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ARTICLE

Effect of Ta_2O_5-Y_2O_3 Dopants on Phase Structure, Fracture Toughness and Thermophysical Properties of Zirconia

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Abstract: A broad range of Ta_2O_5-Y_2O_3 doped ZrO_2 (TYSZ) compounds were synthesized. The effects of dopant content on phase structure, phase stability, fracture toughness, coefficient of thermal expansion (CTE), and thermal conductivity were investigated. The TYSZ response mechanism under stress conditions was also explored. Result suggests that the lattice distortion caused by Ta_2O_5 and Y_2O_3 doping favors t phase stabilization. However, as the doping content increases, the high-temperature stability and fracture toughness decrease due to the suppressed stress-induced phase transformation and precipitation. The variation in CTE and thermal conductivity is due to the chaotic and expansive crystal structure. The 16TYSZ might be the potential candidate for advanced thermal barrier coating materials for its good phase stability, stress-sensitive phase transferability, and thermophysical properties.

Key words: thermal barrier coatings; phase stability; fracture toughness; thermo-physical properties

Because of the critical need for higher operating efficiency, longer operating lifetime, and reduced emissions, the hot components in advanced gas turbine engines have led to increasingly harsh operating environments[1,2]. The advanced thermal barrier coatings (TBCs) coupled with cooling schemes, can provide a significant temperature drop (over 150 K), which is the only way to enable the superalloy hot components to meet the standard requirements for the advanced gas engines[3]. Yttria stabilized zirconia (YSZ) that predominates in a non-transformable metastable tetragonal structure is identified as a suitable ceramic topcoat material, and has been applied for the last 40 years[4,5]. However, the tetragonal phase structure is not stable at temperatures above 1200 ºC. The long-term exposure above this temperature will lead to the conversion from non-transformable tetragonal structure to a low-yttria tetragonal phase and a high-yttria cubic phase. The low-yttria tetragonal phase will further transform to a monoclinic phase and result in a volume increase, which promotes the formation and growth of cracks in the ceramics, finally increasing the risk of spallation[6-8].

To improve the efficiency and durability of gas turbines, great effort has been made to develop alternative topcoat ceramics suitable for application above 1200 ºC. Trivalent doping of YSZ introduces the oxygen vacancy defect which has severe phonon scattering in the system, thus significantly reducing the thermal conductivity and improving phase stability[9-11]. However, high-level oxygen vacancy concentration will also increase oxygen permeability at high temperature and accelerate the formation of TGO, which is an important reason for TBC failure[12-14]. For this reason, some researchers have attempted to add equimolar trivalent oxides and pentavalent oxides to ZrO_2, which will not introduce oxygen vacancies[15]. At the same time, the larger Y^{3+} ions and the heavier Ta^{5+} ions and its cation sublattice association reduce the phonon mean free path as well as the thermal conductivity[16]. Ta_2O_5 and Y_2O_3 co-doped ZrO_2 is insensitive to the tetragonal-monoclinic transformation upon thermal cycling and exhibits much better corrosion resistance in S/V melts than YSZ[17]. The doping content has a significant effect on the performance of the doped zirconia-based material[18]. Hence, systemic research of the association of the dopant concentration and crystal structure and its effects on the thermal physical properties in TYSZ, which is instructive for further research and application, needs to be fully understood.

Despite the superior thermophysical properties, many new TBC materials have a deterioration in thermal cycling

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performance due to the restricted mechanical properties (especially fracture toughness) [1,19,20]. Therefore, the fracture toughness is also one of the crucial factors to evaluate its suitability for the novel thermal barrier coating material. The most commonly discussed toughening mechanisms of the tetragonal phase in zirconia are the t-m phase transformation toughening and the ferroelastic toughening[21,22]. The former inhibits crack growth by volume expansion caused by the t-m phase transition, while the latter depends on the reorientation of random orientation of grains. In theory, the severe distortion caused by large substituting ion wil increase the tetragonality and promote ferroelastic toughening. Previous works reported that the ZrO_2 doped with +5/+3 cations exhibit undiminished fracture toughness[23,24]. Hence, it is assumed that the good fracture toughness comes from large tetragonality. However, previous work did not report whether the t-phase in TYSZ also possesses a phase transformation toughening mechanism under stress conditions.

