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Microstructure and mechanical properties of ZTA fabricated by liquid phase sintering

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Abstract

Zirconia-toughened alumina (ZTA) ceramics with ZrO_2 volume fraction from 0 to 50 vol.% were pressurelessly prepared with the addition of 1 wt.% TiO_2–1 wt.% MnO_2 and 2 wt.% CaO–Al_2O_3–SiO_2 (CAS) as sintering aids. The influence of ZrO_2 content and sintering temperature on microstructure and mechanical properties of the composites were investigated. All samples can be fully densified at as low as 1400 °C. For pure Al_2O_3 sample, platelike grains appeared. With the addition of ZrO_2, platelike grains of Al_2O_3 conversed to equiaxed grains and their sizes decreased gradually. Mechanical properties increased with ZrO_2 content. When 50 vol.% was added, strength and toughness of composite reached 619 ± 36 MPa and 7.02 ± 0.06 MPam$^{1/2}$, respectively. The toughening mechanism was phase transformation based on analyzing the transformable ZrO_2 content.

Keywords: B. Microstructure-final; C. Mechanical properties; D. Al_2O_3; D. ZrO_2; Liquid phase sintering

1. Introduction

Among the different works devoted to the enhancement of the mechanical properties and reliability of high performance ceramic materials, the most promising results are obtained by the synthesis of composite materials made of a ceramic matrix and a second phase: long or short fibers, whiskers, particles [1]. In the case of ZrO_2 particles in Al_2O_3 matrices improved fracture properties, especially fracture toughness (K_{IC}), were observed due to phase transformation of t-ZrO_2 [2,3].

However, previous studies show that Al_2O_3/ZrO_2 powder compacts require a higher sintering temperature (>1550 °C) to achieve a comparable density relative to their constituents because the densification is significantly retarded by the presence of ZrO_2 inclusions [4,5]. Besides, stresses arising from the presence of the heterogeneities and agglomerates give rise to differential sintering rates within the compact during sintering [6,7]. Thus, the composite can only be densified by hot-pressing or post-hot isostatic pressing in most cases.

Conversely, the densifications of polycrystalline matrices containing a liquid phase are much less affected by the second-phase inclusions [8]. The spreading liquid penetrates the solid-solid interfaces, which can disintegrate the solid grain structure (agglomerates) in some extent [9]. Furthermore, the lower sintering temperature by the presence of liquid phase can save the fabrication cost. However, liquid-phase sintering of zirconia-toughened alumina has received little attention.

The objective of this work is to develop a processing method to the low-cost fabrication of high-performance zirconia-toughened alumina (ZTA) materials. 3Y-TZP and Al_2O_3 powders are starting materials, TiO_2–MnO_2 and CaO–Al_2O_3–SiO_2 glass are used as liquid forming additives. The microstructure and mechanical properties of the composite are characterized in detail.

2. Experimental procedure

High-purity commercial (99.9%) 3Y-TZP and Al_2O_3 were used as starting powders. CaO–Al_2O_3–SiO_2 glass (CAS), reagent-grade TiO_2 and MnO_2 were used as sintering additives. CAS glass was derived from reagent-grade $CaCO_3$, Al_2O_3 and SiO_2, which were

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mixed thoroughly, precalcined and then melted at 1500 °C for 2 h. Clear transparent glass was obtained and powdered to a final size of 3.4 μm (d_{50}). Mechanical milling of 3Y-TZP, Al_2O_3 and additives was performed in distilled water for 24 h. Content of 3Y-TZP varied from 0 up to 50 vol.%. Amount of additives was 1 wt.% TiO_2, 1 wt.% MnO_2 and 2 wt.% CAS glass. After drying, the mixture was uniaxially pressed and followed by isostatic pressing at 200MPa, and then pressurelessly sintered at 1300-1500 °C for 2h. Bulk density was measured by the Archimedes method.

The specimens were machined into rectangular bars with dimensions of 3 mm by 4 mm. Bending strength was measured by the three-point method with a span of 30 mm and cross-head speed of 0.5 mm/min. At least five specimens were tested. The fracture toughness measurement was carried out on the polished surfaces by microindentation method using Shetty's equation [10]. XRD was performed on the polished surfaces to determine the phase compositions of the sintered materials. The fraction of monoclinic ZrO_2 was calculated using the following equation [11]:

$$X_m = \frac{I_m(111) + I_m\left(11\bar{1}\right)}{I_m(111) + I_m\left(11\bar{1}\right) + I_{t,c}(111)}$$

The microstructure of the sintered bodies was observed by scanning electron microscope on the polished surfaces after thermally etched.

