

Mechanical Properties Durability of Sc_2O_3 - Y_2O_3 Co-Stabilized ZrO_2 Thermal Barrier Materials for High Temperature Application

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Abstract: The poor phase stability of conventional 6–8 wt.% yttria-partially stabilized zirconia (YSZ) results in the formation of detrimental cracks in thermal barrier coatings (TBCs) as well as the decrease of fracture toughness, limiting its long-term application above 1200 °C. Here, we try to prove that a higher t' -phase stability is the prerequisite for the mechanical properties durability of ZrO_2 -based TBC materials. Compared with YSZ ceramic, 7.0 mol.% Sc_2O_3 and 0.5 mol.% Y_2O_3 co-stabilized ZrO_2 (ScYSZ) shows a superior t' phase stability at 1300 °C. In addition, the fracture toughness of ScYSZ is nearly stable after being annealed at 1300 °C for 0–40 h, while the value of YSZ gradually declines during the aging process. The stable fracture toughness of ScYSZ is closely related to its prominent t' phase stability. The elastic modulus of ScYSZ is nearly unchanged and lower than that of YSZ. The excellent stability of the phase structure and mechanical properties makes ScYSZ a great potential material for next generation high-temperature TBCs.

Keywords: thermal barrier coatings; ScYSZ; phase stability; fracture toughness; heat treatment



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1. Introduction

Thermal barrier coatings (TBCs) are indispensable in protecting the key hot-section components of high-temperature gas turbines as well as high-power diesel engines [1–4]. The TBC system deposited on the super-alloys includes a metallic bond coating layer, a thermally grown oxide (TGO) layer that forms as a result of in-service bond-coat oxidation, and a thermal barrier ceramic layer [5–7]. 6–8 wt.% yttria-partially stabilized zirconia (YSZ) is employed intensively as thermal barrier material due to its relatively low thermal conductivity, proper coefficients of thermal expansion and prominent mechanical properties [8–10]. However, during the long-time operation above 1200 °C, the phase structure of plasma-sprayed YSZ coating transforms from the metastable tetragonal prime (t') phase to the tetragonal (t) phase and cubic (c) phase. Subsequently, the t -phase further transforms into the monoclinic (m) phase during cooling, resulting in not only a 3–5% volume expansion but also the degradation of the fracture toughness [11–16]. These changes are the main reasons for the easy generation and propagation of detrimental cracks as well as the premature failure of TBCs [17–19].

Up to now, numerous studies have demonstrated that t' phase zirconia exhibits a superior fracture toughness to the c phase due to the existence of the ferroelastic toughening effect, which can inhibit crack propagation by domain switching [20–22]. For instance, Pan et al. [11] confirmed that the fracture toughness of conventional YSZ declined when decreasing the t' phase content. Jiang et al. [23] found that the phase composition of 16

mol.% CeO₂ and 4 mol.% Gd₂O₃ co-doped ZrO₂ (16Ce-4Gd) was a mixture of t phase and c phase at 1500 °C, and their contents were kept nearly constant when increasing the aging time. Accordingly, the fracture toughness of sample 16Ce-4Gd was also stable during heat treatment. Therefore, a TBC material that has an excellent t' phase stability is preferable for an effective application at elevated temperatures. The previous research demonstrated that 7.0 mol.% scandia and 0.5 mol.% yttria co-stabilized zirconia (ScYSZ) was fully t' phase, even when annealed for 336 h at 1500 °C, while t'-YSZ fully changed to the m phase and c phase under the same conditions [24]. In addition, the as-sintered ScYSZ ceramic showed superior or comparable thermophysical and mechanical properties to its YSZ counterpart, suggesting that ScYSZ was a potential alternative material for high-performance TBCs [25,26]. However, present studies on the performance of thermal barrier materials are not enough because TBCs operate at an elevated temperature, which will result in the variation of the structures as well as the mechanical properties [27,28]. Therefore, the investigation of the mechanical behavior after high-temperature annealing is of significant importance.

In this work, the mechanical properties durability of dense YSZ and ScYSZ bulk materials after a high-temperature heat treatment was comparatively studied by selecting an appropriate annealing temperature and time to control the phase composition and grain size. This study further confirmed that t' phase stability was a prerequisite for the mechanical properties durability of ZrO₂-based thermal barrier coatings, and provided a very promising future for the next generation of high-temperature thermal barrier coating materials.

