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Preparation and thermophysical properties of CeO_2 doped La₂Zr₂O₇ ceramic for thermal barrier coatings

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Abstract

Lanthanum zirconate ($La_2Zr_2O_7$, LZ) and CeO_2 doped $La_2Zr_2O_7$ (LCZ) ceramic were synthesized by the coprecipitation–calcination method. The chemical compositions, phase compositions, thermophysical properties of these materials were investigated. Inductively coupled plasmaatomic emission spectrometry (ICP-AES) and XRD results revealed that the compositions of all prepared ceramic materials were in the range of the synthesis of single $La_2Zr_2O_7$ with pyrochlore structure. After the prepared ceramic powders were mechanically ball-milled, vacuum dried, molded by cold pressure and densified by sinter at 1650 °C for 10 h, the bulk density of the sample was measured by the Archimedes method with an immersion medium of deionized water, a high-temperature dilatometer, DSC and laser thermal diffusivity method were used to analyze its thermal expansion coefficient, specific heat and thermal diffusivity. The results showed that, with the temperature increasing, the thermal expansion coefficient (TEC) of these ceramics increased, while the thermal conductivity decreased. The thermal expansion coefficient of $La_2Zr_2O_7$ was enhanced clearly by adding CeO₂, and its thermal diffusivity and specific heat were all changed slightly. The thermophysical results also indicated that TEC of LCZ was slightly higher than that of conventional Y_2O_3 –8 wt.% ZrO₂ (8YSZ), but its thermal conductivity was lower than that of 8YSZ. The lower thermal conductivity of LCZ was mainly attributed to more oxygen vacancies and larger atomic weight of substitutional atom (La, Ce). These results imply that LCZ can be explored as the candidate material for the ceramic layer in TBCs system. © 2006 Elsevier B.V. All rights reserved.

Keywords: Lanthanum zirconate; Coprecipitation-calcination method; Thermal barrier coatings; Thermal properties; CeO2

1. Introduction

In order to improve the reliability and durability of hotsection metal components in advanced engines and enhance engine performance, thermal barrier coatings (TBCs) were applied on the surface of these components. The use of TBCs can result in a significant temperature decrease between the hot gas and the surface of these components. In the next generation of advanced engines, further increases in thrust-to-weight ratio will require even higher gas temperatures [1,2]. This means that the surface temperatures of the components will increase. In order to meet this ambitious goal, three major methods can be used. The first is to ameliorate the cooling technique [3]. However, the excessive internal and external cooling will be harmful to the overall thermal efficiency of the engine and engine per-

0925-8388/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2006.08.005 formance. The second method is the usage of more advanced superalloys [4], but the melting point of the superalloys clearly marks the limit for future developments. The third method is to explore new generations of advanced ceramic TBCs with much lower thermal conductivity [5,6]. Therefore, the most feasible and economic method is to further reduce the thermal conductivity of new ceramic TBCs on the premise of the usage of advanced superalloys and cooling technique [7].

At present, thermal barrier coatings (TBCs) of partly Y_2O_3 stabilized ZrO₂ (PYSZ) films [8–10] are widely used to protect hot section parts of aircraft and land-based turbines by reducing the temperature of metal substrates. However this standard material has a limited temperature capability due to accelerated sintering and phase transformations at high temperatures. As a result, a worldwide effort has been undertaken to identify new candidates for a TBC application [11–14].

In recent studies, the rare earth zirconates with the type of $Ln_2Zr_2O_7$ have been investigated and the results show that these materials are significant for the top ceramic materials for

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future TBCs. Several interesting zirconates, such as $Gd_2Zr_2O_7$, $Sm_2Zr_2O_7$, $Nd_2Zr_2O_7$ and $La_2Zr_2O_7$ were investigated. It is found that, $La_2Zr_2O_7$ has excellent thermal stability, low thermal conductivity, chemical resistance, low sintering rate, and become a very promising candidate for new TBCs. However, compared to partly Y_2O_3 stabilized ZrO_2 , its thermal expansion coefficient is relatively low [15–17]. It is well know that, CeO_2 has high thermal expansion coefficient, which indicates that the thermal expansion coefficient of $La_2Zr_2O_7$ may be enhanced by CeO_2 doping.

