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Preparation, characterization and thermophysical properties of $(Sm_{1-x}Gd_x)_2Ce_2O_7$ solid solutions

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Abstract

$Sm_2Ce_2O_7$ has low thermal conductivity and relatively high thermal expansion coefficient which make it suitable for application as high-temperature thermal barrier coatings. $(Sm_{1-x}Gd_x)_2Ce_2O_7$ solid solutions were synthesized by solid state reaction in this paper. The influence of Gd_2O_3-doping on the phase structure and thermophysical properties were investigated. The synthesized $(Sm_{1-x}Gd_x)_2Ce_2O_7$ ceramics exhibit a defect-fluorite structure, which is mainly determined by ionic radius ratio $r(A_{av}^{3+})/r(B^{4+})$. The linear thermal expansion coefficients and thermal conductivities of different $(Sm_{1-x}Gd_x)_2Ce_2O_7$ decrease with the increasing value of x in the measuring temperature. Their thermal expansion coefficients are higher than that of 8YSZ, the thermal conductivities of $(Sm_{1-x}Gd_x)_2Ce_2O_7$ ceramics at 1000 °C are located within the range of 1.07–1.69 W/m K. The composition dependence of thermal conductivity was discussed by taking into account the phonon scattering by mass and strain fluctuations at the A site.

Keywords: C. Thermal conductivity; C. Thermal expansion; Oxides; Thermal barrier coatings

1. Introduction

Thermal barrier coatings (TBCs) have been widely used to protect turbine engines operating in high temperature environment. Traditional TBCs consist of a ceramic top-coat (usually 100–400 µm thick) and an oxidation resistant bond-coat (~100 µm thick) which is usually deposited on nickel-based superalloy [1,2]. Due to low thermal conductivity, high phase stability, high thermal-expansion coefficient and high toughness compared to other ceramics, yttria-stabilized zirconia (YSZ) has been known as the most favorite top-layer material for many years [3,4]. The metallic coating acts not only as bond-coat but also as barrier against oxidation and corrosion of substrate at high temperature. The top-coat is mainly processed by air plasma spray (APS) and/or by electron beam physical vapor deposition (EB-PVD), while the bond-coat is deposited by various methods such as APS, high velocity oxy-fuel spray (HVOF), low pressure plasma spray (LPPS) and Pt-plating/chemical vapor deposition (CVD) or EB-PVD [5–7]. However, two flaws have been reported when YSZ are exposed to high temperature (above 1200 °C) for long time, i.e., phase transformation and sintering. Metastable tetragonal phase decomposes into tetragonal and cubic phase above 1200 °C. Upon cooling, tetragonal phase transforms to monoclinic phase, causing about 3.5% volume change and resulting in crack formation in the TBCs. In addition, volume fraction of pores decreases due to the significant sintering of YSZ at high temperature, which leads to an increase in the thermal conductivity as well as the in-plane stiffness and thus decreases the strain compliance of TBCs [5,6].

Due to the described shortcomings of YSZ, considerable efforts have been made to seek alternatives to further increase the gas turbine inlet temperature. However, the selection of TBCs materials is restricted by some basic requirements such as high melting point, low thermal conductivity, high thermal expansion coefficient, high phase stability, and low sintering rate [8–10]. It is found by many researchers that rare earth oxides with general composition of $A_2B_2O_7$ show promising thermophysical properties. In the type of $A_2B_2O_7$, A is a 3^+ cation (La–Lu) and B is a 4^+ cation (Zr, Hf, Sn, Ce, etc.) [11–13].

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The rare earth zirconates have excellent thermal stability, low sintering rate and low thermal conductivity. However, the low thermal expansion coefficient of rare earth zirconates leads to high thermal stress between the rare-earth zirconate coating and the metallic bond coat, resulting in a short thermal cycling life [8,10,12]. A few of rare-earth $A_2Hf_2O_7$ oxides have been proved to have lower thermal conductivity, better temperature phase stability compared to YSZ [14–17]. Unfortunately, most of current research results about thermophysical properties of rare-earth $A_2Hf_2O_7$ oxides are predicted by theoretical simulation calculation, there has been no further systemic experimental evidence to confirm the calculations [18,19]. Rare-earth stannates are a series of compounds with similar structures to the rare-earth zirconates. Interestingly, these compounds, $A_2Sn_2O_7$, constitute a complete series of isostructure compounds with a pyrochlore structure, whereas the rare-earth zirconates undergo a pyrochlore–fluorite transition, i.e. pyrochlores can only form for the lanthanide series from La to Gd, with the remainder existing as defective fluorites [20,21]. Thermophysical properties of some interesting rare-earth stannates, such as $La_2Sn_2O_7$, $Nd_2Sn_2O_7$, $Sm_2Sn_2O_7$, $Gd_2Sn_2O_7$, $Er_2Sn_2O_7$ and $Yb_2Sn_2O_7$, have been reported. However, their thermal conductivities are higher compared to 8YSZ (2.5–2.7 W/m K at 800 °C for $A_2Sn_2O_7$ and 2.1 W/m K at 1000 °C 8YSZ), and their thermal expansion coefficients are low compared to 8YSZ ($8.4–9.2 \times 10^{-6}$ K^{-1} at 1000 °C for $A_2Zr_2O_7$ and 10.1×10^{-6} K^{-1} at 1000 °C for 8YSZ) [22]. These thermophysical properties imply that the stannates can not be explored as candidate materials for the ceramic layer in TBC system.

