Preparation and thermophysical properties of fluorite-type samarium–dysprosium–cerium oxides

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Abstract

In the present study, $(Sm_{1-x}Dy_x)_2Ce_2O_7$ solid solutions were synthesized by solid reaction at $1600\,°C$ for $10\,h$ in air. The phase structure, micromorphology and thermophysical properties of $(Sm_{1-x}Dy_x)_2Ce_2O_7$ oxides were examined. XRD results indicated that pure $(Sm_{1-x}Dy_x)_2Ce_2O_7$ oxides with fluorite structure were prepared. SEM revealed that their microstructures were very dense and there were no other phases among the particles. The thermal conductivity and thermal expansion coefficient of the ceramics remarkably decreased through Dy-doping. Their thermal expansion coefficients were higher than that of YSZ, and their thermal conductivities were much lower than that of 8YSZ. Their excellent thermophysical properties imply that these solid solutions are potential materials for the ceramics layer in thermal barrier coatings.
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1. Introduction

Thermal barrier coatings (TBCs) are widely used in gas turbine engines and other components which must endure high temperature.[1–3] Generally, a typical TBC consists of a thermally insulating ceramic top layer and intermediate oxidation resistant metallic bond-coat layer. The main purpose of this dual layer system is to provide thermal protection of the superalloy components, thus improving performance or lifetime.[4] Now, the demand for improved performance in high-temperature mechanical systems has led to increasingly harsh operating environments. Further improvements in gas turbine performance will require even higher thermal efficiencies, longer operating lifetimes, and reduced emissions.[4,5] Currently, yttria stabilized zirconia (YSZ), especially zirconia containing 8 wt.% yttria coatings are still the mostly used TBCs on rotating parts in the turbine, showing an amazing balance of all required properties.[6] However, the major disadvantage of YSZ is the limited operation temperature of 1473 K for the long-term application. At higher temperatures, the t'-tetragonal phase transforms into the tetragonal and the cubic ($t + c$) phases. During cooling, the t-phase will further transform into the monoclinic (m) phase, resulting in the volume increase and leading to the formation of cracks in the coating.[7] Moreover, the sintering-induced volume shrinkages would degrade the columnar structure of EB-PVD coatings and increase the elasticity modulus and, as a result, reduce the favorable strain tolerance of the coating.[8] In order to overcome the shortcomings and meet to the ambitious development goal of TBCs, 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. This would have a dual benefit of increased engine efficiency and increased reliability. With this objective, recent development efforts have focused toward identifying new ceramic materials for TBCs.[9]

The selection of TBC material is restricted by some basic requirements, such as: (1) high melting point, (2) no

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phase transformation between room temperature and operating 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.[10,11] Therefore, the number of materials that can be used as TBCs is very limited. In recent years, the rare earth oxides with type of $Ln_2B_2O_7$ (Ln = rare earth elements, B = Zr, Hf, Hf or Ce), have been developed for advanced turbine engines, which are intended to operate at temperatures as high as possible.[12] The rare earth zirconates with general formula $Ln_2Zr_2O_7$ with pyrochlore structure or defect fluorite-type structure have been regarded as the most potential ceramic materials for thermal barrier coatings. The thermal conductivities of $Ln_2Zr_2O_7$ (Ln = La, Nd, Sm, Eu, Gd, Dy, etc.) ceramic materials are in the range from 1.1 to 1.2 W/m K, which are much lower than that of YSZ. Because of their promising thermophysical properties, efforts have been made to investigate the co-doped $Ln_2Zr_2O_7$ ceramics with one or more metal oxides in recent years.[13–16] However, their relative low thermal expansion coefficients (CETs) can result in high thermal stresses in TBC applications, which is very harmful for TBC's performance.

The rare earth hafnate with type of $Ln_2Hf_2O_7$ show typical pyrochlore structure.[17] However, their thermophysical properties were mainly studied by numerical simulation, further report on the thermophysical property of $Ln_2Hf_2O_7$ series was relatively less.[18,19] Thermophysical properties reported by Q. Z. Xue revealed that thermal conductivities of $Ln_2Sn_2O_7$ series were higher than that of 8YSZ, and their thermal expansion coefficients were lower than that of 8YSZ.[20] These results contrary to the requirements of thermal barrier coatings.