However, CeO_2 doped $La_2Zr_2O_7$ ceramic for TBCs has not been investigated in detail up to now. In this research, $La_2Zr_2O_7$ (LZ) and $La_2Zr_2O_7$ doped with CeO_2 (LCZ) ceramic were synthesized by the coprecipitation–calcination method. And the chemical compositions, phase compositions, thermophysical properties of these materials were examined.

2. Experimental

In the present study, lanthanum oxide powder (Rare-Chem Hi-Tech Co. Ltd., purity \geq 99.99%), zirconium oxychloride (Zibo Huantuo Chemical Co. Ltd., Analytical) and cerium nitrate (Rare-Chem Hi-Tech Co. Ltd., Analytical) were chosen as the reactants. CeO2 doped La2Zr2O7 were prepared by coprecipitation of an aqueous solution of LaNO₃, Ce(NO₃)₂ and zirconium oxychloride. For the preparation of LCZ ceramic powder, the lanthanum oxide was dissolved in hydrogen nitrate, cerium nitrate and zirconium oxychloride were dissolved in distilled water, respectively. These solutions were mixed in appropriate proportions and stirred for 30 min. The precursor solution was slowly added to an ammonium hydrate solution with pH 12.5, with stirring, to obtain gel-like precipitates, which were then filtered and washed with distilled water. The washed precipitates were dried at 120 °C for 12 h and heat-treated at 600 °C for 10 h to remove any organics. The remaining solid was then calcined at 1200 °C for 5 h. The densified cake was finally crushed in an agate mortar and subsequently milled in a planetary mill for 24 h with ehanol using zirconia balls and dried at 120°C overnight.

Samples for the determination of thermophysical properties were prepared by uniaxially cold pressing with 100 MPa pressure and pressureless sintering of zirconate ceramic powders at temperatures up to $1650 \,^{\circ}$ C for 10 h.

The chemical compositions of prepared ceramic powders (LZ and LCZ) were determined by an inductively coupled plasma-atomic emission spectrometer (ICP-AES, OPTIMA-4300DV).

Crystal-phase identification of the synthesized sample was determined by X-ray diffractometry (XRD, RIGAKU D/Max-rB) with Ni filtered Cu K α radiation (0.1542 nm) at a scan rate of 4 °C/min. The bulk density of the sample was measured by the Archimedes method with an immersion medium of deionized water.

The linear thermal expansion coefficient (CTE) of the sample was determined with a high-temperature dilatometry (Model NETZSCH DIL 402EP, Germany) operating in a temperature range between ambient and 1000 °C at a heating rate of 5 K/min in air. The sample dimensions were approximately 25 mm \times 4 mm \times 3 mm.

The thermal diffusivity (λ) for the sintered sample was measured, using the laser-flash method (Model NETZSCH LFA 427, Germany), as a function of specimen temperature (in the range between ambient and 800 °C) in an argon atmosphere. The present sample was about 10 mm in diameter and about 1 mm in thickness. Before thermal-diffusivity measurement, both the front and the back faces of the specimen were coated with a thin layer of gold. This coating was done to prevent direct transmission of the laser beam through the translucent specimens. The thermal diffusivity measurement of the specimen was carried out three times at each temperature and the experimental uncertainty is <10%.

The specific heat capacity (C_p), as a function of temperature (in the range between ambient and 600 °C), was measured using differential scanning calorimeter (DSC) (Model NETZSCH DSC204, Germany) at a heating rate of 10 K/min in air.



Fig. 1. Phase diagram of La2O3-ZrO2.

The thermal conductivity k is given by Eq. (1) with the heat capacity C_p , density ρ and thermal diffusivity λ .

$$k = C_p \lambda \rho \tag{1}$$

Because the sintered specimen was not fully (100%) dense, the measured thermal-conductivity value was modified for the actual data k_0 using the Eq. (2) [12]:

$$\frac{k}{k_0} = 1 - \frac{4}{3}\phi$$
 (2)

where ϕ is the fractional porosity.

