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Short communication

Influence of partial substitution of Sc_2O_3 with Gd_2O_3 on the phase stability and thermal conductivity of Sc_2O_3-doped ZrO_2

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Abstract

Multi-rare earth elements doping is one of effective methods to improve the phase stability and thermal barrier property of zirconia for thermal barrier coatings (TBCs) application. In this paper, the phase stability and thermo-physical properties of 7.5 mol% Sc_2O_3 and Gd_2O_3 co-doped ZrO_2 (ScGdSZ) were investigated. ScGdSZ after 150 h heat-treatment at 1400 °C exhibited no monoclinic phase, showing high phase stability. The substitution of Sc_2O_3 with Gd_2O_3 increased the fraction of c-phase, however, t′-phase was still the dominant phase when the substitution amount was less than 2 mol%. The thermal conductivities of ScGdSZ gradually decreased with the increasing Gd_2O_3 proportion. 3.7 Sc_2O_3 and 3.7 Gd_2O_3 co-doped ZrO_2 (in mol%) showed the lowest thermal conductivity, which was 20% lower than 7.5 Sc_2O_3-doped ZrO_2 and 40% lower than 4.5 Y_2O_3-doped ZrO_2.

Keywords: A. Powders: chemical preparation; C. Thermal conductivity; D. ZrO_2; E. Thermal applications

1. Introduction

Thermal barrier coatings (TBCs) are extensively used to protect the metal alloy components in the hot-sections of the gas turbine engine from high-temperature gas [1,2]. Among those researched TBC ceramic materials, 3.5∼4.5 mol% Y_2O_3 stabilized ZrO_2 (YSZ) has been considered as the state-of-the-art material, owing to its satisfactory properties, including high melting point, low thermal conductivity, high thermal expansion coefficient and high hardness [3]. However, YSZ coatings cannot long-term operate above 1200 °C, due to sintering and metastable tetragonal phase (t′-ZrO_2) transformation [4,5].

Co-doping trivalent rare earth oxides is considered as one of the effective ways to develop alternative ceramic materials with high phase stability and low thermal conductivity. Liu et al. [6,7] found that the thermal conductivities of $Sm_xZr_{1-x}O_{2-x/2}$ and $Nd_xZr_{1-x}O_{2-x/2}$ were lower than those of YSZ. The phase structures were mixtures of monoclinic and tetragonal phases when $x=0.1$, while fluorite structure when $x=0.2$, 0.3. Doping of Gd_2O_3 and La_2O_3, which have larger cation radii than Y_2O_3, could obviously decrease thermal conductivity of ZrO_2, but accelerated the destabilization of t′-phase [8–10]. 7 mol% Sc_2O_3,Y_2O_3 co-doped ZrO_2 exhibited excellent tetragonal phase stability even at 1400 °C, when Sc_2O_3 dominated the dopants [11,12]. It can be supposed that the high doping level may introduce more oxygen vacancies than 3.5∼4.5 mol% YSZ, thereby lowering thermal conductivity. With respect to these, Sc_2O_3 seems to be a better stabilizer to ZrO_2 than Y_2O_3. However, the high-temperature thermal conductivity of Sc_2O_3 doped ZrO_2 (ScSZ) has been seldom reported so far. In the present study, Gd_2O_3, with both larger cation radius and heavier atomic mass than Sc_2O_3, was chosen to partially substitute Sc_2O_3 in ScSZ. The influence of the substitution on phase stability at 1400 °C and thermal conductivity between 20 °C and 1400 °C were investigated. The total doping amount of Gd_2O_3, Sc_2O_3 co-doped ZrO_2 (ScGdSZ) was selected to be 7.5 mol% within the tetragonal phase region, according to the Sc_2O_3–ZrO_2 phase diagram [13].

