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Sintering densification and properties of Al_2O_3/PSZ(3Y) ceramic composites①

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Abstract: The content of partially stabilized zirconia has remarkable influence on densification and mechanical properties of Al_2O_3/PSZ(3Y) ceramic composites. When 15% PSZ(3Y) is added to Al_2O_3, after vacuum sintering for 2 h at 1 550 ℃, the fracture toughness and bending strength of the Al_2O_3/PSZ(3Y) ceramic composite reaches 8.2 MPa·$m^{1/2}$ and 884 MPa, respectively. The effect of the content of PSZ(3Y) on relative density and mechanical properties was investigated. The change of *m*-ZrO_2 and *t*-ZrO_2 phases content before and after fracture was measured by X-ray diffraction quantitative phase analysis. It is confirmed that improvement in bending strength and fracture toughness of the Al_2O_3/PSZ(3Y) ceramic composite is due to the phase transformation toughening mechanism of PSZ(3Y).

Key words: Al_2O_3/PSZ(3Y) ceramic composite; vacuum sintering; transformation toughening; mechanical properties
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1 INTRODUCTION

Al_2O_3 ceramics is one of the wide-spreading materials because it holds good features such as resistance to high temperature, oxidation, corrosion and abrasion. However, the brittle nature of Al_2O_3 ceramics has prompted us to explore a variety of approaches to enhance its fracture toughness. Since Garvie et al[1] advanced a theory in 1975, that is to improve the fracture toughness and flexural strength of ZrO_2 ceramics with martensitic transformation, ZrO_2 has been receiving considerable attention. Adding MgO, CaO, Y_2O_3 and CeO_2 respectively to ZrO_2 can take advantage of phase transformation effectively to increase the fracture toughness and flexural strength of ceramic materials. As a structured ceramic composite, a number of investigations have been carried out on ZrO_2 over the years[2]. The authors show in this paper that the content, relative density and sintering temperature of PSZ(3Y) have effect on the fracture toughness and flexural strength of Al_2O_3 ceramics and that the phase transformation increases and the microscopic structure is associated with the mechanical properties in vacuum sintering condition.

2 EXPERIMENTAL

2.1 Fabrication

Powder with average grain size of 200 nm (soft agglomerated), and purity of 99.99% for Al_2O_3 was used[3]. Y_2O_3(3%, mole fraction) was 99.99% pure and the particle size was close to 200 nm in partially-stabilized ZrO_2. Media containing high-purity Al_2O_3 balls and pure ethyalcohol milled composite powder for 48 h. Five composite series were fabricated for this study: these, respectively, containing 10%, 15%, 20%, 25% and 30% volume fractions. All powders were dried, loaded with two-face model and then cold isostatically pressed at 200 MPa. The green body reaches the relative density of 55%. The specimens were firstly heated at 600 ℃ in a box-furnace for 2 h. Secondly, they were sintered respectively at 1 500, 1 550, 1 600, 1 650 and 1 700 ℃ for 2 h in a VSF-7 vacuum sintering furnace with a vacuum degree < 1×10^{-3} Pa. After the treatments above, the specimens were sintered at selected temperatures for 2 h and cooled to room temperature. Finally, the dimension of specimens reached 5 mm × 5 mm × 30 mm.

2.2 Mechanical properties measurement

The densities of specimens were measured with Archimedes method and changed into relative density through calculation. Strength measurements were obtained by three-point bending method using an Instron4206 materials testing machine with a speed of 0.05 mm/min. By using Single Edge Notched Beam (SENB) techniques, the fracture toughness was giv-

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en by[4] $K_{IC}= Y\frac{3pL}{2bW^2}\sqrt{a}$, where Y is a geometrical constant, p is the fracture load(kN), L is the length of the span between two points, b and W are related to the width and thickness respectively, and a is the depth of specimens center crack. The phases were analyzed by using the D/max-RB type X-ray diffractometer and the phase contents before and after cracking were calculated. Based on the relative diffraction strength of t-ZrO_2(111), m-ZrO_2 and $(11\bar{1})$ peak, the relative content of t-ZrO_2 and m-ZrO_2 was obtained from[5]

$$X_m= \frac{I_{m(111)}+ I_{m(11\bar{1})}}{I_{m(111)}+ I_{m(11\bar{1})}+ I_{t(111)}} \times 100\%$$

and

$$\varphi_m= \frac{1.311X_m}{1+ 0.311X_m} \quad (1)$$

where X_m is the integrated intensity ratio, and the subscripts m and t represent the intensities of the m and t phases after the peak separation and fitting procedures, φ_m is volume fraction of the monoclinic phase.