2. Materials and Methods

2.1. Samples Preparation

ScYSZ and YSZ powders were synthesized utilizing the Sol-Gel method. Sc(NO₃)₃·6H₂O (99.9%, Beijing Hwrkchemical Co., Ltd., Beijing, China), Y(NO₃)₃·6H₂O (99.9% purity, Beijing Hwrkchemical Co., Ltd., Beijing, China) and ZrOCl₂·8H₂O (99.9% purity, Beijing Hwrkchemical Co., Ltd., Beijing, China) were used as the original materials. Firstly, the stoichiometric hydrates were dissolved in distilled water and stirred continuously for 20 min. Then, citric acid (CA) monohydrate and ethylene glycol (EG) were successively added to the above nitrate aqueous solution to prepare the wet gel. Herein, the molar ratio of CA or EG to total metal ions is 1:1. The obtained wet gel was baked at 90 °C for 24 h in a drying oven. The calcination process of the dried precursor was conducted in a muffle furnace (Hefei Kejing Materials Technology Co., Ltd., Hefei, China) at 1000 °C for 2 h. Finally, the powder was wet ball milled for 24 h using ZrO₂ milling balls and then dried at 90 °C. Specimens for the phase compositions and mechanical properties measurements were fabricated utilizing a plasma-activated sintering (PAS, Ed-PASIII, Elenix Ltd., Kanagawa, Japan) method. The detailed information on the PAS process can be found in our previous work [24]. The porosity and density of the samples were tested by the Archimedes method. In order to observe the grain size variation of the heat-treated specimens, thermal etching was performed at 1300 °C for 3 h.

2.2. Phase Composition

To evaluate the high-temperature phase stability of the samples, the as-sintered bulks are heat treated at 1300 °C for different times. We previously found that, for as-sintered t'-YSZ, a certain amount of m-ZrO₂ was generated after annealing at 1400 or 1500 °C for 20 h. It is well-known that the fracture toughness of m-ZrO₂ is essentially inferior to that of t'-ZrO₂. Additionally, the grain of m-ZrO₂ grows abnormally. A previous study confirmed that the fracture toughness of YSZ was related to the grain size. To eliminate the effect of the grain size on the fracture toughness, 1300 °C was selected as the annealing temperature. The crystal structure of the materials is characterized through X-ray diffraction (XRD, D8 Advance, Bruker, Karlsruhe, Germany) from 20° to 80° utilizing CuKα radiation

($\lambda = 1.5406 \text{ nm}$). To better distinguish the t' , t and c phases, a slow scanning speed of $0.1^\circ \text{ min}^{-1}$ at $72^\circ\text{--}76^\circ$ is performed.

2.3. Mechanical Properties

The toughness of specimens is evaluated utilizing a small load Vickers hardness tester (HV-1000SPTA, Veiye, Laizhou, China). Indentations are carried out on the polished surface with a load of 9.8 N and a holding time of 15 s. The fracture toughness (K_{IC} , $\text{MPa}\cdot\text{m}^{1/2}$) of the bulks is calculated by the following equation [29]:

$$K_{IC} = 2 \times 0.0319 \left(\frac{P}{a\sqrt{L}} \right) \quad (1)$$

where P refers to the applied load (N), a refers to half of the average diagonal length of the indents (μm), and L represents the total length (μm) of the radial and edge cracks. 10 clear indentations are utilized to calculate the toughness.

The elastic modulus (E) of ceramic bulks is evaluated through the Knoop hardness (HK). The microhardness tester is employed to measure the Knoop hardness under a load of 4.9 N and a holding time of 15 s. The elastic modulus is obtained as follows [30]:

$$E = \frac{0.45HK}{b/a - b'/a'} \quad (2)$$

where a or b ($b/a = 1/7.11$) is the diagonal length before the elastic recovery of the Knoop indentation (μm), and a' or b' refers to the diagonal length after the elastic recovery of the Knoop indentation. The scheme of the measurement of the mechanical properties is presented in Figure 1. It is worth noting that each test was repeated 3 times to lower the experimental error.