In the present study, 8mol%~24mol% ($TaO_{2.5}$-$YO_{1.5}$)-ZrO_2, here abbreviated as 8~24TYSZ, were synthesized and investigated. Their phase structure and phase evolution were conducted, and the TYSZ response behavior under stress conditions was explored via ball milling. The effects of lattice defects on fracture toughness and thermal properties were discussed. The possibility of developing TYSZ as a ceramic coating material for TBCs was evaluated.

1 Experiment

1.1 Materials and specimen preparation

The powders for Ta_2O_5-Y_2O_3-ZrO_2 samples were synthesized by the solid-state reaction. The starting materials used in this study were Ta_2O_5 (99.9%), Y_2O_3 (99.95%), and ZrO_2 (99.9%). All oxide powders were heated at 900 ºC for 2 h before weighing. The mixed oxides in the corresponding amount were ball-milled with high-purity YSZ balls in a polyamides container for 24 h in a planetary mill. The suspensions obtained were dried completely and then calcined at 1500 ºC for 6 h for the solid-state reaction. The calcined powders were ball-milled in ethanol and crushed to the size below 0.5 μm. The commercial yttria-stabilized zirconia (7wt%~8wt% Y_2O_3-ZrO_2, marked as YSZ) was employed for comparison. The ceramic bulks were prepared by hot pressing under a pressure of 30 MPa at 1600 °C for 2 h.

1.2 Fracture toughness test and ball milling process

Single-side-notched beam method (SENB) and a three-point bending method were used to test the fracture toughness of ceramic materials. The sample was a long strip of the small rectangular beam (2 mm×4 mm×22 mm) with a U groove (0.3 mm in width and 2 mm in depth). The powder was ball-milled (350 r/min, 24 h) with high purity zirconia grinding balls in 1-liter nylon grinding pot (Jingpu Ceramic Material Co., Ltd). The grinding ball to powder ratio was 1:6, and the grinding balls with diameters of 2, 5, 8, and 10 mm had a ratio of 2:4:2:1.

1.3 Characterization

The phase structure of the specimens was characterized by X-ray diffraction (XRD, Cu Kα, X’pert PRO, PANalytical B. V., Almelo, Netherlands). The specific heat capacity was measured using a differential scanning calorimeter (Netzsch STA 449C) at a heating rate of 10 ºC·min^{-1} from room temperature to 1400 ºC in air, in a corundum crucible. The linear thermal expansion coefficient (CTE) was measured with a high-temperature dilatometer (Netzsch DIL 402C). Measurements were taken from room temperature to 1400 ºC at a heating rate of 5 ºC·min^{-1} in air.

The thermal diffusivity was measured using a laser-flash apparatus (Netzsch LFA 427) in an argon atmosphere. The thermal diffusivity measurement was performed from room temperature to 1400 ºC at a temperature interval of 200 ºC and each sample was measured three times at each corresponding temperature. The thermal conductivities were calculated according to the relationship[25]:

$$\lambda_{(T)}=\rho\alpha_{(T)}C_{p(T)} \quad (1)$$

2 Results and Discussion

2.1 Phase structure and phase stability

Fig. 1 shows the XRD patterns of the 8~24TYSZ powder. There are no diffraction peaks of Y_2O_3 and Ta_2O_5 in the powders patterns, which means that Y_2O_3 and Ta_2O_5 are completely dissolved to ZrO_2 crystal and stabilize ZrO_2. It can be seen that 8TYSZ and 12TYSZ are composed of monoclinic phases while 16TYSZ, 20TYSZ, and 24TYSZ are the tetragonal phase. Unlike trivalent doping zirconia, the stabilization effect in the tetragonal-ZrO_2 of TYSZ mainly comes from lattice distortion rather than oxygen vacancy[23,26]. The radius of Ta^{5+} and Y^{3+} is 64 and 101.1 pm, respectively, while the radius of Zr^{4+} is 72 pm. Therefore, the substitutional cations and its association will produce larger local distortion in the lattice. The lattice parameter and tetragonality of TYSZ increase with increasing the dopant content, as shown in Table 1, confirming lattice distortion. When the dopant content is less than 12mol%, the lattice stabilization is not sufficient to form a stable tetragonal phase. As the stabilizer content increases, the stabilization effect becomes stronger, so 16TYSZ, 20TYSZ, and 24TYSZ comprise the stable tetragonal phase.

One of the major issues in YSZ TBCs is that the t’ phase is unstable over 1200 ºC, i. e., decomposition accompanied by volume change, which leads to the formation of cracks[27,7]. Although the thermal stability of all the TYSZ is much higher than that of YSZ which experiences significant decomposition at 1400 ºC[28], it does not increase monotonically as expected. In fact, with a high stabilizer content, the thermal stability of the t phase of TYSZ at elevated temperatures decreases. After sintering at 1400 ºC for 50 h (Fig.2a), small reflections, which correspond to the YTO_4 phase, are observed in 24TYSZ. As the heat treatment prolongs to 100 h (Fig.2b), a slight similar decomposition occurs in 16TYSZ and 20TYSZ. At high temperatures, the diffusion rate of stabilizer atoms increases

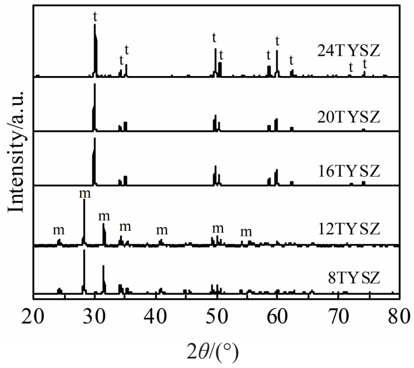

Fig.1 XRD patterns of TYSZ powders

Table 1 Lattice parameters of TYSZ powders

Material	Phase structure	Lattice parameters		
		a/×10^{-1} nm	c/×10^{-1} nm	$c/\sqrt{2}a$
8TYSZ	m	-	-	-
12TYSZ	m	-	-	-
16TYSZ	t	3.6127	5.2333	1.024
20TYSZ	t	3.6145	5.2416	1.025
24TYSZ	t	3.6154	5.2505	1.027

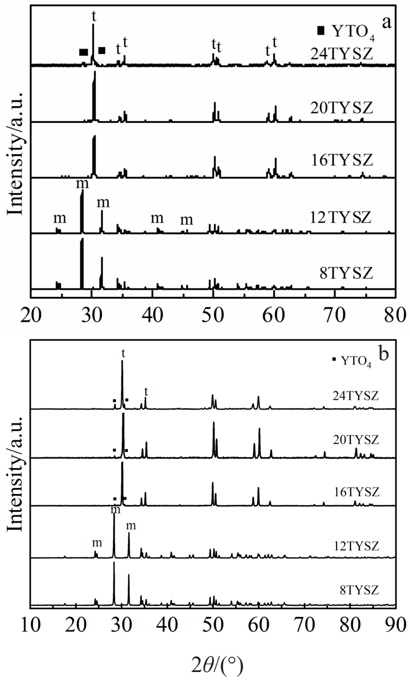

Fig.2 XRD patterns of TYSZ powders after heat treatment: (a) sintering at 1400 °C for 50 h and (b) sintering at 1400 °C for 100 h

and tends to converge at grain boundaries and other defects[29]. When the local region Y^{3+} and T^{5+} are excessive, small amounts YTO_4 are precipitated out and the precipitation becomes severe with increasing the dopant content.