Microstructures of specimen were observed under EPM-810Q Scanning Electron Microscope.

3 RESULTS AND ANALYSES

3.1 Effect of PSZ(3Y) conten and sintering temperature on relative density and strength

Figs. 1(a) and (b) illustrate that the relative density and linear shrinkage gradually increase with the rise of sintering temperature and that the relative density and linear shrinkage exhibit a trend to be low with the rise of PSZ(3Y) content. The critical reason is that ZrO_2 grains have produced t-$ZrO_2 \rightarrow m$-ZrO_2 phase transformation during sintering, which results in m-ZrO_2 phase insufficient to basic thermal expansion factor. High internal stress occurs on the grain boundary, which causes larger size cracks. High ZrO_2 content, as reported by Kreher et al[6], can induce network crack, while ZrO_2 grains growth can induce larger size and dangerous cracks, and cause low linear shrinkage, which directly results in relative density and sintering properties decreasing.

Fig. 2 illustrates that the fracture toughness is related to sintering temperature. Namely, the fracture toughness, for the different volume fraction of PSZ(3Y) investigated, holds the trend to increase, corresponding with the sintering temperature rising from 1 500 ℃ to 1 550 ℃. The fracture toughness reaches the maximum of 884 MPa at 1 550 ℃. For the different PSZ(3Y) content materials investigated, the fracture toughness reaches respective maximum(as shown in Fig. 2) at 1 550 ℃ and gradually decreases, corresponding to PSZ(3Y) content increasing. According to Ref. [7], the pressure of potential oxygen decreases with PSZ(3Y) content increasing during vacuum sintering. Therefore, there is a considerable number of oxygen vacancies, which results in low fracture toughness.

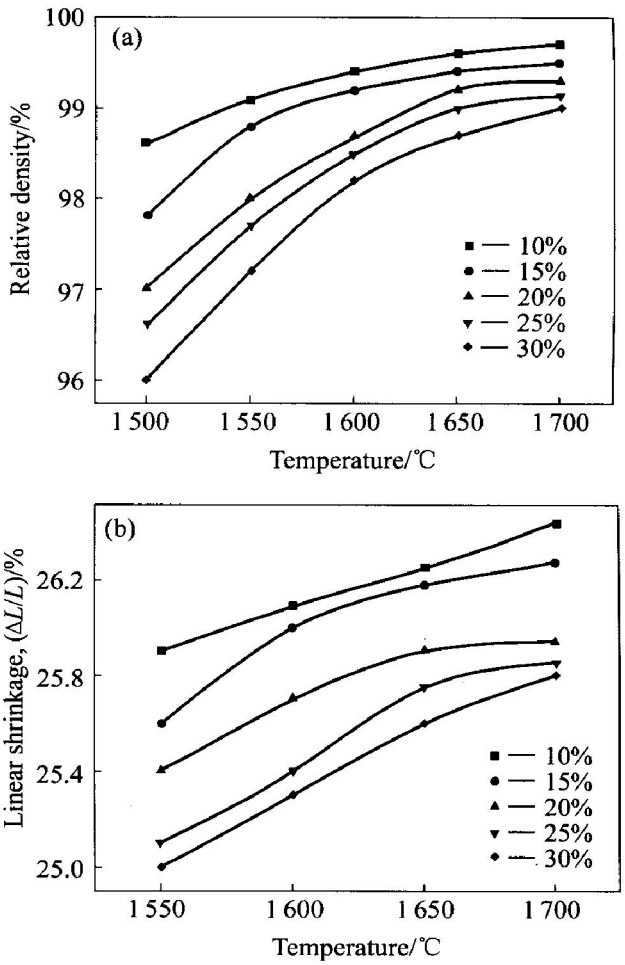

Fig. 1 Relative density and linear shrinkage vs sintering temperature for Al_2O_3 ceramics containing different volume fractions of PSZ(3Y)