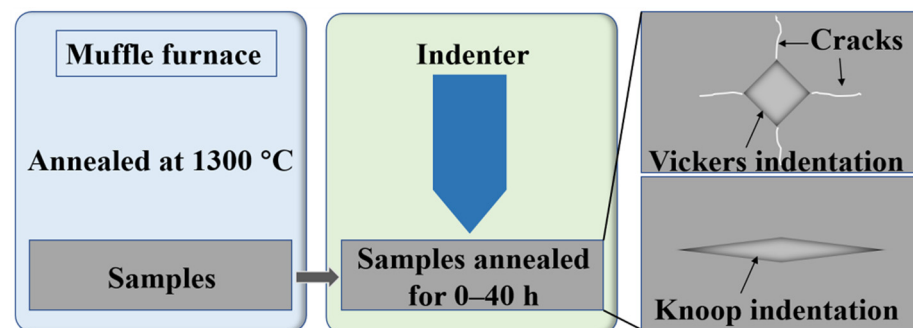


Figure 1. Scheme of the measurement of the mechanical properties.

3. Results and Discussion

Figure 2 displays the phase structures of the YSZ and ScYSZ bulks before and after heat treatment at 1300°C for different times. One can see that the as-sintered YSZ sample exhibits a pure t' phase. With the heat treatment process going on, a certain amount of t' -YSZ gradually decomposes into the t phase and c phase. However, the phase composition of the ScYSZ sample maintains a pure t' phase even when annealed for 40 h at 1300°C . Utilizing the diffraction peaks' integrated intensity for different phases of the XRD spectrum, their volume percent can be calculated by the following formulas [31]:

$$C_m = \frac{I_m(111) + I_m(111)}{I_m(111) + I_m(111) + I_{c,t/t'}(111)} \quad (3)$$

$$C_t = \frac{(1 - C_m) \times (I_t(400) + I_t(004))}{I_t(400) + I_t(004) + I_c(400) + I_{t'}(400) + I_{t'}(004)} \quad (4)$$

$$C_{t'} = \frac{(1 - C_m) \times (I_{t'}(400) + I_{t'}(004))}{I_t(400) + I_t(004) + I_c(400) + I_{t'}(400) + I_{t'}(004)} \quad (5)$$

$$C_c = 1 - C_m - C_t - C_{t'} \quad (6)$$

where C_m , C_t , $C_{t'}$ and C_c represent the volume percent of the corresponding phases, respectively, and I is the integrated intensity of different peaks in the XRD patterns.

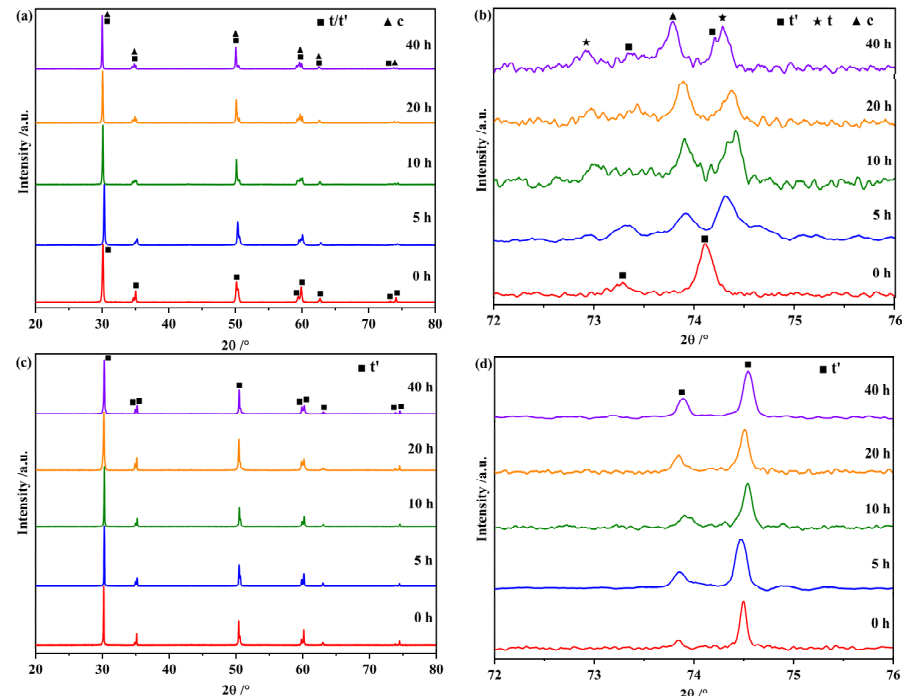


Figure 2. The phase structures of (a,b) yttria-partially stabilized zirconia (YSZ) and (c,d) scandia and yttria co-stabilized zirconia (ScYSZ) bulks before and after being heat-treated at 1300 °C.