3. Results and discussion

3.1. Preparation of LZ and LCZ ceramic powders

According to the diagram of La_2O_3 –ZrO₂ [18], the pyrochlore $La_2Zr_2O_7$ exists in a rather large range (P area in Fig. 1), and the mol ratio range of La and Zr is 0.87–1.15.

The chemical compositions of prepared ceramic powders (LZ and LCZ) were determined by an inductively coupled plasmaatomic emission spectrometer. Table 1 shows the results of chemical composition analyses for LZ and LCZ.

It can be seen from Table 1, the mol ratio of La and Zr in LZ and LCZ is 0.98 and 0.97, respectively, which are all in the range of 0.87–1.15, which indicates that LZ and LCZ with pyrochlore structure are synthesized. The XRD results of LZ and LCZ ceramic powders prepared by coprecipitation–calcination method are shown in Fig. 2.

Table 1 Chemical composition of the prepared LZ and LCZ ceramic powders

Ceramic powders	Mol ratio La:Ce:Zr	mass%/wt.%		
		La ₂ O ₃	CeO ₂	ZrO ₂
LZ	0.98:0:1	56.43	0	43.57
LCZ	0.97:0.14:1	51.75	7.88	40.37



Fig. 2. XRD patterns of LZ and LCZ ceramic powders.

Fig. 2 indicates that the XRD spectrum of the synthesized LZ is coincident with the standard XRD spectrum of La₂Zr₂O₇ and no other phases exist in the product. According to the standard XRD spectrum of La₂Zr₂O₇ (73-0444), a piece of pure La₂Zr₂O₇ with pyrochlore structure was synthesized. From the powder X-ray diffraction pattern at room temperature of the sample, it is found that the cubic pyrochlore type single phase La₂Zr₂O₇ with the space group of Fd-3m is obtained in the present study. The lattice parameters evaluated from the Xray diffraction pattern are a = 1.0823 nm, b = 1.0823 nm and c = 1.0823 nm. Subramanian [19] reported that, La³⁺ is packed in the vacancy of the octahedron constituted by six ZrO₆ in the pyrochlore crystal structure of La₂Zr₂O₇, which is stable and can contain many La³⁺ ion and oxygen vacancy. Under the conditions of satisfying electroneutrality of the lattice, La³⁺ ion may be substituted by other ion (such as Ce⁴⁺ ion) with closed ion radium to La^{3+} ion. It can be seen from Fig. 2 that, the XRD spectrum of the synthesized La₂Zr₂O₇ doped with CeO₂ (LCZ) is also coincident with the standard XRD spectrum of La₂Zr₂O₇ with pyrochlore structure, which indicates that CeO have been dissolved in the La₂Zr₂O₇ crystal through substitution solid solution. The lattice parameters of CeO2 doped La2Zr2O7 evaluated from the X-ray diffraction pattern are a = 1.0768 nm, b = 1.0768 nm and c = 1.0768 nm. The substitution of Ce⁴⁺ ions for the La³⁺ sites makes the lattice parameter shrink because the ionic radius of Ce^{4+} (0.097 nm) is smaller than that of La^{3+} (0.116 nm).

3.2. Sintered samples

The prepared LZ and LCZ ceramic powders were crushed in an agate mortar and subsequently milled in a planetary mill for 24 h with ethanol using zirconia balls and dried at 120 °C overnight. Then these treated ceramic powders were uniaxially cold pressing with 100 MPa pressure and pressureless sintering of zirconate ceramic powders at temperatures up to 1650 °C for 10 h. Finally, the densified samples of LZ and LCZ for the determination of thermophysical properties were obtained. The densities of these samples determined by the Archimedes method with an immersion medium of deionized water were shown as Table 2.

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Relatively densities of LZ and LCZ ceramic block

Ceramic block	LZ	LCZ
Density (g/cm ³)	5.74	5.84
Relative density (%)	94.8	95.3

It can be seen from Table 2 that, the relative density of the LZ and LCZ ceramic samples is 94.8 and 95.3%, respectively.