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2. Experimental procedure

2.1. Powder synthesis

YSZ, ScSZ and ScGdSZ powders were synthesized by a chemical co-precipitation technique. The chemical compositions can be found in Table 1. Firstly, the zirconium oxychloride powders were dissolved into deionized water while gadolinia and scandia powders were dissolved into nitric acid. The cation-containing solutions were mixed in the required proportions, and then added dropwise into ammonium hydroxide while stirring vigorously and controlling pH > 9. The precipitants were washed and ultrasonically re-dispersed, finally, dried at 75 °C for 24 h and then calcined at 800 °C for 4 h to obtain molecularly mixed oxide powders. X-ray diffraction (XRD, Rigaku Diffractometer, Cu K_α radiation) was performed for the phase identifications of the synthesized powders.

2.2. Phase stability

To investigate the phase stability of the synthesized powders, they were annealed at 1400 °C for 150 h. The phase evolutions were identified by X-ray diffraction. In the range of $2\theta = 72° \sim 76°$ corresponding to {4 0 0} peaks, the scanning speed was as low as 0.2°/min to distinguish cubic and tetragonal phase. Mole fraction of each phase was calculated using the common Eq. [14].

$$M_m/M_{c,t/t'} = 0.82[I_m(\bar{1}\ 1\ 1) + I_m(1\ 1\ 1)]/I_{c,t/t'}(1\ 1\ 1)$$
$$M_c/M_{t/t'} = 0.88 I_c(4\ 0\ 0)/[I_{t/t'}(4\ 0\ 0) + I_{t/t'}(0\ 0\ 4)] \quad (1)$$

2.3. Thermal properties

The synthesized powders were uniaxially pressed at 80 MPa into disc-shaped compacts, further densified by isostatic cool pressing at 200 Mpa, followed by sintering at 1500 °C for 15 h. The bulk densities were measured using Archimedes's method.

The thermal diffusivity between 20 °C and 1400 °C was measured using a laser-flash apparatus (Netzsch LFA 427). Prior to measurements, both the front and rear surfaces were coated with a thin film of graphite to increase the absorption of laser pulses. The specific heat capacities were calculated according to the Neumann–Kopp law, with the value of the constituent oxides obtained from the thermodynamic database [15]. The thermal conductivity λ was calculated from density ρ, heat capacity C_p and thermal diffusivity α, using the equation:

$$\lambda = \rho \alpha C_p \quad (2)$$

Then the results were corrected for the actual data λ_0 of fully dense samples, using [16]:

$$\lambda/\lambda_0 = 1 - 4\Phi/3 \quad (3)$$

where Φ is the fractional porosity.

3. Results and discussion

3.1. Phase stability

The XRD patterns of the synthesized 4.5YSZ, 7.5ScSZ and ScGdSZ powders are shown in Fig. 1. All the spectra are coincident with the XRD spectrum of tetragonal or cubic zirconia and have no evidence for other phases, indicating that the dopants had been dissolved into ZrO_2 crystal and stabilized tetragonal or cubic phase. Specifically, the synthesized 4.5YSZ and 7.5ScSZ compose of only t′-phase zirconia while ScGdSZ compose of both t′-phase and c-phase.

Fig. 2a shows the XRD spectra of 4.5YSZ, 7.5ScSZ and ScGdSZ powders after 150 h heat treatment at 1400 °C.

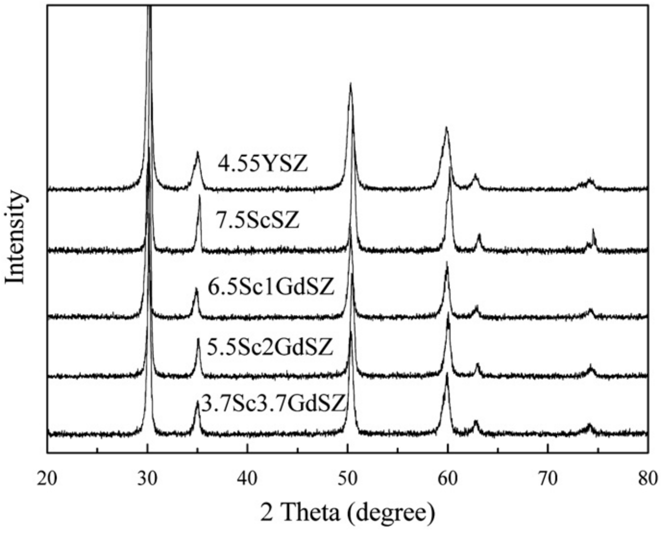

Fig. 1. XRD patterns of the synthesized powders.

