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The mechanical and thermophysical properties of $La_2(Zr_{1-x}Ce_x)_2O_7$ ceramics

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ABSTRACT

The $La_2(Zr_{1-x}Ce_x)_2O_7$ ($x = 0, 0.3, 0.5, 1.0$) powders were synthesized by coprecipitation-calcination method. The XRD results indicated that $La_2(Zr_{0.5}Ce_{0.5})_2O_7$ comprised of $La_2Ce_2O_7$ and $La_2Zr_2O_7$, whereas single phase $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ with pyrochlore structure was synthesized at 1400 °C. The bulk $La_2(Zr_{1-x}Ce_x)_2O_7$ ($x = 0.3, 0.5, 1.0$) were sintered at 1600 °C and showed excellent phase stability at 1450 °C. The $La_2Ce_2O_7$ possessed the highest microhardness both in as-sintered state and after heat treatment at 1450 °C for different times, followed by $La_2(Zr_{0.5}Ce_{0.5})_2O_7$ and $La_2(Zr_{0.7}Ce_{0.3})_2O_7$. The $La_2(Zr_{0.5}Ce_{0.5})_2O_7$ had the highest fracture toughness of 3.8 ± 0.2 MPa $m^{1/2}$ in as-sintered state, followed by $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ (3.5 ± 0.2 MPa $m^{1/2}$) and $La_2Ce_2O_7$ (2.6 ± 0.3 MPa $m^{1/2}$), which are much higher than that of $La_2Zr_2O_7$ and 8YSZ. The sudden thermal expansion decrease of $La_2Ce_2O_7$ was fully suppressed in $La_2(Zr_{0.7}Ce_{0.3})_2O_7$. The $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ also had the lowest sintering rate of 1.13×10^{-7} s^{-1} at 1400 °C, as well as the lowest thermal conductivity of 1.06 $Wm^{-1}K^{-1}$ at 900 °C.

1. Introduction

Thermal barrier coatings (TBCs) are applied on the superalloy components in order to increase the operating temperatures and reduce the cooling requirements of gas turbine engines, thus achieving higher engine efficiency, lower emissions, and increased practical performance [1,2]. State-of-the-art TBCs are based on 7–8 wt.% Y_2O_3-stabilized ZrO_2 (8YSZ), that is limited to be used at ~1200 °C for long-term operation due to the phase transformations and sintering effect [3,4]. Therefore, much effort was devoted to develop new ceramic TBCs candidates which can be operated at higher temperatures. Among the investigated ceramic TBCs candidates, $La_2Zr_2O_7$ (LZ) with pyrochlore structure shows promising thermophysical properties, such as low thermal conductivity, high phase stability, as well as high sintering resistance compared to YSZ, thus LZ has been proposed as a promising TBC material [5,6]. However, the relatively low thermal expansion coefficient (TEC) and low fracture toughness of LZ lead to high thermal stress generated between LZ coating and metallic bond coat, resulting in a premature failure of the LZ TBC system.

It is well known that CeO_2 has high TEC, and the TEC of LZ can be enhanced by doping with CeO_2 [7–9]. However, the TEC of LZ doped with CeO_2 does not linearly increase with increasing doping amount of CeO_2. Zhang et al. reported that 10 mol% CeO_2 substituted LZ ($La_2(Ce_{0.1}Zr_{0.9})_2O_7$) had a highest TEC of 11.61×10^{-6} K^{-1} (25–1400 °C) [9]. In addition, $La_2Ce_2O_7$ (LC) is also considered as a promising TBC material due to its low thermal conductivity, high TEC, as well as high phase stability at higher temperatures compared to 8YSZ [10–12]. However, the dramatic TEC decrease of LC at ~280 °C can cause higher thermal stress between ceramic top coat and underneath metallic bond coat, as well as substrate, giving rise to a premature failure of the LC TBC system. Fortunately, the dramatic TEC decrease of LC at ~280 °C can be suppressed by either doping with Ta_2O_5/WO_3 or increasing Ce/La ratio [13]. Another undesired property of LC is relatively low sintering resistance.