2.2 Fracture toughness and stress response

Since the TBC failures are mainly attributed to crack initiation, propagation coalescence[30], improved fracture toughness helps to prolong its service life. As shown in Table 2, the fracture toughness of TYSZ decreases with the increase of the doping content. It is noticeable that the fracture toughness (5.72 MPa·m$^{1/2}$) of 16TYSZ is comparable to that of YSZ (5.97 MPa·m$^{1/2}$). To explain the differences in fracture toughness of TYSZ and identify the toughening mechanism, the ceramic powder was stressed by ball milling. As shown in Fig. 3, 16TYSZ and 20TYSZ exhibit a mixed phase of the t phase and m phase after ball milling, and the content of the m phase in 16TYSZ and 20TYSZ is 46.12% and 15.92%, respectively. In contrast, there are only a few m phases in YSZ (3.98%) and 24TYSZ, which means that t-m transformation toughening effect of YSZ and 24TYSZ is small. Regardless of the presence of a free surface or irregular shape grains, the change of total free energy ($\Delta G_{\text{t-m}}$) for the t-m transformation of the particle can be expressed by[31]:

$$\Delta G_{\text{t-m}}=\Delta G_{\text{c}}+\Delta U_{\text{SE}}+\Delta U_{\text{s}} \tag{2}$$

where ΔG_{c} (ΔG_{c}<0 at temperatures below the equilibrium M_{S} temperature) is the difference in chemical-free energy between the tetragonal and monoclinic phases and is dependent on temperature and composition, implicitly including the oxygen vacancy content. The ΔU_{SE} (ΔU_{SE}>0) refers to the change in elastic strain energy associated with the transformation of particles and ΔU_{s} is the change in energy associated with the formation of new interfaces when the transformation occurs. These two factors are dependent on the surrounding matrix, the size and shape of the particle, cracks and monoclinic variants, and the presence of internal or external stresses,

Table 2 Fracture toughness of TYSZ and YSZ specimens

Material	K_{IC}/MPa·m$^{1/2}$
YSZ	5.97
16TYSZ	5.72
20TYSZ	3.09
24TYSZ	1.98

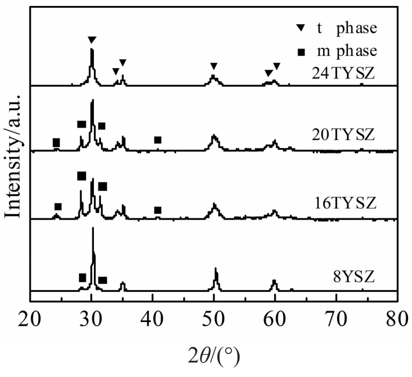

Fig.3 XRD patterns of TYSZ after ball milling

which can be considered constant in this study due to the same experimental condition. The high doping content in 24TYSZ improves the stability of the t phase and increases ΔG_c, resulting in a decrease of driving force $\Delta G_{t\text{-}m}$. Thus, the stress-induced phase transformation is suppressed and the fracture toughness of 24TYSZ is smaller than that of 16TYSZ and 20TYSZ. Combined with the above fracture toughness results and tetragonality, it can be concluded that transformation toughening dominates the fracture toughness in the TYSZ rather than the ferroelastic toughening and content of dopant having a significant effect on it. Effective transformation toughening requires the retention of the maximum amount of *t*-ZrO_2 at the service temperature, with optimum transformability[32]. As shown in Fig.4, 16TYSZ, and 20TYSZ transform back to the t phase again after reheating at 1100 ºC for 2 h, proving that the reason for the previous t-m phase transformation is stress and the t-phase is the thermodynamically stable phase. This transfor-mation ensures that TYSZ has a high content of t phase and sustain high fracture toughness under thermal cycle conditions.

