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Effects of TiO_2 doping on the defect chemistry and thermo-physical properties of Yb_2O_3 stabilized ZrO_2

Lei Guo[a,b,c,*], Chenglong Zhang[a,b], Luming Xu[a,b], Mingzhu Li[a,b], Qi Wang[a], Fuxing Ye[a,b,c], Chengyi Dan[d], Vincent Ji[d]

[a] School of Materials Science and Engineering, Tianjin University, China
[b] Tianjin Key Laboratory of Advanced Joining Technology, Tianjin University, China
[c] Key Lab of Advanced Ceramics and Machining Technology of Ministry of Education, Tianjin University, No. 92, Weijin Road, Tianjin 300072, China
[d] ICMMO/SP2M, UMR CNRS 8182, Université Paris-Sud, 91405 Orsay Cédex, France

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ABSTRACT

Yb_2O_3 stabilized ZrO_2 (YbSZ) doped with different TiO_2 contents were produced, and their phase structure, thermal conductivities and thermal expansion coefficients were investigated. A new solid-solution model is proposed, i.e. Ti^{4+} would take the interstitial sites when its content is below a critical value (≤2.5 mol%) and then substitute for Zr^{4+}. The abnormal lattice volume and thermo-physical properties of 2.5 mol% TiO_2 doped YbSZ, and the positive effects of TiO_2 doping on the thermal conductivity at moderate doping level are consistent with the new defect model. However, monoclinic phase is formed when the TiO_2 content reaches to 10 mol% and its content increases with doping content, which have negative influence on the thermo-physical properties. Considering the comprehensive properties, 10 mol% TiO_2 doped YbSZ is considered as a promising thermal barrier coating ceramic.

1. Introduction

Thermal barrier coatings (TBCs) are strongly required for hot-section metallic components in advanced gas-turbine engine, which can protect the hot section from oxidation, corrosion and erosion wear and increase the engine inlet gas temperature, leading to enhanced engine performance and efficiency [1,2]. Up to now, the successfully and widely used TBCs are made of 7–8 wt% Y_2O_3 stabilized ZrO_2 (YSZ), owing to its desirable attributes including high melting point, low thermal conductivity, large thermal expansion coefficient (TEC) and good toughness [1–3]. Various methods have been developed to prepare TBCs, such as air plasma spray (APS), electron beam physical vapor deposition (EB-PVD) and plasma spray physical vapor deposition (PS-PVD) [4–7]. The as-fabricated YSZ TBCs usually crystallize as a non-transformable metastable tetragonal (t') phase. This phase has high toughness resulting from a ferroelastic toughening and is remarkably stable at temperatures below ~1200 °C [1,2,8–10].

Even-increasing demands on TBC temperature capability impose severe limitations on YSZ TBCs. At temperatures higher than 1200 °C, t' phase loses its stability and suffers a disastrous phase partitioning to cubic (c) and equilibrium t phases. The latter transforms on cooling to monoclinic (m) phase accompanied with excessive volume expansion, which severely damages the TBCs [1,2,11]. Another less stringent but equally significant issue is the low sintering resistance of the YSZ TBCs. Sintering leads to a loss of strain tolerance and an increased thermal conductivity, reducing the high-temperature capability and the thermal insulation of the coatings [1,2,4,12]. Additionally, in anticipation of better thermal insulation, there is a practical requirement for TBCs with even lower thermal conductivity. Therefore, the search is underway for TBC materials that have even better phase stability, higher sintering resistance and lower thermal conductivity. Several high-temperature ceramics with low thermal conductivity (for example, $La_2Ce_2O_7$, $LaTi_2Al_9O_{19}$, $Gd_2Zr_2O_7$ and $GdPO_4$) are being pursued, some of which have been considered as prospective TBC materials [13–16]. However, their applications are restricted by unsatisfactory mechanical properties, especially low toughness.