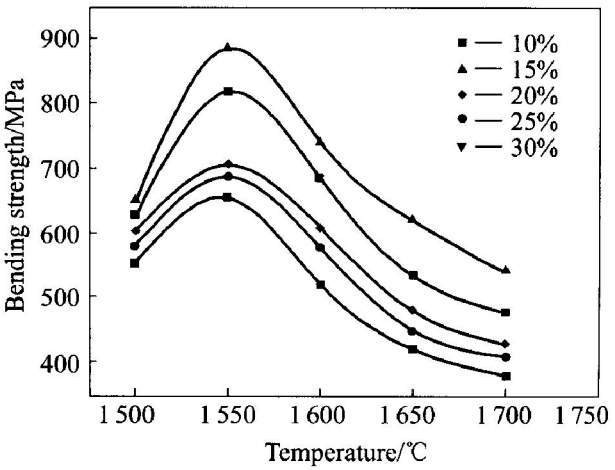

Fig. 2 Bending strength vs sintering temperature for Al_2O_3 matrix ceramics containing different volume fractions of PSZ(3Y)

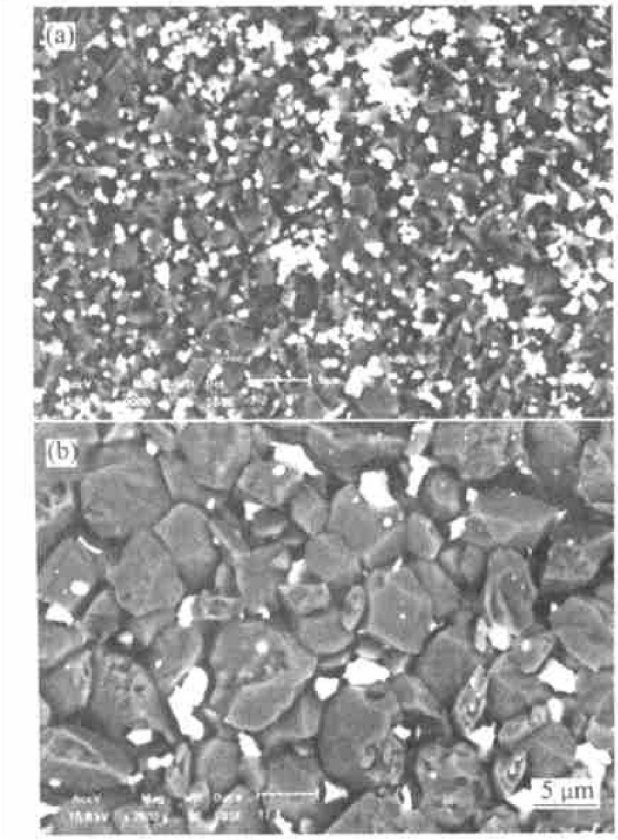

Fig. 3 Fracture surfaces (SEM) of Al_2O_3/15% PSZ(3Y) composite sintered at 1 550 ℃(a) and 1 700 ℃(b) (ZrO_2 is white-phase, Al_2O_3 is dark-phase)

Fig. 3 shows the SEM photographs of fracture surfaces of specimen for Al_2O_3/15% PSZ(3Y) at several sintering temperatures. Based on energy spectrum analysis, the white phase is ZrO_2 and the dark one is Al_2O_3. Fig. 3 shows that the grain size of specimen at 1 550 ℃ grows fine and evenly, however, that the specimen at 1 700 ℃ appears abnormal growing up phenomenon. The grain size growth weakens the strength of grain boundary, which leads to decrease of bending strength. Therefore, effectively controlling the speed ratio of the grain size growth and choosing proper sintering temperature and PSZ (3Y) content can play important roles on bending strength of Al_2O_3/PSZ(3Y) ceramics composite.