Figure 3 displays the phase content variation of YSZ and ScYSZ samples when increasing the annealing time. For the conventional YSZ material, the t' phase content decreases rapidly before the first 5 h, and it decreases to approximately 32 vol.% after being annealed for 40 h. No m phase is detected during this thermal exposure process. Different from the free-standing coatings, the substrate in TBCs leads to compressive stress in the coating, reducing the amount of m phase. Similarly, the dense YSZ bulk exhibits compressive stress, which can effectively inhibit the formation of m phase. Our previous study showed that the m phase content of YSZ bulks was only about 5.40 vol.% even when heat-treated at 1500 °C for 100 h [24]. Therefore, the m phase is not easy to generate in such a short annealing time at 1300 °C.

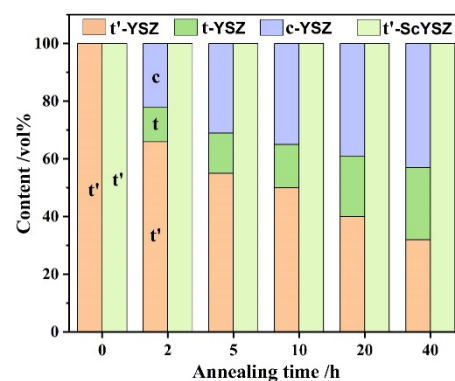


Figure 3. The phase content variation of YSZ and ScYSZ bulks at different annealing times.

The fracture toughness value is an important factor for determining the performance of TBCs. Figure 4 shows the fracture toughness evolution of different samples during the heat treatment process. The value of the as-sintered pure t' -YSZ sample ($5.00 \pm 0.30 \text{ MPa}\cdot\text{m}^{1/2}$) is higher than that of t' -ScYSZ ($4.30 \pm 0.30 \text{ MPa}\cdot\text{m}^{1/2}$). The toughness value of ScYSZ shows a prominent stability during the high-temperature thermal exposure. However, the value of the fracture toughness of the YSZ sample gradually declines with the increase of the annealing time, and it becomes lower than the value of ScYSZ after annealing for 5 h. The value is about 3.20 ± 0.24 or $4.22 \pm 0.18 \text{ MPa}\cdot\text{m}^{1/2}$ for the YSZ or ScYSZ sample after being heat-treated for 40 h, respectively, which suggests that ScYSZ has more potential advantages for the long-term operation of high-temperature TBCs. It is well-known that the fracture toughness of nano-sized YSZ is related to the grain size [32]. Figure 5 shows the SEM images of bulks before and after annealing at 1300°C . It can be seen that the grain size of the as-sintered YSZ or ScYSZ is in the range of $1\text{--}5 \mu\text{m}$. A slight grain growth is observed after annealing for 40 h. However, the grain size of YSZ is close to that of ScYSZ. Therefore, the effect of the grain size on the fracture toughness of the YSZ or ScYSZ sample is negligible. As mentioned in Figures 2 and 3, ScYSZ bulks remain pure t' phase during the high-temperature annealing process, while the content of the t phase or c phase of YSZ bulks gradually increases with the heat treatment going on, indicating that the content of t' - ZrO_2 is the decisive factor for the durable fracture toughness of ScYSZ. Due to the larger tetragonality of the as-sintered t' -YSZ, the fracture toughness is higher than that of as-sintered t' -ScYSZ, which is also consistent with the results of the literature [22,24]. A previous study [20] demonstrated that the fracture toughness of t' - ZrO_2 was higher than that of c - ZrO_2 due to the unique ferroelastic domain-switching toughening mechanism of the former. The external stress causes the c -axis re-orientation of the t' - ZrO_2 in the unit cell, which dissipates the fracture energy at the crack tip and thus inhibits the crack propagation. Therefore, the fracture toughness of YSZ gradually decreases during the annealing process. These results further indicate that ZrO_2 -based ceramics with a high t' -phase stability are preferable for high-performance TBCs.