Table 1
The designed compositions and phase fractions after heat treatment of the researched samples.

Sample ID	Y_2O_3 (mol%)	Sc_2O_3 (mol%)	Gd_2O_3 (mol%)	m-phase (mol%)	t′-phase (mol%)	c-phase (mol%)	Tetragonality $c/\sqrt{2}a$
4.5YSZ	4.5	–	–	40	0	60	–
7.5ScSZ	–	7.5	–	–	95	5	1.0171
6.5Sc1GdSZ		6.5	1	–	86	14	1.0062
5.5Sc2GdSZ		5.5	2	–	65	35	1.0049
3.7Sc3.7GdSZ		3.7	3.7	–	0	100	–

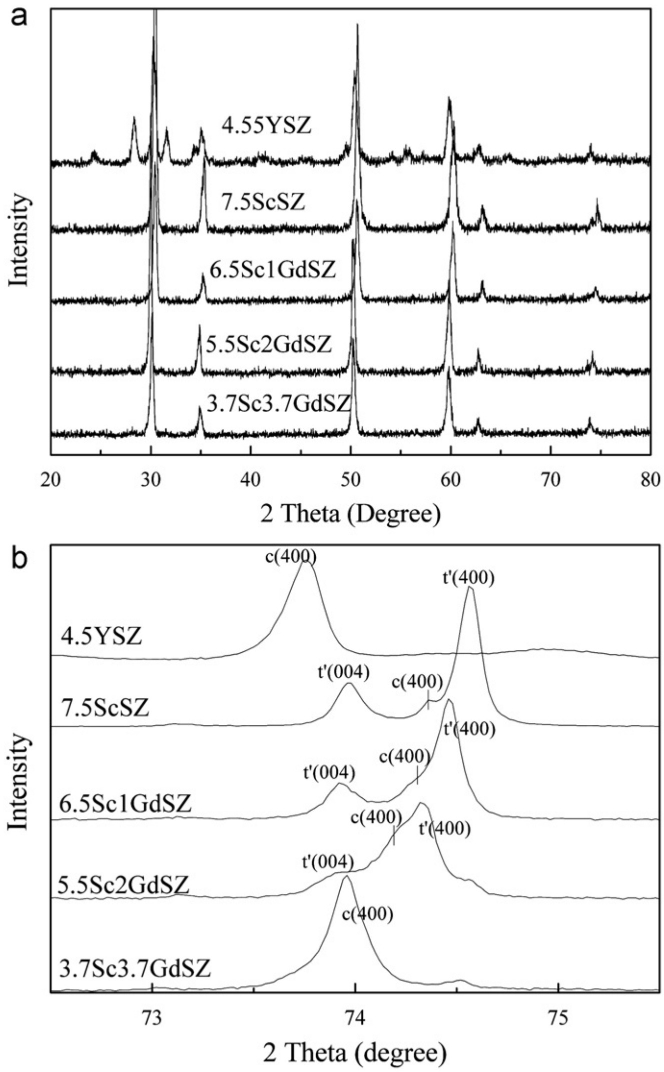

Fig. 2. XRD patterns of the powders after 150 h heat treatment at 1400 °C;.(a) 2θ values of 20°∼80°; (b) 2θ values of 72.5°∼75.5°.

