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Investigation of a new type of composite ceramics for thermal barrier coatings

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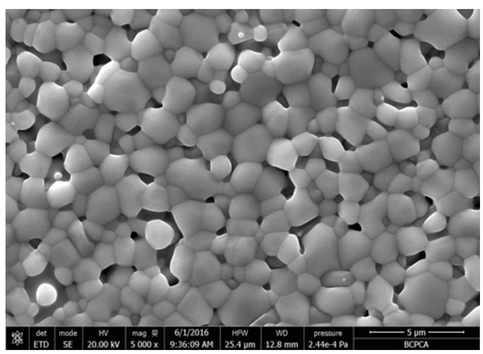
HIGHLIGHTS

- The $La_2Zr_2O_7/LaPO_4$ composite ceramics were prepared.
- $La_2Zr_2O_7/LaPO_4$ composite ceramics have good thermal physical properties.
- $La_2Zr_2O_7/LaPO_4$ composite ceramics have good mechanical properties.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to explore a novel material for thermal barrier coatings (TBCs), the composite ceramic materials of lanthanum zirconate ($La_2Zr_2O_7$) and lanthanum phosphate ($LaPO_4$) were prepared by calcining. The phases and micro-structures of $La_2Zr_2O_7/LaPO_4$ composite ceramic materials were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The properties of $La_2Zr_2O_7/LaPO_4$ material, such as thermal conductivity, coefficient of thermal expansion (CTE) and mechanical properties of $La_2Zr_2O_7/LaPO_4$ were investigated using laser flash method, high-temperature dilatometer and micro-hardness test. Based on XRD patterns, the pyrochlore and monazite phases were obtained in $La_2Zr_2O_7/LaPO_4$ composite ceramic material without any chemical reaction. According to SEM morphology, the $La_2Zr_2O_7$ was closely near to $LaPO_4$ along with a lot of pores, it might cause the decrease of thermal conductivity. The thermal conductivities of composite ceramics were similar to that of $La_2Zr_2O_7$. The CTE of them were about $10 \times 10^{-6}\ K^{-1}$, which was close to the value of $LaPO_4$. Because of doping $LaPO_4$, hardness and Young's modulus of samples were lower than that of $La_2Zr_2O_7$. The studies revealed that the $La_2Zr_2O_7/LaPO_4$ composite ceramics had good mechanical and thermal physical properties and could be applied as new candidate materials for TBCs in the future.

1. Introduction

Thermal barrier coatings (TBCs), which can protect the metallic components from corrosion and oxidation at high temperature, have been widely applied in all kinds of gas turbine due to enhancing the inlet temperature for increasing of engine efficiency with the

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development of demand [1–4]. The traditional TBCs contain metallic bonding coating and ceramic top coat, which can form a heat insulation (from 100 °C to 300 °C) to reduce the surface temperature of the substrates [5]. The heat insulation ceramic top coat plays an important role in these systems, so the selection of materials is very important. The main criteria for the materials used in the ceramic top coat includes low thermal conductivity, high thermal expansion and no phase transformation during service lifetime [6,7].

Yttria-stabilized zirconia (YSZ), with low density, low thermal conductivity and high coefficient of thermal expansion (CTE), was widely used as the ceramic top coat of TBCs [8,9]. Although the application of YSZ can improve heat insulation capability and increases the lifetime of TBCs, it faces three challenges. Firstly, when phase transformations occur at sintering temperature (about 1200 °C) from the t′-tetragonal to tetragonal and cubic (t + c) and then to monoclinic (m) structure, cracks form in the top coat [10–12]. Secondly, due to high temperature sintering, the reduction of porosity increases the thermal conductivity of top coat [1]. Finally, at operating temperature oxygen permeation in YSZ coat leads to the growth of thermally grown oxide (TGO), which accelerates spalling of top coat [13,14].

Recently, Lanthanum zirconate ($La_2Zr_2O_7$), which has lower thermal conductivity (1.6 W/(m·K), at 1000 °C) than that of YSZ (2.12 W/(m·K), at 1000 °C) and higher hardness, is a promising candidate material to be used as the top coat for TBCs [15]. Because its pyrochlore structure ($A_2B_2O_7$) produces large quantities of oxygen ion vacancies, the phonon scattering in $La_2Zr_2O_7$ is increased and its thermal conductivity is reduced [14]. However, when $La_2Zr_2O_7$ is used at high temperatures, its relatively low coefficient of thermal expansion accelerates crack formation and delamination [16–18]. To improve its properties, the attempts have been made to substitute A site or B site of $A_2B_2O_7$ structure in $La_2Zr_2O_7$ by some elements, e.g., $(Sm_{0.5}La_{0.5})_2Zr_2O_7$, $(Sm_{0.5}La_{0.5})_2(Zr_{0.8}Ce_{0.2})_2O_7$, $(Y_{0.05}La_{0.95})_2(Zr_{0.7}Ce_{0.3})_2O_7$, $La_2(Zr_{1-x}B_x)_2O_7$ (B = Hf, Ce, 0 < x < 0.5), $(Yb_{0.1}La_{0.9})_2(Zr_{0.7}Ce_{0.3})_2O_7$, $La_{1.7}Gd_{0.15}Yb_{0.15}Zr_2O_7$, $La_{1.7}Dy_{0.3}(Zr_{0.8}Ce_{0.2})_2O_7$, $La_{2-x}Lu_xZr_2O_7$, $(La_{1-x}Er_x)_2Zr_2O_7$, $La_2Zr_{2-y}Pu_yO_7$, $(La_{1-x1}Y_{x1})_2(Zr_{1-x2}Y_{x2})_2O_{7-x2}$ [19–27]. While its problem has not been solved completely, the new ways to improving the $La_2Zr_2O_7$ properties have been paid more attention.