3.2 Effect of PSZ(3Y) content on fracture toughness

For the measurement of fracture toughness K_{IC}, Hannink et al[8] found that the indentation technique is usually unfit for increasing toughness of ceramics, especially for phase transformation-toughening ceramics. The cracks caused by pressure are controlled utterly. In this paper, fracture toughness K_{IC} values of different contents of PSZ(3Y) in the Al_2O_3 matrix were achieved by SENB method at 1 550 ℃. Fig. 4 illustrates that K_{IC} values of the specimens Al_2O_3/PSZ(3Y) and bending strength are related to the volume fraction of PSZ(3Y) at 1 550 ℃ during vacuum sintering. Fig. 4 presents that the curve of bending strength is similar to that of fracture toughness, which corresponds with Griffth relational expression:

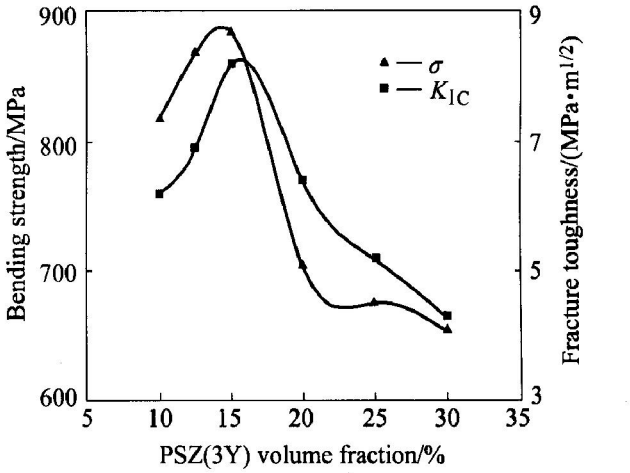

Fig. 4 Fracture toughness and bending strength as functions of volume fraction PSZ(3Y)

$$\sigma = Y \cdot K_{IC} \cdot C^{-1/2}$$

where C is the final flaw size, Y is a geometric factor, and K_{IC} values increase with high σ values.

Fig. 5 is a SEM micrograph showing the microstructure forms of Al_2O_3 matrix ceramics specimens with different PSZ(3Y) contents. Fig. 5(b) presents that the Al_2O_3 grains with the contents of PSZ(3Y) < 15% volume fraction, become distinctly fine and distribute well. As the content increase to 30%, Al_2O_3 grains become coarse and irregular, and cracks appear among grain sizes. In other aspect, too many contents of PSZ(3Y) result in weakening the dispersion of Al_2O_3 matrix, which induces cracks to occur. These phenomena illustrate that adequate PSZ (3Y) content can take roles on refining basic grain sizes and improving the microstructure of the Al_2O_3 matrix. For the effect of microstructure on two-phase ceramics properties, according to Claussen's[9] application energy absorbing mechanism, it is suggested that the existence of a few evenly distributed microcracks structure is a necessary condition to obtain high fracture toughness and bending strength. The secure method to limit microcrack growth is to use the second phase grain size lower than basic thermal expansion coefficient to composite. So too many contents of PSZ(3Y) can result in decreasing ceramics mechanical properties.

In addition, the larger ZrO_2 particles beyond 0.8 μm take place $t \rightarrow m$ phase transformation during the cooling of the agglomerates. Volume expansions resulted from phases transformation cause residual microcracks appearances, which take important roles in absorbing the crack energy and improving flexural strength. Meanwhile, the remained tensile stresses occur due to the relation between thermal expansion