It can be found that only 4.5YSZ exhibits evident monoclinic phase reflection peaks of m($\overline{1}$ 1 1) and m(1 1 1) after heat treatment, however, the others have no sign of monoclinic phase. To distinguish the tetragonal phase from cubic phase, the high angle region ($2\theta = 72° \sim 76°$) XRD patterns are depicted in Fig. 2b. 4.5YSZ shows only a single peak of c-phase; whereas 7.5ScSZ exhibits evident tetragonal (0 0 4) and (4 0 0) double peaks, showing high tetragonal phase stability at 1400 °C. The presence of m-phase and c-phase in 4.5YSZ could be explained by the general principle that t′-phase transformed to t-phase and c-phase at high temperature and then t-phase transformed to m-phase during cooling. Jade 5.0 software package was used to split the overlapping peaks and calculate the integral intensity. The phase compositions and tetragonality of the heat treated powders are calculated and listed in Table 1. The tetragonality, below 1.020, reflects t′-phase [12]. 4.5YSZ contains 40 mol% monoclinic phase, indicating that 4.5YSZ had undergone almost complete t′-phase partitioning.

The t′-phase of Gd_2O_3-doped ZrO_2 was reported [8] easy to decompose and form m-phase at 1400 °C. However, in our investigation, when Gd_2O_3 was doped to ScSZ, the undesired m-phase transformation didn't occur at 1400 °C. Actually the influence of Gd_2O_3 on the phase structure was the changed proportion of c-phase, indicated by Fig. 2b and Table 1. Specifically, the fraction of c-phase gradually increased with Gd_2O_3 content. In considering of the identical total doping amount they containing, Gd_2O_3 seemed to be more effective to stabilize c-phase zirconia than Sc_2O_3. Two of the possible reasons are considered: The concentration at the phase boundary of c and $(c+t)$ in Gd_2O_3–ZrO_2 may be lower than that in Sc_2O_3–ZrO_2; the radius of Gd^{3+} is larger than that of Sc^{3+}. However, t′-phase was still the dominant phase when the substitution amount did not exceed 2 mol%.

3.2. Thermal conductivity

Fig. 3a shows the measured thermal diffusivities of the sintered compacts between 20 °C and 1400 °C. The corresponding thermal conductivities are calculated using Eq. (2) and corrected for porosity according to Eq. (3) to represent full dense samples, as shown in Fig. 3b. The thermal conductivities of 7.5ScSZ and ScGdSZ are nearly constant from 20 °C to 1400 °C. It is notable that the thermal conductivities of ScGdSZ gradually decrease with the increasing Gd_2O_3 content. 3.7Sc3.7GdSZ shows the lowest thermal conductivity, 1.47∼1.58 W m^{-1} K^{-1}, which is about 20% lower than that of 7.5ScSZ, 1.86∼1.96 W m^{-1} K^{-1}.

According to the thermal conductivity theory for electrical-insulating solids, thermal transfer is decided by the scattering of phonons [17], which can decrease the phonon mean free path and thereby reduce thermal conductivity. As the cation radius difference between Gd^{3+} and Zr^{4+} is much larger than that between Sc^{3+} and Zr^{4+}, doping of Gd_2O_3 can reasonably cause larger elastic strain field. In addition, co-doping of two oxides can introduce defect clusters [18] and thereby more significant defect scattering, leading to lower thermal conductivity. On the other hand, for the case of cations occupying Zr^{4+}, the scattering coefficient is decided by this Eq. [19]:

$$\Gamma = \sum_i x_i[(M_i - M_{Zr})/M_{Zr}]^2 \qquad (4)$$

where x_i is the concentration of the dopant, M_i is the corresponding atomic mass. It is obvious that $(M_{Gd} — M_{Zr})^2$ is bigger than $(M_{Sc} — M_{Zr})^2$. In summary, the substitution of Sc_2O_3 with Gd_2O_3 can enhance the scattering and thereby lead to lower thermal conductivity, which is in good agreement with the experimental results.