Lanthanum phosphate ($LaPO_4$) is an interesting material that exhibits high melting point with 2072 ± 20 °C and high CTE of about $10.5 \times 10^{-6}\ K^{-1}$ at 1000 °C, relatively. Furthermore, $LaPO_4$ has high thermal and chemical stability, excellent hardness and a suitable modulus [28–30]. $LaPO_4$ is also expected to show good corrosion resistance in environments containing sulfur and vanadium salts. It does not react with alumina, which is a positive attribution. On the other hand, it has poor interface bonds, which is a limitation to its application [6].

However, $LaPO_4$ has been widely used in machinable ceramics to improve the machinability due to aluminium oxide (Al_2O_3)/$LaPO_4$ or zirconium dioxide (ZrO_2)/$LaPO_4$ ceramic composites possessing excellent bending strength and Young's modulus in recent years [31–33]. Thus, the composite ceramics have excellent properties, which can develop the advantage properties and overcome shortcoming of pure ceramic. Previous research results show that the doping of $LaPO_4$ can not only enhance the thermal shock resistance of ZrO_2 ceramics in ZrO_2/$LaPO_4$ composite ceramics but also reduce the thermal conductivity and improve high temperature stability in 3YSZ/$LaPO_4$ composite ceramics [34,35]. Liu prepared the $La_2Zr_2O_7$/YSZ composite ceramic and found that the YSZ exhibited tensile stress while the $La_2Zr_2O_7$ possessed compressive stress in composite ceramic to relax thermal stress at sintering time [36]. Therefore, composite ceramic will become one of ways to improve the $La_2Zr_2O_7$ properties.

Considering the composite ceramics have excellent thermophysical and mechanical properties, the composite ceramics consist of $La_2Zr_2O_7$ and $LaPO_4$ with different mass ratios was designed in this work. The thermophysical and mechanical properties of $La_2Zr_2O_7$/$LaPO_4$ composite ceramics have been investigated systematically.

2. Experimental procedure

2.1. Preparation of composite ceramics

The raw materials are corresponding to zirconium oxide (99.99%), lanthanum oxide (99.9%) and lanthanum phosphate (>99%) in this study. Before the preparation of composite ceramics, the oxide powders were dried by calcination at 1000 °C for 2 h. Then they were mixed by ball-milling for 24 h and dried. Finally, they were compressed into plates and sintered at 1550 °C for 12 h. Composite ceramics composed of $La_2Zr_2O_7$ and $LaPO_4$ with different mass ratios, including 10 wt.%, 20 wt.%, 30 wt.% and 40 wt.% of $LaPO_4$, and they were named Sample 1, 2, 3 and 4, respectively, in this paper.

2.2. Characterization of microstructures and mechanical properties

The phase structure of $La_2Zr_2O_7$, $LaPO_4$ and the composite ceramics with different mass ratio were characterized by X-ray diffraction (XRD, D8 Advance, CuK_α radiation) with the scanning rate of 6°/min. Scanning electron microscopy (SEM, HITACHIS-4800) was used to analyze the morphology of cross-section of samples. The bulk composite ceramics materials were mounted by epoxy resin, ground and polished before testing. The hardness and Young's modulus were measured by nano-indentation tester (MCT, CSM Switzerland). Nano-indentation tester with 30 mN loading and 10 s loading time was employed to test the hardness and Young's modulus of the bulk composite ceramics materials during testing.

2.3. Characterization of thermal physical properties

The thermal diffusivity was measured by laser flash method (Netzsch LFA 427, Germany). The specimens for measurement were machined to tablets with a diameter of 12.7 mm and a thickness of about 1 mm. Archimedes' principle was applied to determine the sample density. The specific heat capacity (Cp) at different temperatures was calculated by Neumann-Kopp rule according to the chemical composition of the $LaPO_4$ and $La_2Zr_2O_7$ composite ceramics [37]. The thermal conductivity was calculated by following equation:

$$\kappa = \lambda \cdot \rho \cdot Cp \tag{1}$$

Where κ is the thermal conductivity, λ is the thermal diffusion, ρ is the density and Cp is the specific heat capacity.

The CTE was tested by high-temperature dilatometer (NETZSCH DIL 402C, Germany). Specimens used for measurements were fabricated by bulk materials with the dimensions of 13.5 mm × 8 mm × 3 mm. The operations of measurements were conducted from room temperature to 1400 °C with the heating rate of 10 °C/min. The CTE is defined as [38]:

$$\alpha = \frac{1}{L_0}\frac{\Delta L_k - \Delta L_0}{T_k - T_0} \tag{2}$$

where L_0 is the length of the specimen at T_0 (room temperature), ΔL_0 is the change in length at T_0, and ΔL_k is the corresponding length change at T_k.

3. Results and discussion

3.1. Structure of composite ceramics

Fig. 1 shows the XRD patterns of pure $LaPO_4$ and $La_2Zr_2O_7$, respectively. From Fig. 1, it can be seen that pure $La_2Zr_2O_7$ prepared by the solid state reaction possesses the typical phase of pyrochlore, which belongs to $Fd\bar{3}m$ space group. This type of pyrochlore structure have a lot of vacant position, which can scatter the phonon. Due to the phonon scattering, its thermal conductivity is very low. At the same time pure