Figure 6 depicts the evolution of the elastic modulus during the heat treatment. It can be seen that the elastic modulus of all samples is nearly stable and that the value of ScYSZ is approximately 50 GPa lower than that of YSZ. The reduced elastic modulus is beneficial to lowering the thermal mismatch stress between the ceramic layer and the bond coat and to thus improving the service life of TBCs. Additionally, the elastic modulus of a certain solid compound is an intrinsic property, which is closely related to the cohesive energy of the lattice [11]. It is not sensitive to the microstructure except for porosity. The porosities of as-sintered YSZ and ScYSZ bulks are 0.92% and 0.96%, respectively. After annealing for 40 h, the values of the porosity decrease slightly to 0.87% and 0.88%. Since the as-sintered samples are relatively dense and no obvious porosity change occurs during the aging process, the elastic modulus of YSZ or ScYSZ is stable at elevated temperatures.

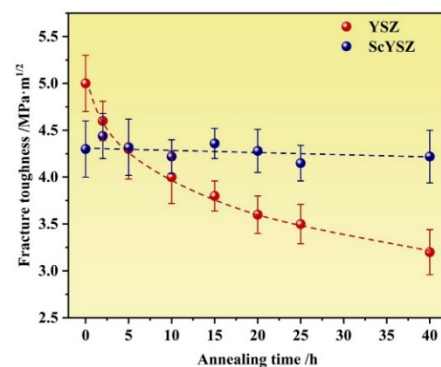


Figure 4. The fracture toughness evolution of different samples during the heat treatment.

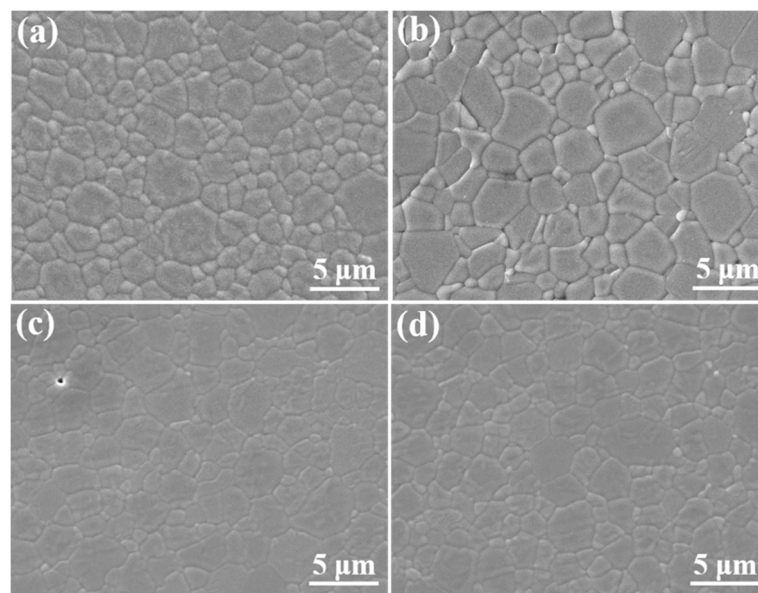


Figure 5. The surface morphologies of grains before and after heat treatment: YSZ bulks (a) as-sintered and (b) annealed for 40 h; ScYSZ bulks (c) as-sintered and (d) annealed for 40 h.

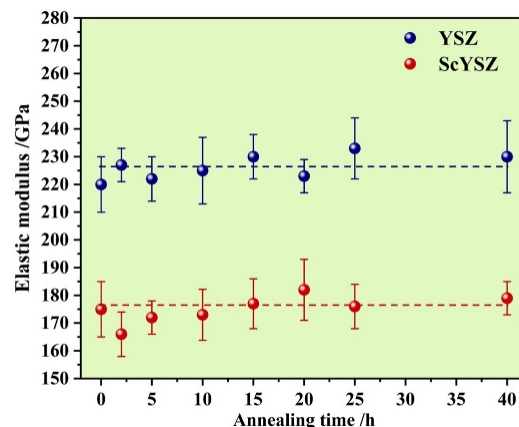


Figure 6. The evolution of the elastic modulus of different samples during the heat treatment.

4. Conclusions

The durable mechanical behavior of the ceramic layer is a key element that determines the service lifetime and efficiency of TBCs. Compared with the conventional YSZ ceramic, ScYSZ has a superior t' phase stability at 1300 °C. In addition, the fracture toughness of ScYSZ is nearly stable during the heat treatment process, while the value of YSZ gradually decreases. The stable fracture toughness of ScYSZ can be attributed to its prominent t' phase stability. The elastic modulus of ScYSZ is nearly unchanged and lower than that of YSZ. The excellent stability of the phase structure and mechanical properties makes ScYSZ a great potential material for next generation high-temperature TBCs.

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