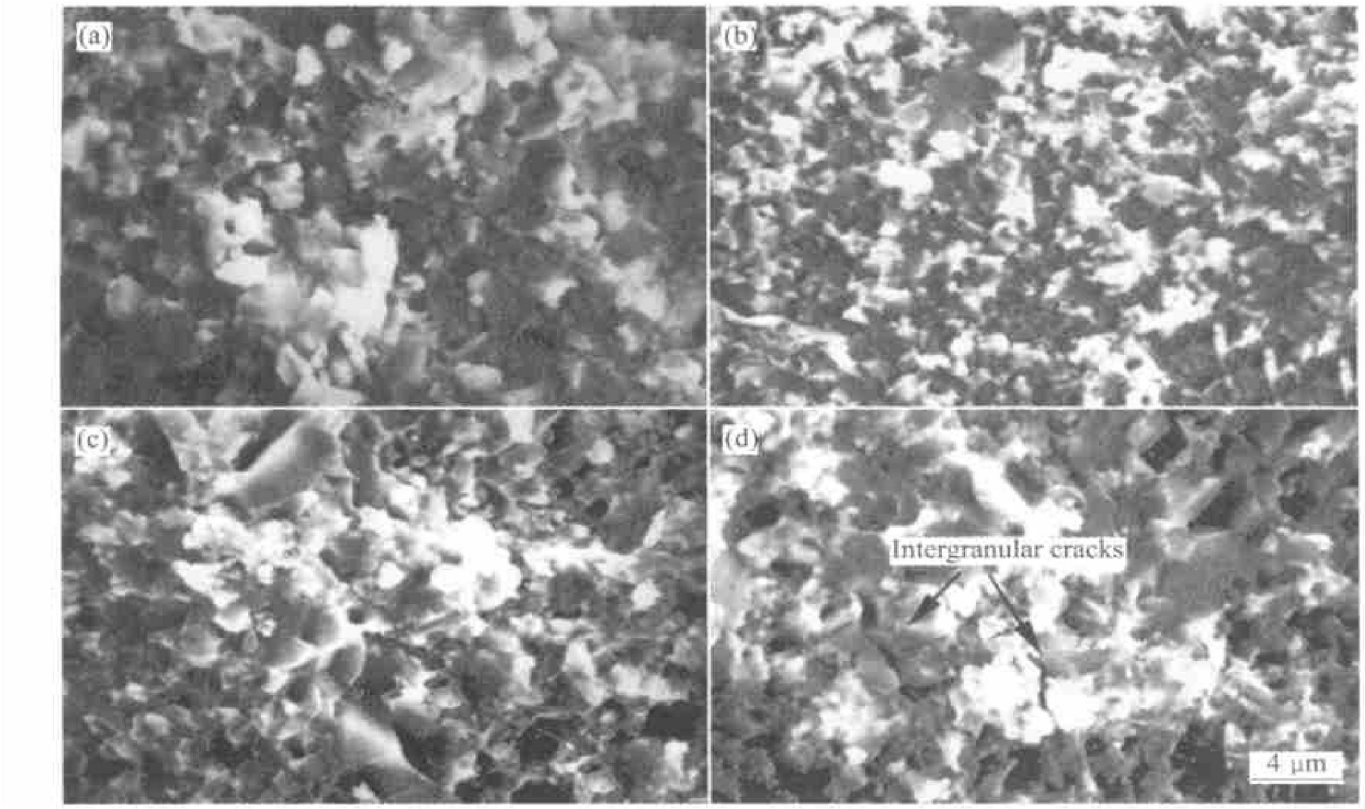

Fig. 5 Fracture surfaces (SEM) of Al_2O_3/ PSZ(3Y) ceramics containing ZrO_2 volume fractions of 10% (a), 15% (b), 25% (c) and 30% (d)

coefficients of Al_2O_3 and ZrO_2 (m-phase transformed): $\alpha_{Al_2O_2} > \alpha_{m\text{-}ZrO_2}$, which weakens Al_2O_3 phases forces of constraint and induces microcracks in a small part of Al_2O_3 phase to appear. The agglomerate [15% PSZ(3Y) content] appear fracture toughness peak and bending strength peak in Fig. 4. Fig. 5(b) presents that spread evenly around Al_2O_3 phases, which effectively controls grain growth to make the grain sizes of agglomerates more even . The PSZ (3Y) content continually rising to 30% causes microcrack density, in phase transformation zone, to increase and microcracks to integrate into net-like cracks, which leads bending strength and fracture toughness to decrease obviously.

3.3 Effect of PSZ(3Y) on transformation toughening mechanism of Al_2O_3 matrix ceramics

The stress-induced phase transformation bring about microcracks during fracture process[10]. After agglomerates being cooled, the grain size of remained t-ZrO_2 phase is usually smaller than that of critical transformation at room temperatures. t-$ZrO_2 \rightarrow m$-ZrO_2 phase transformation induces thinner microcraks to occur while the samples sintered are loaded by stresses outside and residual tensile stress as mentioned above. Affected by elastic strain energy and cracks extending to stress-induced microcracks formation zone, both the bending strength and fracture toughness of Al_2O_3 matrix are enhanced.

