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Phase structure, thermophysical properties and thermal cycling behavior of novel $(Sm_{0.2}La_{0.8})_2(Zr_{0.7}Ce_{0.3})_2O_7$ thermal barrier coatings

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ABSTRACT

Samarium-lanthanum-zirconium-cerium composite oxide ($(Sm_{0.2}La_{0.8})_2(Zr_{0.7}Ce_{0.3})_2O_7$, SmLZC) as a candidate material for novel thermal barrier coatings (TBCs) was prepared by electron beam-physical vapor deposition (EB-PVD). The phase structure, thermophysical properties, sintering-resistance and thermal cycling behavior of SmLZC ceramics and coatings were investigated in detail. The SmLZC ceramics consist of mixture structures of pyrochlore and fluorite, and no new phase appears after long-term annealing. The thermal conductivities of SmLZC ceramics first decrease gradually with the increment of temperature below 1273 K and then increase slightly above 1273 K. The minimum value of $\sim 0.85\ W\,m^{-1}\,K^{-1}$ is detected at 1273 K. Thermal expansion coefficient of SmLZC is $\sim 10.78 \times 10^{-6}\,K^{-1}$, which is larger than those of $La_2Zr_2O_7$ ($9.18 \times 10^{-6}\,K^{-1}$) and $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ (LZC, $10.51 \times 10^{-6}\,K^{-1}$). The volume shrinkages of LZC and SmLZC are basically identical, only a bit of sintering-resistance improvement of SmLZC ceramics observed above 1773 K. The failure of the SmLZC coating is mainly a result of the occurrence of microcracks within ceramic coat, which cause the abnormal oxidation of bond coat. The microcracks of the ceramic coating are probably improved in a way both by adjusting the compositional ratio of ceramic ingot and by optimizing the process parameters.

1. Introduction

Thermal barrier coatings (TBCs), which can provide thermal, corrosion, and erosion protections for the underlying metallic components, are playing increasingly important roles in advanced gas-turbine engines used for aircraft propulsion and power generation [1]. The application of TBCs enables engines to be operated at higher gas inlet temperature, giving rise to the improvement of the thrust-to-weight ratio and fuel efficiency of the aerospace engines [2]. State-of-the-art TBCs consist of a (Ni,Pt)Al diffusion or MCrAlY overlay bond coat (BC) as the oxidation resistant layer and a ceramic topcoat as the heat resistant layer. Up to now, the most studied and commercially used ceramic top coat is based on 6–8 wt% yttria stabilized zirconia (YSZ) which shows superior thermophysical and mechanical properties such as low thermal conductivity, high thermal expansion coefficient and high fracture toughness. However, the maximum operation temperature of YSZ is limited to 1473 K for long-term application. At higher temperatures, YSZ coating suffers serious sintering and martensitic phase transformation accompanied by a 4–6% volume expansion, which tend to lead to early spallation failure of TBCs [3–7].

In the next generation of advanced engines, further increases in thrust-to-weight ratio will require even higher gas temperature. To meet the development of advanced gas turbine engines, great efforts have been done to identify new alternative TBC materials to YSZ for applications above 1473 K. The selection of TBCs materials is restricted by some basic requirements such as: (1) high melting point, (2) no phase transformation between room temperature and operation temperature, (3) low thermal conductivity, (4) chemical inertness, (5) thermal expansion match with the metallic substrate, (6) good adherence to the metallic substrate, and (7) low sintering rate of the porous microstructure [3,8,9]. Therefore, the number of materials that can be used as TBCs is very limited. Several ceramic materials such as pyrochlores ($Re_2Zr_2O_7$, Re = La, Nd, Sm and Gd), fluorite-type $Re_2Ce_2O_7$ (Re = La and Nd), and magetoplumbite-type $LaMgAl_{11}O_{19}$ have been evaluated as TBC materials [8–11]. Some new complex oxide ceramics with even lower thermal conductivity and better thermal stability, such as those materials with the mixture of pyrochlore and fluorite structures, have been also proposed as new TBC candidate materials [3,8]. Bulk $La_2(Zr_{0.7}Ce_{0.3})_2O_7$ (LZC) has a lower thermal conductivity than that of YSZ [12,13]. It is thermally stable up to its melting point (2413 K) and it has been proposed as a promising TBCs material [12,14]. However, the relatively low thermal expansion

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coefficient of LZC leads to high thermal stress between LZC top coat and metallic bond coat, and the thermal expansion curve appears a sudden decrease at moderate temperature [14,15].

In our former work [16,17], we reported that the addition of ytterbia (or yttria) could increase the thermal expansion and reduce the thermal conductivity of LZC. However, LZC ceramic material doped by Sm_2O_3 for new TBCs has not been investigated in detail up to now, and no thermal cycling life result is available. In this work, the phase structural stability, thermophysical properties, and sintering-resistance behavior of the SmLZC composite ceramics were investigated. Meanwhile, SmLZC coating was prepared by EB-PVD technique and the durability of the coating was evaluated by thermal cycling testing at 1373 K.

2. Experimental procedure

In the present study, SmLZC powders were synthesized by a solid state reaction method. Commercially available powders of La_2O_3, ZrO_2, CeO_2 and Sm_2O_3 with stoichiometric ratio were ball-milled and were calcined at 1773 K for 48 h to obtain the pure products. Then the acquired powders were uniaxially pressed into pellets and then were further compacted by cold isostatic pressing. Finally, some of the compacts were sintered at 1923 K for 24 h in air to be used for thermophysical properties measurement and the others were sintered at different annealing temperatures for 6 h to evaluate the sintering-resistance behavior.