Another approach being pursued is focused on the ZO_2-based system with alternative stabilizers to Y_2O_3. Investigation on different rare earth oxides (RE_2O_3) doped or co-doped ZrO_2 has revealed that the t' phase stability increases with the decrease of the RE^{3+} size [17–23]. The rationale behind this phenomenon might be the reduced driving force for t' phase partitioning. During prolonged

* Corresponding author at: School of Materials Science and Engineering, Tianjin University, Tianjin 300350, China.
E-mail addresses: glei028@163.com, glei028@tju.edu.cn (L. Guo).

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exposure to high temperatures, a RE-rich phase (t") forms first, followed by decomposition to equilibrium t phase. The driving force for the formation of the t" phase scales with the size misfit between the RE^{3+} and Zr^{4+} ions [18–20]. Doping smaller rare earth reduces the size misfit, leading to lower driving force for t" phase formation and thus better t' phase stability. Among the rare earth cations, except Sc^{3+}, Yb^{3+} has the smallest size. Compared with Yb_2O_3, Sc_2O_3 doping in ZrO_2 might lead to good phase stability, but Sc_2O_3 cannot be widely used as the stabilizer due to its high cost. Therefore, from the t' phase stability point of view, Yb_2O_3 might be the most promising dopant for ZrO_2.

In addition to better phase stability, Yb_2O_3 doped ZrO_2 (YbSZ) also have lower thermal conductivity than YSZ [24,25]. However, systemic research on this promising TBC candidate is still lacking. Especially, effects of doping on the properties of YbSZ are limitedly investigated. Many previous studies have focused on ZrO_2-Y_2O_3-TiO_2 system, and indicated that a superior comprehensive properties, including phase stability, thermal conductivity, TECs and toughness, compared with YSZ could be obtained in the TiO_2 doped YSZ series [26–29]. In this study, different amounts of TiO_2 doped YbSZ compounds are produced, aiming to investigate the effects of TiO_2 doping on the phase structure, thermal conductivity and TEC of YbSZ. A new Ti^{4+} solid-solution model is proposed. The variation of thermal conductivity and TEC with TiO_2 doping content is discussed based on the proposed defect model.

2. Experimental procedures

2.1. Samples preparation

3.5 mol% Yb_2O_3 doped Zirconia (YbSZ) powders were synthesized by a chemical co-precipitation method, using Yb_2O_3 (purity 99.99%) and $ZrOCl_2{\cdot}8H_2O$ (purity 99.95%) as raw materials. The appropriate quantity of Yb_2O_3 powders and $ZrOCl_2{\cdot}8H_2O$ were dissolved in nitric acid and deionized water, respectively. The obtained solutions were mixed in accordance with the compositional requirement and stirred to yield homogeneous solution. Then, the mixed solution was added drop by drop to excess ammonia water (pH > 12) to obtain gel-like precipitate. The resultant precipitate was filtered and washed repeatedly with distilled water and alcohol until a neutral pH was achieved. After wash, the precipitate was dried at 120 °C for 10 h followed by calcination at 800 °C for 5 h for crystallization. The obtained powders were ground and sieved to eliminate the coarse agglomerates.

TiO_2 doped YbSZ powders were produced by a solid state reaction method, using TiO_2 and the fabricated YbSZ powders as raw materials. YbSZ and x mol% TiO_2 (x = 0, 2.5, 5, 7.5,10, 15, 20) powders were mixed by ball milling with zirconia media for 8 h. Then, the suspension was dried at 150 °C for 12 h and calcined at 1400 °C for 10 h. The acquired powders were cold pressed at ~250 MPa and sintered at 1500 °C for 10 h to obtain bulks for thermo-physical and mechanical properties measurements.