Throughout this paper the nomenclature ZA*XX* has been used. ZA represents zirconia-toughened alumina ceramics and *XX* represents the volume fraction of alumina present in the specimen.

3. Results and discussion

The effect of sintering temperature on the densities of Al_2O_3 and ZTA specimens is shown in Fig. 1. The relative densities were calculated on the basis of the theoretical densities of 6.08 and 3.98 g/cm^3 for 3Y-TZP and Al_2O_3, 4.25, 5.026 and 2.579 g/cm^3 for TiO_2, MnO_2 and CAS glass, respectively. It shows that a complete sintering of Al_2O_3 can be achieved at temperature as low as 1300–1350 °C. A slight reduction of density occurs at higher temperatures. The decrease in density is most likely due to the formation and evolution of gaseous species caused by pore coarsening [12] as evinced by bloating and blistering in some of the materials. ZTA specimens exhibit significant difference in densification. The sintered densities ranged between 95 and 98% attained at 1350–1450 °C. In general, Al_2O_3 and ZTA can only be densified above 1550 °C by solid-state sintering. It is evident that liquid-phase sintering has advantages in lowering sintering temperature and enhancing densification.

Fig. 2 shows the microstructure of the composites sintered at 1400 °C. It can be seen that platelike grains formed in the sintered body of specimen Al_2O_3 (as shown in Fig. 2a). Wang et al. [13] indicated that platelike grains of Al_2O_3 can be found when the body contained small amount of impurities, especially when SiO_2 is present with other oxides. However, the formation of platelike grains usually needs higher temperature ($\geqslant$1500 °C) and longer holding time [14]. In present work platelike grains with a large aspect ratio forms at 1400 °C/2h.

From Fig. 2b–e, it can be seen that the pinning effect of ZrO_2 on the grain growth of Al_2O_3 is distinct. That is, with the increase of ZrO_2, two phenomenons are obvious. One is the morphology change of Al_2O_3 grain. It changed gradually from platelike to equiaxed. The suppressing effect of ZrO_2 on the formation of platelike Al_2O_3 grains is great. The other is the decrease of Al_2O_3 grain size. At low volume fractions of 3Y-TZP the ZrO_2 particles (white grains) are ineffective in pinning the Al_2O_3 grain boundaries, so that abnormal or exaggerated grain growth occurs readily, as shown in Fig. 2b (10 vol.% 3Y-TZP). Some ZrO_2 particles are trapped into Al_2O_3 grains. Lange [15] reported that abnormal growth of Al_2O_3 was prevented by the ZrO_2 inclusions at volume fractions $\geqslant$5%. The discrepancy suggests that other factors besides ZrO_2 volume fraction affect microstructural evolution. Kibbel et al. [16] observed breakaway grain growth in a ZTA with a higher volume fraction of ZrO_2 than that supposedly needed to prevent exaggerated grain growth. They show that the reason is related to impurities altering the properties of the

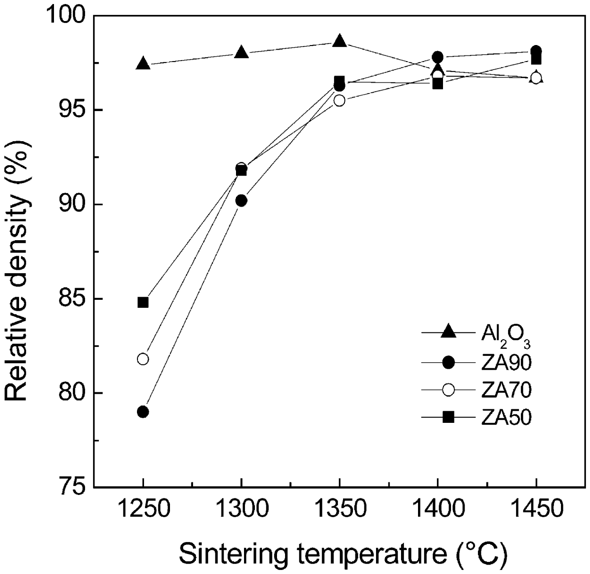

Fig. 1. Relative density as a function of sintering temperature for the Al_2O_3/3Y-TZP composites codoped with 2 wt.% TiO_2–MnO_2 and 2 wt.% CAS glass.