3.3. Thermal expansion

The linear thermal expansion coefficients of LZ and LCZ are presented in Fig. 3, together with the data of 8YSZ [20].

It can be seen that the linear thermal expansion coefficient of LZ and LCZ increase with the temperature increasing. The essence of the linear thermal expansion coefficient of solid materials increasing with the increase of temperature is that, the average distance between particles among the lattice increases with the temperature increasing. With the increasing of temperature, the crystal lattice vibration of solid materials is intensified, which results in the increase of the linear thermal expansion coefficient.

Fig. 3 also indicates that the thermal expansion coefficient of LZ is lower than that of 8YSZ, but the thermal expansion coefficient of LCZ is higher than that of 8YSZ when the temperature is over 400 °C, which indicates the thermal expansion coefficient of LZ can be evaluated by adding CeO₂. This result is beneficial to reduce the residual stresses due to thermal expansion mismatch at the interface between a top ceramic layer and a bond coat.

3.4. Thermal conductivity

The specific heats of LZ and LCZ for various temperatures are illustrated in Fig. 4, which indicates nearly a linear temperature dependence, i.e., $C_p \propto T$, and increases with the temperature increasing. Due to the limitation of the measurement apparatus, the data of specific heat were determined only in the range



Fig. 3. The linear thermal expansion coefficient of La₂Zr₂O₇, LCZ and 8YSZ.



Fig. 4. Specific heat of La₂Zr₂O₇ and LCZ for various temperatures.

between ambient and 800 °C. The specific heats can be fitted as the following equations in this temperature range:

$$C_p(\text{LZ}) = 0.37 + 1.92 \times 10^{-4} T - 2.95 \times 10^{-8} T^2$$
 (2)

$$C_p(\text{LCZ}) = 0.37 + 1.91 \times 10^{-4} T - 1.51 \times 10^{-10} T^2$$
 (3)

The thermal diffusivities of LZ and LCZ decrease with the increasing of temperature in the range between ambient and 800 °C, which is plotted in Fig. 5. Fig. 5 shows an inverse temperature dependence, i.e., $\lambda \propto T^{-1}$, in this temperature range. The T^{-1} -dependence diffusivity for LZ and LCZ suggests a dominant phonon conduction behavior, which resembles most polycrystalline materials [21].

The values of thermal conductivity are thus obtained by multiplying the thermal diffusivity, density and specific heat according to Eq. (1), and are observed in Fig. 6.

It can be seen that thermal conductivity decreases gradually with the temperature increasing. The value of thermal conductivity of LCZ decreases from 1.75 to 1.52 W/(m K) in this temperature range. According to the micro-mechanism of thermal conduction, the thermal conduction of inorganic non-metallic material is the results of phonon impacting. The thermal con-



Fig. 5. Thermal diffusivity of La₂Zr₂O₇ and LCZ for various temperatures.



Fig. 6. Thermal conductivity of La2Zr2O7 and LCZ for various temperatures.

ductivity of phonon is shown as formula (4) [22]

$$k = \frac{1}{3}C_v \overline{v}\overline{l} \tag{4}$$

where, C_v is the specific heat capacity of phonon, \bar{v} is the average speed of phonon, \overline{l} is the mean free path of phonon. C_v is almost a constant when temperature is upon Debye temperature. The value of \bar{v} is related with elastic ratio (E) and density (ρ), because of the effect of temperature on the elastic ratio and density is not obviously, so the value of \bar{v} may be also as a constant approximately. Consequently, the value of the crystal thermal conductivity (k) is decided by the law that the mean free path of phonon decreases with the increasing of temperature among most polycrystalline ceramic materials. With the increasing of temperature, the shaking energy of phonon increases, the frequency increases, the impact probability increases and the mean free path of phonon decreases, which results in the decrease of the thermal conductivity (k). This is the main reason of the thermal conductivity of most inorganic non-metallic materials decreases with the increasing temperature at upper temperature.