2.2. Phase characterization

Phase analysis was conducted by an X-ray diffraction (XRD; Rigaku Diffractometer, Tokyo, Japan), with a scanning range of 2θ = 20–90°. In order to distinguish the t' (t_1', t_2') and c phases, slow scans were performed over the range of 2θ = 72–76° with a step size of 0.01° and a dwell time of 20 s. The mole fractions of m, c and t' (t_1', t_2') phases could be calculated using the following equations [20,23,30]:

$$\frac{M_m}{M_{c,t'}} = 0.82\frac{I_m(\bar{1}11) + I_m(111)I_{c,t'}(111)}{} \quad (1)$$

$$\frac{M_c}{M_{t'}} = 0.88\frac{I_c(400)}{I_{t'_1}(004) + I_{t'_1}(400) + I_{t'_2}(004) + I_{t'_2}(400)} \quad (2)$$

$$\frac{M_t 1' M_{t'_2}}{} = \frac{I_{t'_1}(004) + I_{t'_1}(400)}{I_{t'_2}(004) + I_{t'_2}(400)} \quad (3)$$

$$M_{t'} = M_{t'_1} + M_{t'_2} \quad (4)$$

$$M_m + M_c + M_{t'_1} + M_{t'_2} = 1 \quad (5)$$

Where M_m, M_c and $M_{t'}$ (M_{t1}', $M_{t2'}$) are the mole fractions of the m, c and t' (t_1', t_2') phases, respectively, the $M_{c,t'}$ is the sum of the mole fractions of the c and t' (t_1', t_2') phases, and I refers to the integral intensity corresponding to the peaks concerned. The lattice volume of each phase was calculated from the lattice parameters obtained from the diffraction peak positions. Raman spectrum was recorded by a microscopic confocal Raman spectrometer (RM2000; Renishaw, Gloucestershire, UK) using an argon ion laser with radiation at 514.5 nm. The spectrum was collected at a rate of 600 cm^{-1}/30 s and accumulated by triple scanning.

2.3. Thermal diffusivity and thermal expansion measurements

Thermal diffusivity (α) measurement was carried out using a laser-flash apparatus (Netzsch LFA 427, Bavaria, Germany) from 20 °C to 1200 °C, at an interval of 200 °C. Prior to the measurement, thin graphite films were coated on both the front and rear surfaces of the sample for thermal absorption of laser pulses. Each sample was measured three times at the selected temperature. According to the Neumann-Kopp rule, specific heat capacity (C_p) was calculated from the heat capacity values of the constituent oxides [31]. Density (ρ) was measured by Archimedes method. Thermal conductivity (λ) was calculated using the following equation:

$$\lambda = \rho \cdot \alpha \cdot C_p \quad (6)$$

The uncertainty of the thermal conductivity was estimated to be ±5%, considering the uncertainties for the density (ρ), the thermal diffusivity (α) and the specific heat capacity (C_p). Since the bulk for thermal diffusivity measurement was not fully dense, the obtained thermal conductivity was corrected for the actual data (λ_0) using the following equation [32]:

$$\frac{\lambda}{\lambda_0} = 1 - \frac{4}{3}\varphi \quad (7)$$

Where φ is the fractional porosity.

Thermal expansion coefficient (TEC) was measured using a high-temperature dilatometer (Netzsch DIL 402E, Bavaria, Germany). The engineering TEC is the average value from room temperature to 1200 °C. The data were corrected using the known TEC of a certified standard alumina. To avoid systematic errors, the specime ns were fabricated to the same dimension of 4 mm × 4 mm × 25 mm.

3. Results and discussion

3.1. Phase structure and defect chemistry of TiO_2 doped YbSZ

Fig. 1 shows the XRD patterns of the samples. YbSZ basically consists of t' phase. In the patterns of the compositions with 2.5, 5, 7.5 and 10 mol% TiO_2, characteristic diffraction peaks of c-ZrO_2 could be observed at 2θ ≈ 35.2° and 60.1°. The inset image in Fig. 1 clearly depicts the presence of $(200)_c$ peak in the range of 33–38°. With the increase of the TiO_2 content, the peak shifts toward higher angle and its intensity becomes weak. 10 mol% TiO_2 doped YbSZ shows low-intensity m-ZrO_2 peaks. Notably, an increase in the m-ZrO_2 to t'-ZrO_2 peak intensity ratio is found with further increasing the TiO_2 content, indicative of an increased amount of m phase.

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