When compared with 4.5YSZ, 7.5ScSZ and ScGdSZ showed attractive thermal conductivities for TBC applications. Especially, the thermal conductivities for 3.7Sc3.7GdSZ and 5.5Sc2GdSZ (1.61∼1.73 W m^{-1} K^{-1}) were about 30% and 40% lower than those for 4.5YSZ (2.35∼2.65 W m^{-1} K^{-1}), respectively. Obviously, the higher total doping amount of 7.5ScSZ and ScGdSZ (7.5 mol%) had introduced higher

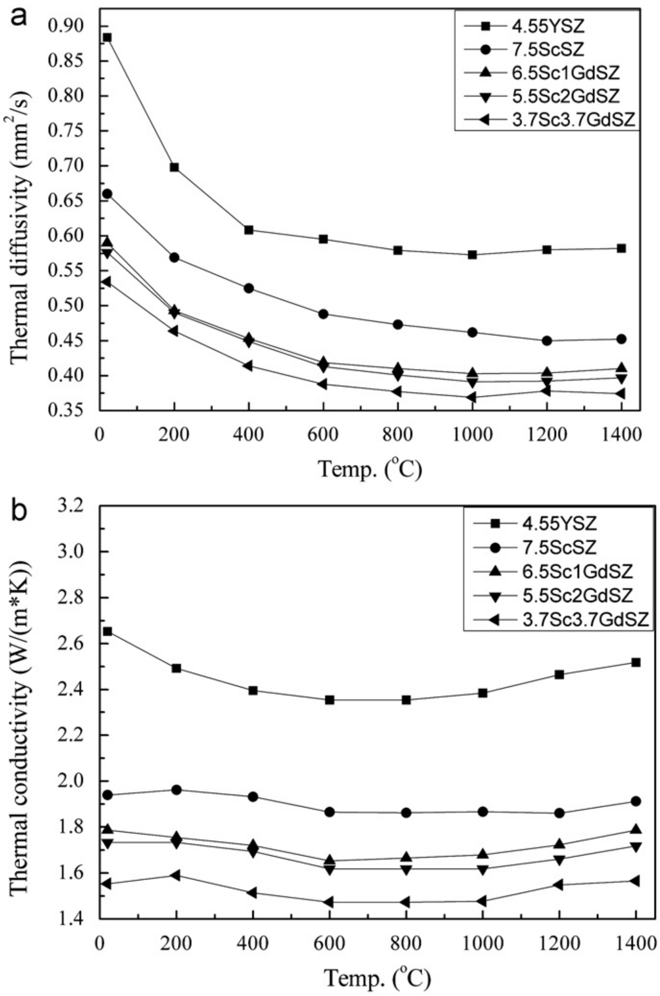

Fig. 3. Thermal diffusivities (a) and thermal conductivities (b) of the sintered compacts.

concentration of oxygen vacancies and substitutional defects which enhanced the phonon scattering.

4. Conclusions

In 7.5 mol% Sc_2O_3-doped ZrO_2, the effects of substitution of Sc_2O_3 with Gd_2O_3 on the phase stability and thermal conductivity were investigated. Some conclusions can be drawn as follows:

1) After 150 h heat treatment at 1400 °C, there was no monoclinic phase in Sc_2O_3 and Gd_2O_3 co-doped ZrO_2, indicating high phase stability of ScGdSZ. The substitution of Sc_2O_3 with Gd_2O_3 resulted in increased fraction of cubic phase, however, t′-phase was still the dominant phase when the substitution amount was less than 2 mol%.
2) The thermal conductivity of ScGdSZ gradually decreased with increasing the Gd_2O_3 proportion, owing to the larger cation radius and heavier atomic mass of Gd^{3+}. 3.7 Sc_2O_3 and 3.7 Gd_2O_3 co-doped ZrO_2 (in mol%) had the lowest thermal conductivity, which was 20% lower than 7.5 ScSZ and 40% lower than 4.5 YSZ, respectively.

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