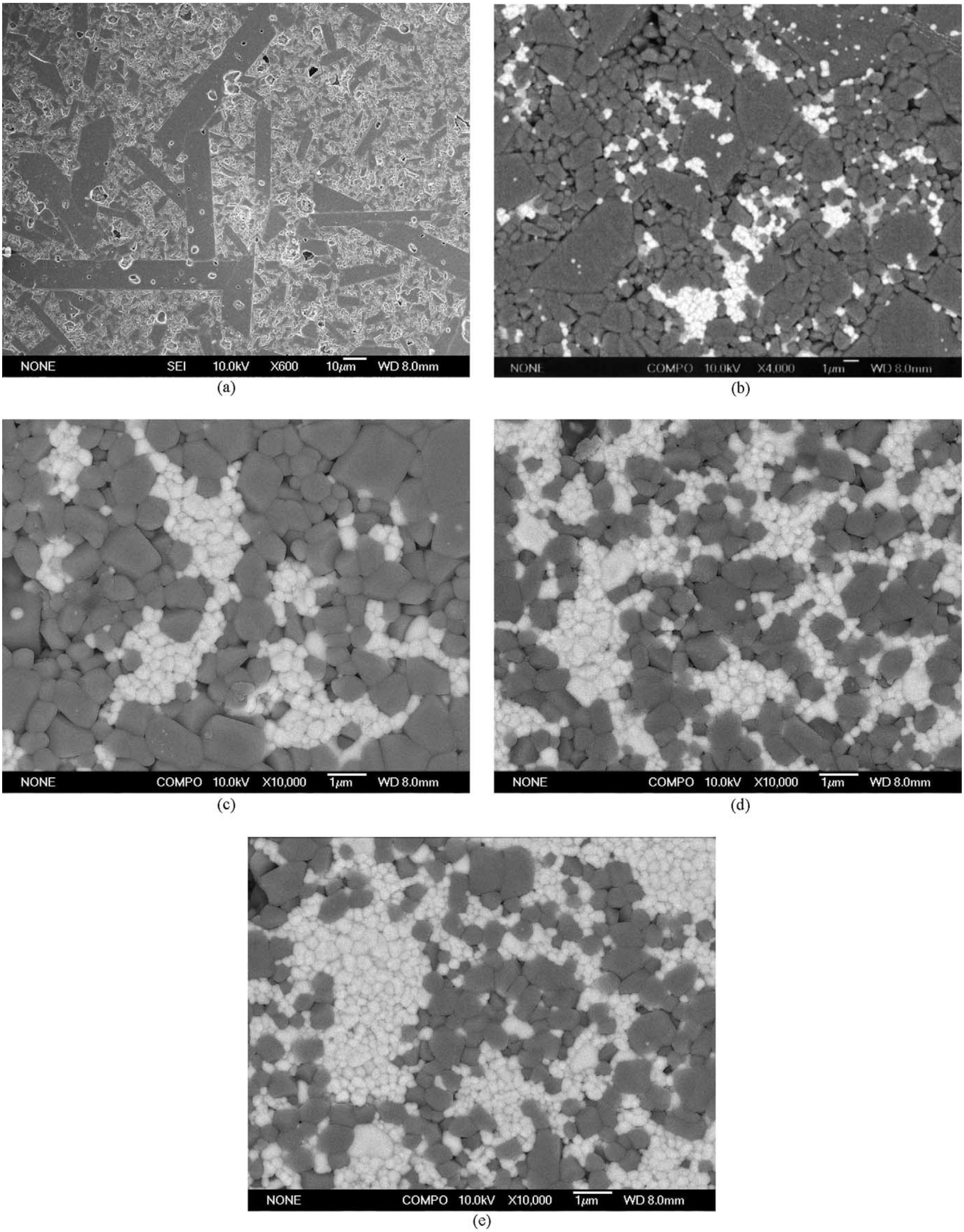

Fig. 2. SEM micrographs of polished and thermally etched surfaces for the Al_2O_3/3Y-TZP composites sintered at 1400 °C: (a) Al_2O_3, (b) ZA90, (c) ZA80, (d) ZA60 and (e) ZA50.

ubiquitous and continuous glassy grain-boundary phase. In our work, ZrO_2 particles located at Al_2O_3 grain junctions migrate with Al_2O_3 grain boundaries, impede their motion, and can become trapped inside Al_2O_3 grains when rapidly migrating grain boundaries break away during grain growth, which is resulted from the existing of TM-CAS liquid (TM: TiO_2–MnO_2). This is agreement with Kibbel's [16] results.