It is a common knowledge that the use of second phase particle can not only retard the grain growth with higher sintering resistance, but also improve fracture toughness of the ceramic. In this paper, the $La_2(Zr_{1-x}Ce_x)_2O_7$ ($x = 0, 0.3, 0.5, 1.0$) ceramics were in-situ synthesized as a solid solution or a composite by

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coprecipitation-calcination method. The mechanical and thermophysical properties of the $La_2(Zr_{1-x}Ce_x)_2O_7$ ceramics were investigated.

2. Experimental procedure

$La(NO_3)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$ and $Zr(NO_3)_4 \cdot 5H_2O$ (Tianjin Guangfu Fine Chemical Institute, AR, Tianjin, China) were used as starting materials. For the preparation of the $La_2(Zr_{1-x}Ce_x)_2O_7$ (x = 0, 0.3, 0.5, 1.0) (short denomination: LZ, LZ7C3, LZ5C5, LC) ceramic powders, $La(NO_3)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$ and $Zr(NO_3)_4 \cdot 5H_2O$ dissolved in deionized water in appropriate proportions and stirred for 30 min. The precursor solution was dropwise added to ammonia solution with continuous stirring, keeping pH value as 10. The obtained precipitates were centrifugated and washed using deionized water until pH value reaches about 7, followed by vacuum drying at 120 °C for 12 h. The precursor powders were calcined in a muffle furnace with heating rate of 3 °C/min to 1200 °C, followed by soaking at 1200 °C for 3 h, and then cooled down to room temperature by shutting down the furnace.

The $La_2(Zr_{1-x}Ce_x)_2O_7$ bulk materials were prepared by cold pressing followed by sintering at 1600 °C for 6 h in air. The sample dimensions for TEC and thermal diffusivity measurements were $3 \times 4 \times 25$ mm and $\Phi 10 \times 1$–2 mm, respectively.

The thermal behavior of the precursor powders was studied from 25 °C to 1300 °C using a simultaneous thermal analysis apparatus (TG-DSC, Model STA 449PC, Netzsch, Germany). The TECs and thermal diffusivities of the $La_2(Zr_{1-x}Ce_x)_2O_7$ bulk materials were recorded by a high-temperature dilatometer (Model DIL 402E, Netzsch, Selb, Germany) and a laser flash method (Model THETA, Netzsch, Selb, Germany), respectively. The densities (ρ) of the sintered samples were measured according to the Archimedes' principle. The porosity of the bulk $La_2(Zr_{1-x}Ce_x)_2O_7$ used for measuring thermal diffusivity is ~11%. The thermal conductivities of the sintered samples were calculated with the Eq. (1) and then calibrated with Eq. (2):

$$\lambda = D_{th}(T)C_p(T)\rho(T) \tag{1}$$

$$\lambda/\lambda_0 = 1 - 4P/3 \tag{2}$$

whereλ, $D_{th}(T)$, $C_p(T)$, $\rho(T)$, λ_0 and P are the thermal conductivity, the thermal diffusivity, the specific heat capacity, the measured density, the calibrated value of the thermal conductivity and the porosity, respectively. The specific heat capacities of the bulk $La_2(Zr_{1-x}Ce_x)_2O_7$ were calculated using Neumann-Kopp rule [14].

For measurements of the mechanical properties, the disk-shaped bulk $La_2(Zr_{1-x}Ce_x)_2O_7$ samples were polished to <1 μm with double surfaces. The microhardness and fracture toughness of the bulk $La_2(Zr_{1-x}Ce_x)_2O_7$ samples were determined by using a conventional hardness tester (Model HXD-1000TM/LCD, Shanghai Taiming Optical Instrument Co., Ltd, Shanghai, China) with applied loads of 1.96 N and 294 N, respectively. 10 indents were performed on each sample to reduce the experimental uncertainty. The fracture toughness (K_{IC}) was assessed using Eq. (3) [15]:

$$K_{IC} = 0.16Ha^{1/2}\left(\frac{c}{a}\right)^{-3/2} \tag{3}$$

where H is the hardness, a is the half-length of diagonal, and c is the crack length measured from the middle of the indent to the tip of crack ($c/a \geq 2.5$).