2.3 Thermal expansion coefficient

Considering these results, the CTE and thermal conductivity of 16TYSZ and 20TYSZ were further explored. As mentioned above, as the radius of Ta^{5+} is smaller than Zr^{4+}, the lattice expansion of the TYSZ system mainly comes from the contribution of Y^{3+}. The increase of the Y_2O_3 content will decrease Zr-O and Y-O distance, increase the binding energy of the crystal, and decrease the thermal expansion coefficient[33]. Hence, as shown in Fig. 5, the CTE ($10.9\sim11.1\times10^{-6}$ K^{-1}) at 25~800 °C of TYSZ is lower than that of YSZ and slightly decreases with increasing the YTO_4 content. In addition, as the higher dopant content leads to unit cell expansion, the crystal energy of TYSZ decreases, and thus the CTE increases. With the increase of the temperature, this effect on thermal expansion becomes much more obvious, which can explain the fact that CTE of 16TYSZ and 20TYSZ from 25 °C to 1400 °C is comparable to that of YSZ.

2.4 Thermal conductivity

The thermal conductivity is plotted as a function of temperature from 200 ºC to 1000 ºC in Fig.6. The thermal conductivity of TYSZ is 1.6~2.0 W/(m·K), which is 20% lower than that of YSZ (1.91~2.4 W/(m·K)), and the thermal conductivity of the TYSZ system decreases with the increase of doping amount.

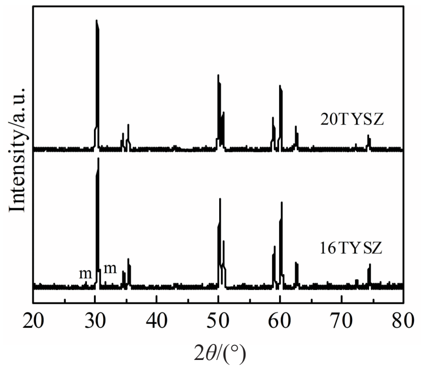

Fig.4 XRD patterns of TYSZ after annealing

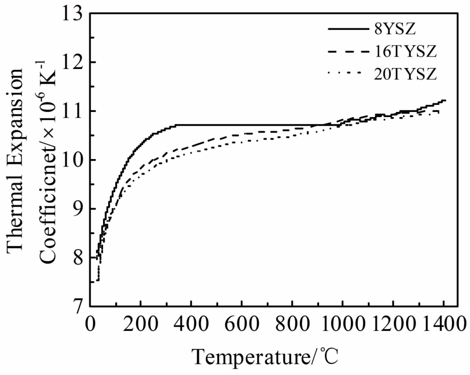

Fig.5 Thermal expansion coefficient curves of TYSZ and YSZ bulks

The point defect scattering caused by substituting atoms on the phonon mean path affects thermal conductivities mostly and can be described by the following equation[9,34]:

$$\Gamma_i=f_i[(\Delta M/M)^2+\varepsilon(\Delta R/R)^2] \tag{3}$$

where Γ_i characterizes the phonon scattering coefficient of defect *i*; f_i is the defect concentration of atom *i*; *M* and *R* are the average values of the atomic mass and the ionic radius on the corresponding defective crystalline site, respectively; ΔM is the difference in the atomic mass between the substituting atoms and *M*; ΔR is the difference in the ionic radii between the substituting atoms and *R*; ε is a strain field factor, which is related to the Grüneisen parameter and Poisson ratio, and it reflects the relative mass of mass difference and radius difference on phonon scattering. In this study, the stress field factor is considered to be a constant due to the lack of data, which leads to some uncertainty in the results. Fig. 7 shows the phonon scattering coefficients (Γ) of Ta^{5+} and Y^{3+}, as well as combination substitutions. With the increase in stabilizer content, the Γ_Y, Γ_T, and Γ_{TY} increase, which means that the phonon