In recent years, rare-earth $A_2Ce_2O_7$ oxides have attracted extensive attention due to their excellent electrical, catalytic, mechanical properties, low thermal conductivities and high thermal expansion coefficients at high temperature. Thermophysical properties of several interesting rare earth cerium oxides, such as $La_2Ce_2O_7$ [23,24], $Nd_2Ce_2O_7$ [25], $Gd_2Ce_2O_7$ [26,27], $Y_2Ce_2O_7$ [28], $Dy_2Ce_2O_7$ [29], $Sm_2Ce_2O_7$, $Er_2Ce_2O_7$ and $Yb_2Ce_2O_7$ [30] have been investigated. Results indicate that these rare earth cerium oxides have potential to be used as new candidate materials for future TBCs. It is well known that materials with lower thermal conductivity and higher thermal expansion coefficient can be prepared by doping or co-doping with one more oxides (Yb_2O_3, Gd_2O_3, Sm_2O_3 and Nd_2O_3) due to defect cluster formation, which indicates that the thermal conductivity of $A_2Ce_2O_7$ oxides can be reduced further by doping with other elements in the cation of A or Ce [31,32]. Clarke and coworkers also point out that substituted cations, especially the atom with large atomic weight, at site A or B creates mass disorder on the cation sublattice, which results in the lowering of thermal conductivity [31]. Meanwhile the thermal expansion coefficient is proved to be higher by Cao et al. [25]. According to this theroy, thermophysical properties of Gd-doped $La_2Ce_2O_7$ have been reported in Ref. [24], the evident differences in ionic radius and mass weight lead to the decreasing thermal conductivity of $(La_{1-x}Gd_x)_2Ce_2O_7$, and their thermal expansion coefficients are still higher than that of 8YSZ. In the lanthanide elements, ionic radius and mass weight of samarium and gadolinium are very close, $(Sm_{1-x}Gd_x)_2Zr_2O_7$ ($x=0$, 0.2, 0.4, 0.6, 0.8 and 1) and $(Sm_xGd_{1-x})_2Zr_2O_7$ ceramics have been synthesized and their thermophysical properties were studied, the relatively mass differences (mass fluctuation), and size and interatomic coupling force differences (strain filed fluctuations) contribute the decreasing thermal conductivities of $(Sm_{1-x}Gd_x)_2Zr_2O_7$ and $(Sm_xGd_{1-x})_2Zr_2O_7$ ceramics [33]. The $(Sm_{1-x}Gd_x)_2Zr_2O_7$ or $(Sm_xGd_{1-x})_2Zr_2O_7$ ceramics are rare earth zirconates, however, the influence of $(Sm_{1-x}Gd_x)_2Ce_2O_7$ ceramics have not been reported in open literatures.

In this paper, $(Sm_{1-x}Gd_x)_2Ce_2O_7$ ceramics were prepared by the solid reaction method. The structure evolution and thermophysical properties of $(Sm_{1-x}Gd_x)_2Ce_2O_7$ ceramics were investigated in order to understand on co-doped fluorite-structure rare-earth cerium oxides.

2. Experimental

In the present study, CeO_2, Gd_2O_3 and Sm_2O_3 (Rare-Chem Hi-Tech Co., Ltd., Huizhou, China; purityHi-Tec) were chosen as the reactants. The oxides powders were fired at 1000 °C for 5 h before weighting in order to eliminate hydroxide and/or carbonate. After mixed the stoichiometric constituents of $(Sm_{1-x}Gd_x)_2Ce_2O_7$ by ball milling in analytically pure alcohol and dried at 110 °C for 5 h. The dried powder mixtures were then sieved for granulation and compressed into a disk form under uniaxial pressure of 50 MPa by cold isostatic pressing with 150 MPa. The bulks were placed on cerium tiles and sintered at 1600 °C for 10 h in air. The pellets were subsequently cooled in air at the end.

For heat-treated samples, the actual densities were measured by the Archimedes method with an immersion medium of deionized water. The phases of heat-treated samples were identified using an X-ray diffraction (XRD, X'Pert PRD MPD The Netherlands) with Ni filtered CuKα radiation (0.1542 nm) at the scanning rate of 4°/min. The lattice parameters of developed phases were calculated from the XRD results. The theoretical density of each composition was calculated using lattice parameters acquired from XRD results and the molecular weight in an elementary cell. 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 element analysis of various phases was carried out using SEM equipped with energy dispersive spectroscopy (EDS).

The thermal diffusivity (λ) of the synthesized samples was measured using laser-flash method (Model Netzsch LFA 427/) in the range 200–1000 °C in an argon atmosphere 7/G. The sample dimension for thermal diffusivity measurement was about 12.7 mm in diameter and about 1 mm in thickness. Before thermal diffusivity measurement, both the front and back faces of the samples were coated with a thin layer of graphite. These coatings were done to prevent direct transmission of laser beam through the translucent specimens. The specific heat capacity (C_p) as a function of temperature was calculated from the heat