The phase analysis of the synthesized $La_2(Zr_{1-x}Ce_x)_2O_7$ powders and the bulk $La_2(Zr_{1-x}Ce_x)_2O_7$ was characterized by XRD (Model D/MAX 2200, Rigaku Co. Ltd., Japan). The composition of the bulk $La_2(Zr_{1-x}Ce_x)_2O_7$ was investigated by an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Model IRIS Intrepid II XSP, Thermo Fisher, USA). The microstructure of fracture surface of the bulk $La_2(Zr_{1-x}Ce_x)_2O_7$ was carried out using a scanning electron microscopy (SEM) (Model JXA 840, JEOL, Japan).

3. Results and discussion

3.1. Synthesis of the $La_2(Zr_{1-x}Ce_x)_2O_7$ powders

$La_2(Zr_{0.5}Ce_{0.5})_2O_7$ (LZ5C5) was chosen as an example to investigate the thermal behavior by TG-DSC, as shown in Fig. 1. The TG curve shows a total weight loss of 40 wt.% at 1300 °C, in which about 35% weight loss occurs below 600 °C. The broad endothermic band in DSC curve, accompanied by weight loss, indicates dehydration of the hydroxides into different oxides of La, Zr, Ce elements. The small exothermic peak at ~570 °C can be attributed to the crystallization of LC [16]. The small exothermic peak at ~800 °C and the big exothermic peak at ~1250 °C correspond to the crystallization of LZ (Fluorite) and the phase transition from LZ (Fluorite) to LZ (Pyrochlore) [17].

The XRD patterns of the $La_2(Zr_{1-x}Ce_x)_2O_7$ (x = 0.3, 0.5, 1) powders calcined at 1200 °C and 1400 °C for 3 h are shown in Fig. 2. The diffraction peaks of LC (fluorite) shifted to the large diffraction angle with decreased lattice parameter, and those of LZ (pyrochlore) shifted to the small diffraction angle with increased lattice parameter, especially for x = 0.3 and 0.5, indicating that Ce^{4+} and Zr^{4+} are replaced by each other [16]. After calcination at 1200 °C or 1400 °C, both LC and LZ7C3 were single phase with fluorite structure and pyrochlore structure, respectively. However, LZ5C5 had a single phase with fluorite structure (LC) after calcination at 1200 °C, while the second phase with pyrochlore structure (LZ) has been developed at 1400 °C. The pyrochlore LZ is normally distinguished from fluorite structure by typical super-lattice peaks at 2θ around 36° (331) and 43° (511) (PDF#17-0450).

It is reported that the solubility of LZ in LC is close to 30% (i.e. composition $La_2(Zr_{0.3}Ce_{0.7})_2O_7$), but the solubility of LC in LZ is lower than 10%, and LZ7C3 is a composite comprising fluorite LC and pyrochlore LZ [7,18,19]. In this case, LZ7C3 is a single phase LZ with pyrochlore structure. The different phase constitutes in LZ7C3 are attributed to the different synthesis methods, the single phase LZ7C3 was prepared by coprecipitation method in contrast to solid-state reaction method for composite LZ7C3. However, even the

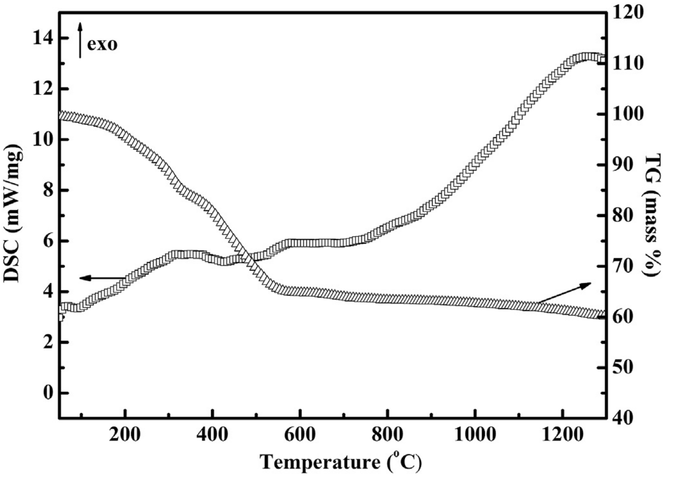

Fig. 1. TG-DSC curves of the $La_2(Zr_{0.5}Ce_{0.5})_2O_7$ precursor.