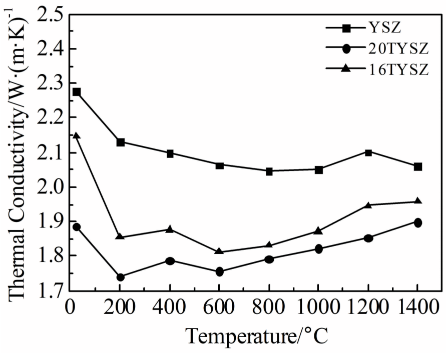

Fig.6 Thermal conductivities versus temperature curves of TYSZ and YSZ bulks

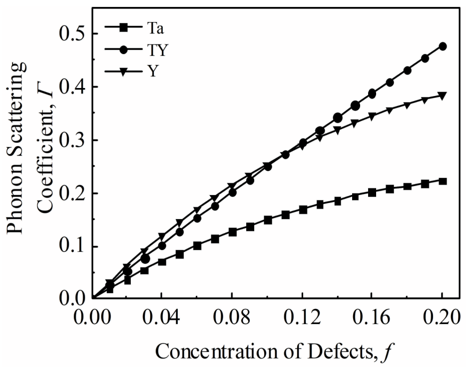

Fig.7 Phonon scattering coefficient caused by Ta^{5+} and Y^{3+} substitutions in zirconia

scattering becomes stronger. It should be noted that the increased rate of Γ_Y and Γ_T gradually decreases with increasing the content, while Γ_{TY} increases almost linearly. Because the heavier Ta^{5+} and larger Y^{3+} provide larger $\Delta M/M$ and $\Delta R/R$, respectively, the lattice disorder caused by multi-substitution is enhanced. Furthermore, the dopant content in 16TYSZ and 20TYSZ (16mol% and 20mol%) is much higher than that of YSZ (3mol%~4mol%). Hence, the experimentally measured thermal conductivity of TYSZ is 1.8~2.0 W/(m·K), about 20% lower than that of YSZ (2.0~2.3 W/(m·K)).

3 Conclusions

1) The lattice distortion that determines the phase structure is related to the doping content. When the doping content is greater than 12mol% , a stable t phase structure can be obtained for TYSZ. Highly doped Ta^{5+} and Y^{3+} can increase precipitation, leading to a decrease in high-temperature stability.

2) The fracture toughness decreases with dopant content, and fracture toughness of 16TYSZ is 5.72 MPa·$m^{1/2}$, which is comparable to that of YSZ. Under stress conditions, the TYSZ undergoes a t-m phase transition, and the content of phase transformation decreases with increasing the dopant content. After heat treatment at 1000 ºC for 2 h, the stress-induced m phase transfers back to the t phase.

3) The CTE of TYSZ from 25 ºC to 1400 ºC is 10.9×10^{-6}~11.1×10^{-6} K^{-1}, close to that of YSZ. Due to the decreased phonon mean free path, the thermal conductivity of 16TYSZ ceramic is approximately 20% lower than that of YSZ.

4) The proper doping of 16TYSZ ceramics makes it stable at high temperatures and stress-sensitive, and the presence of lattice distortion increases the phonon scattering, resulting in low thermal conductivity, which has the potential to become a new TBC material.

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Ta_2O_5-Y_2O_3掺杂剂对氧化锆相结构、断裂韧性和热物理性能的影响

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摘　要：合成制备了一系列的Ta_2O_5-Y_2O_3掺杂的ZrO_2（TYSZ）。研究了掺杂剂含量对处理相结构、相稳定性、断裂韧性、热膨胀系数和导热系数的影响，同时探讨了应力条件下TYSZ的响应机制。结果表明，掺杂Ta_2O_5和Y_2O_3引起的晶格变形有利于t相稳定。但随着掺杂含量的增加，由于应力诱导的t-m相变被抑制和高温下稳定剂析出倾向增加，高温相稳定性和断裂韧性下降。热膨胀系数和热导率的变化则是由晶体结构的混乱程度和晶格膨胀导致的。16TYSZ具有良好的相稳定性、应力敏感性和热物理性能，是先进热障涂层材料的潜在候选材料。

关键词：热障涂层；相稳定性；断裂韧性；热物理性能

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