based multi-scale simulation framework combining molecular dynamics and finite element calculations to study the thermal conductivity of $La_2Zr_2O_7$ thermal barrier coating. Since there is no experimental thermal conductivity data of $La_2Zr_2O_7$ single crystal, a reverse non-equilibrium molecular dynamics approach is first used to compute the temperature-dependent thermal conductivity of $La_2Zr_2O_7$ single crystal. The single crystal data is then passed to a FE model with realistic thermal barrier coating microstructures generated using SEM images. The predicted thermal conductivities from the FE model are compared against experimentally measured thermal conductivity using both flash laser technique and pulsed thermal imaging-multilayer analysis.

2. Method

2.1. Multi-scale simulation of thermal conductivity

For $La_2Zr_2O_7$ single crystal, the RNEMD method is used to predict temperature-dependent thermal conductivity. The $La_2Zr_2O_7$ unit cell is a face-centered cubic pyrochlore structure with a lattice parameter of 10.8 Å [19]. A $La_2Zr_2O_7$ supercell model with the dimension of $324 \times 21.6 \times 21.6$ Å^3 has total 10,560 atoms, including 6720 O atoms, 1920 La atoms and 1920 Zr atoms. The supercell model is sliced into 30 layers with equal thickness. A temperature decay constant 0.1 ps is imposed in each layer. The thermal conductivity follows as the energy flux divided by the temperature gradient [17]:

$$k = \frac{\dot{q}}{dT/dx} \tag{1}$$

where k is thermal conductivity, $\dot{q}$ is heat flux defined by the amount of heat (Q) transferred per unit time per unit area in heat transfer direction; $\partial T/\partial z$ is temperature gradient in the heat transfer direction.

For the image-based FE models, representative SEM images of cross-sectional view of the porous $La_2Zr_2O_7$ thermal barrier coating are converted into binary images using ImageJ software package [29]. In the binary images, white color regions represent solid $La_2Zr_2O_7$ coating phase, and black color regions are pores and