In recent years, rare earth cerium oxides with type of $Ln_2Ce_2O_7$ (Ln = rare earth elements) have attracted considerable attention. H. Dai et al.[21] reported that thermal expansion coefficient of $Nd_2Ce_2O_7$ was higher than that of YSZ and even more interesting was the thermal expansion coefficient change as a function of temperature paralleling that of the superalloy bond coat. Moreover, the thermal conductivity of $Nd_2Ce_2O_7$ was 30% lower than that of YSZ. X.Q. Cao et al.[22] has proposed $La_2Ce_2O_7$ as a new TBC material that has a low thermal conductivity and a large thermal expansion coefficient close to that of the bond coat. After long-term annealing at 1400 °C, $La_2Ce_2O_7$ was still stable without phase transformation. S. J. Patwe et al.[23] reported that thermal expansion coefficient of $Gd_2Ce_2O_7$ was higher than that of $Gd_2Zr_2O_7$ and YSZ. In our laboratory, thermo physical properties of several rare earth cerium oxides, such as $Sm_2Ce_2O_7$, $Yb_2Ce_2O_7$, $Er_2Ce_2O_7$, $Dy_2Ce_2O_7$, $Y_2Ce_2O_7$ and doped-$La_2Ce_2O_7$, have been investigated.[24–28]. Results indicated that their thermal conductivities were 25–40% lower than that of YSZ, and their thermal expansion coefficient were much higher than that of $Ln_2Zr_2O_7$ and YSZ. In these reported rare earth cerium oxides, $Sm_2Ce_2O_7$ has relatively lower thermal conductivity and higher thermal expansion coefficient. It was claimed that the substitution on Ln site by other cations in $Ln_2B_2O_7$ ceramics led to a low thermal conductivity as contrasted with unitary oxides, which also have typical influence on thermal expansion coefficient. However,

no data on phase structure and thermophysical properties of samarium–dysprosium cerium oxides system have been reported up to now. In the present study, $(Sm_{1-x}Dy_x)_2Ce_2O_7$ ceramics were prepared by pressureless sintering. The microstructure and thermophysical properties of different $(Sm_{1-x}Dy_x)_2Ce_2O_7$ ceramics were examined.

2. Experiment

Samarium oxide, dysprosium oxide and cerium oxide powders (Rare-Chem Hi-Tech Co., Ltd., Huizhou, China, purity ≥99.9%) were chosen as raw materials. These rare-earth oxide powders were heat-treated at 800 °C for 2 h before weighting. $(Sm_{1-x}Dy_x)_2Ce_2O_7$ (x = 0, 0.05, 0.15) oxides were prepared by solid-state reaction. For each composition, the weighted powders were mixed by planetary milling with zirconia balls in isopropyl alcohol for 6 h. Subsequently, the dried powder mixtures were then sieved for granulation and compacted into a disk form under uniaxial pressure of 50 MPa followed by cold isostatic pressing with 150 MPa. Finally, the bulks were pressureless-sintered at 1600 °C for 10 h in air.

The phase structures of sintered bulk materials were characterized by X-ray diffraction (XRD, X'Pert PRD MPD The Netherlands) with Cu Kα radiation at a scan rate of 4°/min. Scanning electron microscopy (SEM, Model Hitachi S-4800, Japan) was used to observe the microstructure of bulk ceramics. The specimens were polished with 1 μm diamond paste, and then thermally etched at 1500 °C for 2 h in air for SEM observations. Qualitative X-ray element analysis of various phases was carried out using SEM equipped with energy dispersive spectroscopy (EDS). For heat-treated samples, the actual densities were measured by using Archimedes method with an immersion medium of deionized water. The lattice parameters of developed phases were calculated from the XRD results.

The thermal diffusivity (λ) of the sintered samples was measured using laser-flash method (Model Anter FlashLine™ 3000, USA) from 200 °C to 1000 °C in an argon gas atmosphere. Cylindrical disk-shaped sample was about 12.7 mm in diameter and about 1.2 mm in thickness. Each sample was ground so that both surfaces were coplanar. In order to avoid any transmission of the laser beam through the samples, both the front and back faces of the samples were coated with a thin layer of graphite. Appropriate corrections were made in the thermal diffusivity calculations to account for the presence of these layers. The thermal diffusivity measurements were made at 200 °C intervals from 200 °C to 1000 °C. The thermal diffusivity measurement of these samples was carried out three times at each temperature. The specific heat capacities (C_p) were determined as a function of temperature from the chemical compositions of $(Sm_{1-x}Dy_x)_2Ce_2O_7$ and the heat capacity data of the constituent element (O, Dy, Sm and Ce) obtained from reference.[29,30] in conjunction with the Neumann–Kopp rule. The thermal conductivity (k) of the specimen was calculated by Eq. (1) with specific heat capacity (C_p), density (ρ) and thermal diffusivity (λ) as follows.

$$k = \lambda \cdot \rho \cdot C_P \tag{1}$$