The Ni-based superalloy with the dimension of $30 \times 10 \times 1.5\ mm^3$ was used as the substrate whose nominal composition was shown in Table 1. The superalloy substrates were mechanically polished before deposition of bond coat. The substrates were fixed by the mechanical arm in the Arc Ion-plating unit for the deposition of NiCrAlYSi bond coat (BC). The nominal composition of the BC was also listed in Table 1. After the deposition of BC, the substrates were heat-treated under high vacuum at 1143 K for 3 h. The purpose was that not only averaged the distribution of composition uniformity of coating elements, but also increased the adhesive strength of the interface of bond coat and substrate. The top coating of SmLZC was fabricated by EB-PVD. During the deposition, the single ingot with the designed composition of $(Sm_{0.2}La_{0.8})_2(Zr_{0.7}Ce_{0.3})_2O_7$ was used for EB-PVD original deposition material, and two electron guns were referred to the functions of heating substrate and vaporing of ingot. The deposition power was set to be 15 kW while the substrate pre-heating power was 8 kW. The deposition pressure of EB-PVD working chamber was about 3×10^{-2} Pa and no oxygen was introduced into the vacuum chamber. The substrate temperature for the depositions of SmLZC coating was set to be 1173 ± 25 K by properly controlling of electron beam current. The substrate was rotated at a speed of 7 rpm.

To evaluate the thermal shock resistance of the coating, the cyclic oxidation test of SmLZC TBCs was heated in an air furnace at 1373 K for 30 min followed by removing out and cooling down with airflow for 5 min. The heating-up and then cooling-down make one oxidation cycle, this process was repeated until 5% of the ceramic coat was lost, and the cycling number was then regarded as the thermal cycling life of the coating.

The bulk density (ρ) of the as-prepared SmLZC ceramic was measured by the Archimedes method. Phase composition was identified by X-ray diffraction (XRD, Bruker D8 Advance diffractometer). Microstructures of the sintered ceramics and coating samples were observed via scanning electron microscope (SEM, FEI-Quanta 600). Energy dispersive spectroscopy (EDS, Oxford INCAx-sight 6427) was applied for the composition evaluation. Thermal diffusivity measurement for SmLZC ceramics was carried out on disk shaped specimens, coated with carbon, using a laser flash apparatus (Netzsch LFA 427) in an argon atmosphere. The specific heat capacity (C_p) was calculated from the chemical compositions of SmLZC ceramics with the Neumann-Kopp rule [18] and the heat capacity data of the constituent oxides (La_2O_3, ZrO_2, CeO_2 and Sm_2O_3) obtained from the literature [19]. The linear thermal expansion coefficient (TEC) of bulk material was recorded with a high temperature dilatometer (Netzsch 402C).

3. Results and discussion

3.1. Phase constituent, structural stability and microstructure

The XRD pattern of SmLZC powders by solid state synthesis is shown in Fig. 1a. It can be observed that Sm_2O_3 is possible to be fully solid solution into LZC, and then a mixture of pyrochlore and fluorite structures can be obtained. The main reason is that Sm element has the same valence to La element, and the ionic radius of Sm^{3+} (0.096 nm) is similar to La^{3+} (0.106 nm). The closer is the ionic radii between Sm and La elements, the easier is the occurrence of substitution between them. $(Sm_xLa_{1-x})_2Zr_2O_7$ (SmLZ, pyrochlore) and $(Sm_yLa_{1-y})_2Ce_2O_7$ (SmLC, disordered fluorite) have different crystal structures. The main phase in SmLZC is SmLZ with a small solubility of SmLC, and this phase primarily keeps pyrochlore structure. The second phase is a solid solution of SmLC and SmLZ with fluorite structure. XRD patterns of the SmLZC powders annealed at 1773 K for different dwelling time are shown in Fig. 1b and e. Compared with Fig. 1a, after long-term annealing from 72 h to 240 h at 1773 K (Fig. 1b and e), no significant differences among the XRD patterns are obviously observed, indicating that SmLZC ceramics are thermally stable in the temperature range of interest for TBCs applications at least up to 1773 K.

Fig. 2 shows the typical microstructure of SmLZC ceramics sintered at 1923 K for 24 h. As can be seen from Fig. 2, the averaged grain size of SmLZC ceramics is several micrometers. The microstructure of the sintered products is very dense, only a few micropores are detected. The relative density of SmLZC sintered at 1923 K for 24 h is measured to be ~94.6%, implying that the bulk materials can be used for further characterization of the thermophysical properties.

3.2. Thermophysical properties of SmLZC ceramics

The thermophysical properties of SmLZC ceramic as a function of temperature are plotted in Fig. 3. As shown in Fig. 3, the thermal diffusivity of SmLZC decreases with the increment of temperature below 1273 K followed by a slight increase. The T^{-1}-dependence thermal diffusivity for SmLZC suggests a dominant phonon conduction behavior, which is common for most of the electrical insulating crystalline materials. The thermal conductivity (κ) is calculated from the density (ρ), thermal diffusivity (D_{th}) and heat capacity (C_p) with the relationship $\kappa = D_{th}\rho C_p$. In order to remove the effect of porosity (ϕ), the thermal conductivity is further corrected with Maxwell's relation as $\kappa/\kappa_0 = 1–4/$

Table 1
The nominal compositions (wt%) of substrate and bond coat.

Superalloy	Al	Cr	Co	Y	Si	Ta	Ti	W	Mo	Ni
Substrate	4.8~ 5.4	8.4~ 9.4	9.5~ 10.5	–	–	3.5~ 4.1	0.7~ 1.2	6.5~ 7.5	1.5~ 2.5	bal.
Bond coat	6~ 10	20~ 25	–	0.08~ 0.4	0.4~ 0.8	–	–	–	–	bal.