Low thermal conductivity is one of the most critical requirements for TBCs. The thermal conductivity of current 8YSZ is about 2.5 W/(m K) [23], which is higher than that of LCZ and LZ. It is well known that the substitutional solid solution is formed by the substitution of Zr^{4+} cation by trivalent rare-earth cation when a trivalent rare-earth oxide is doped into ZrO_2 [12]. The substitution of two Zr^{4+} cations with two La³⁺ or Y³⁺ cations is accompanied by the incorporation of one oxygen vacancy, to maintain the electroneutrality of the lattice. The defect chemistry due to codoping can be represented using the Kröger–Vink notation by the following equation:

$$Ln_2O_3 \xrightarrow{ZrO_2} 2Ln_{Zr'} + V_o'' + 3O_o^x$$
⁽⁵⁾

where, $\text{Ln}_{Zr'}$ represents an Ln^{3+} cation that occupies a Zr^{4+} cation site (single negative charge), V_0'' is a doubly charged (positive) oxygen vacancy, and O_0^x is an O^{2-} anion on an oxygen site (neutral charge). The electric charges are defined with respect to the pure $\text{Zr}O_2$ lattice. Ln in Eq. (5) can be either La or Y. Eq. (5) shows that the higher the content of

 Ln_2O_3 is, the more oxygen vacancies are created. The content of La_2O_3 is 33 mol% in $La_2Zr_2O_7$, while that of Y_2O_3 is only 4.02 mol% in 8YSZ. Clearly, the concentration of oxygen vacancies in $La_2Zr_2O_7$ is significantly higher than in 8YSZ. Therefore, the thermal conductivity of $La_2Zr_2O_7$ is much lower than that of 8YSZ due to the scattering of the phonons by the oxygen vacancies.

In addition to the phonon scattering by the oxygen vacancies, another reason of low thermal conductivity of La₂Zr₂O₇ is the scattering of phonons by the substitutional cation. For substitutional atoms existing in the lattice of oxides, the mean free path of phonon \overline{l} is given [24] by

$$\frac{1}{\bar{l}} = \frac{a^3}{4\pi v^4} \omega^4 c \left(\frac{\Delta M}{M}\right)^2 \tag{6}$$

where, a^3 is the volume per atom, v the transverse wave speed, ω the phonon frequency, c the concentration per atom, M the average mass of the host atom, $M + \Delta M$ the average mass of the solute atom. Eq. (6) shows that the phonon mean free path is proportional to the square of the atomic weight difference between the solute and host (Zr) cations. Because atomic weights of Zr and Y are 91 and 89, respectively, the phonon scattering by Y³⁺ solute cations is negligible. On the other hand, the atomic weight of La and Ce is 138.9 and 140.1, respectively; the effective phonon scattering by La³⁺ solute cations is significantly higher than that of Y³⁺ solute cations, which contributes to the lower thermal conductivity of La₂Zr₂O₇.

4. Conclusions

- Lanthanum zirconate (La₂Zr₂O₇, LZ) and CeO₂ doped La₂Zr₂O₇ (LCZ) ceramic were synthesized by the coprecipitation–calcination method. The compositions of all prepared ceramic materials were in the range of the synthesis of single La₂Zr₂O₇ with pyrochlore structure.
- (2) After the prepared ceramic powders were mechanically ballmilled, vacuum dried, molded by cold pressure and densified by sinter at 1650 °C for 10 h, the relative density of the LZ and LCZ ceramic samples is 94.8 and 95.3%, respectively.
- (3) The linear thermal expansion coefficient of LCZ is higher than that of 8YSZ when the temperature is over 400 °C, but the thermal conductivity of La₂Zr₂O₇ is much lower than that of 8YSZ, which indicates the thermal expansion coefficient of LZ can be evaluated by adding CeO₂. With the temperature increasing, the thermal expansion coefficient of these ceramics increased.

- (4) With the temperature increasing, the thermal conductivity of these ceramics decreased. The lower thermal conductivity of La₂Zr₂O₇ can be attributed to the significantly higher concentration of oxygen vacancies and the significantly larger atomic weight of the solute cations in this material.
- (5) LCZ can be explored as a novel prospective candidate material for use in TBCs.

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