Figs. 6(a) and (b), respectively, show XRD patterns of Al_2O_3[15% PSZ(3Y) content] composite phases ceramics specimen surface before fracturing and specimen mouth after fracturing. The calculations present that t-ZrO_2 and m-ZrO_2 phase contents of sample surface unfractured, respectively, are 45.6% and 54.4%, but t-ZrO_2 and m-ZrO_2 phase contents of sample fracture-mouth, respectively, are 45.6% and 54.4%. Therefore, we can find that t and m phase content of samples fractured, separately, decrease and increase by 43.8%. ZrO_2 grain sizes of the specimen [15% PSZ(3Y)] > 0.1 μm (Fig. 5(b)). The critical dimension of t-$ZrO_2 \rightarrow m$-ZrO_2 martensitic transformation is 0.2 – 0.8 μm in ZrO_2 ceramics[11], while Al_2O_3 ceramics [15% PSZ(3Y)] remained ZrO_2 grain sizes close to 0.1 μm(Fig5(b)). Therefore, t-$ZrO_2 \rightarrow m$-ZrO_2 transformation occurring during fracturing produces important role on stresses inducing transformation to increase flexural strengths. In the specimen [30% PSZ(3Y)], the ZrO_2 grains grow abnormally among which the maximum size reaches 2 μm. t-ZrO_2 phases (< 0.2 μm transformation critical size) were remained on the condition of sintering and cooling to room temperatures. For t-ZrO_2 phase (> 0.2 μm), the t-$ZrO_2 \rightarrow m$-ZrO_2 transformation took place in ZrO_2 grains during sintering and cooling processes, which results in larger microcracks that integrate into larger defect cracks. Therefore, t phase content decreases and m phase content increases in the specimens, which

weakens the ability of stress-induced transformation increasing flexural strength. It just interprets why Al_2O_3[30% PSZ(3Y)] two-phase ceramics have the lowest flexural strength.

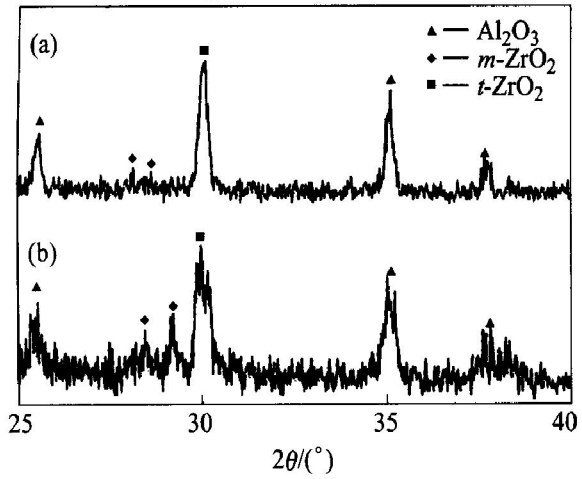

Fig. 6 XRD patterns of Al_2O_3/ 15% PSZ (3Y) composites before (a) and after (b) fracture (Cu K_α)

These results establish that adding 10% - 15% PSZ(3Y) to Al_2O_3 takes important effect on fracture toughness increasing, flexural strength-increasing and stress-induced transformation, and that a few residual cracks play second effect. Based on Griffth's fracture theory, Lange suggested that $t \rightarrow m$ stress-induced transformation of ZrO_2 caused not only flexural strength increasing, but also fracture toughness increasing[12]. While adding 20% - 30% PSZ(3Y) content to Al_2O_3, both fracture toughness and flexural strength tend to decrease. Residual microcrack occuring and combining caused the process of the curve falling in Fig. 4.

According to Ref. [13], combining and jointing the residual microcracks decrease considerably materials fracture toughness. Meanwhile, the bending strength increase, corresponding to high microcracks, but too high microcrack density can cause bending strength to decrease[14]. Therefore, adding proper PSZ (3Y) content to Al_2O_3 ceramics can improve fracture toughness and flexural strength of composite ceramic materials.

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