The average bending strength and fracture toughness of the various specimens sintered at 1400 °C are plotted in Fig. 3. The strength of specimen Al_2O_3 sintered at 1400 °C is lower than the value reported in literature. This is because overfiring of Al_2O_3 has occurred at 1400 °C. It can be noted that the strength of the composites increases with increasing volume fraction of 3Y-TZP. The toughness increases linearly with increasing volume fraction of 3Y-TZP. XRD analysis is shown in Table 1. Data listed in Table 1 indicated that large amount of tetragonal ZrO_2 were transformable. It was therefore concluded that the main toughening mechanism of the composites were from transformation toughening, although the microcrack could also contribute to toughening to some extent, since some ZrO_2 were in the monoclinic form. The X-ray diffraction of compacts sintered at 1400 °C for 2 h is given in Fig. 4. It revealed that peaks were mainly attributed to α-Al_2O_3, *t*-ZrO_2 and *m*-ZrO_2. The rhombohedral phase was also found for sample ZA50.

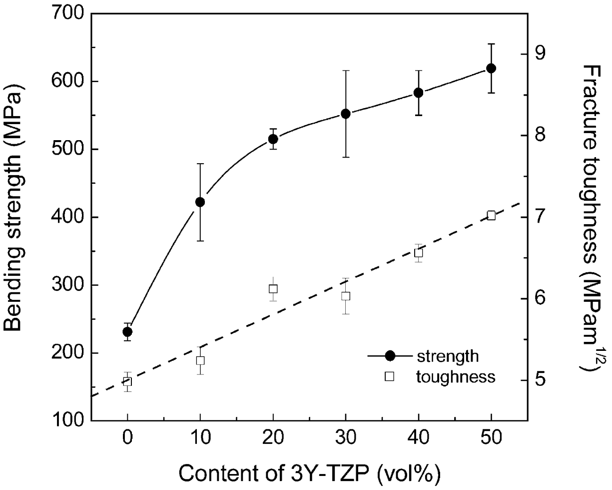

Fig. 3. Bending strength and fracture toughness as a function of 3Y-TZP content for the composites sintered at 1400 °C/2 h.

Table 1
Monoclinic ZrO_2 fraction in ZTA samples

Sample	Sintering temperature (°C)	Mono. ZrO_2 (%)	
		Polished	Fractured
ZA90		28.6	49.4
ZA80		20.8	42.8
ZA70	1400	15.1	50.9
ZA60		5.0	23.8
ZA50		5.0	28.3

An interesting phenomenon is that the amount of monoclinic zirconia phase decreased when the volume fraction of zirconia increased in the composites. According to Lange [17], when increasing the volume fraction of zirconia, the constraint from Al_2O_3 matrix decreased and the grain size of zirconia increased. As a result, the amount of monoclinic phase increased. But our experiment results show a reversible trend. This phenomenon may be related to the sintered densities of the composites. It is found that the relative density of the composite containing more ZrO_2 is slightly higher than that of composite containing less ZrO_2. Higher degree of densification is beneficial to the retain tetragonal ZrO_2 at room temperature.

The dependences of strength and toughness on sintering temperature of zirconia-toughened alumina ceramics are shown in Figs. 5 and 6. It reveals that strength and toughness increased with sintering temperature. This is because densities of samples were raised when sintering temperature increased. However, when the sintering temperature raised to 1450 °C, the bending strength of some samples decreased. This is attributable to the occurrence of excessive grain growth. The transformation of larger ZrO_2 grains from tetragonal phase to monoclinic phase leads to the formation of microcracks in the sintered body. As a result, the bending strength decreased. However, toughness increased with

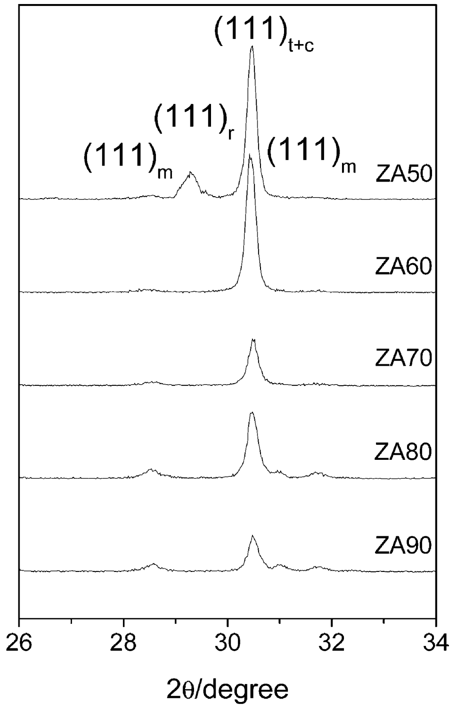

Fig. 4. XRD patterns on the polished surfaces for the composites sintered at 1400 °C/2 h.

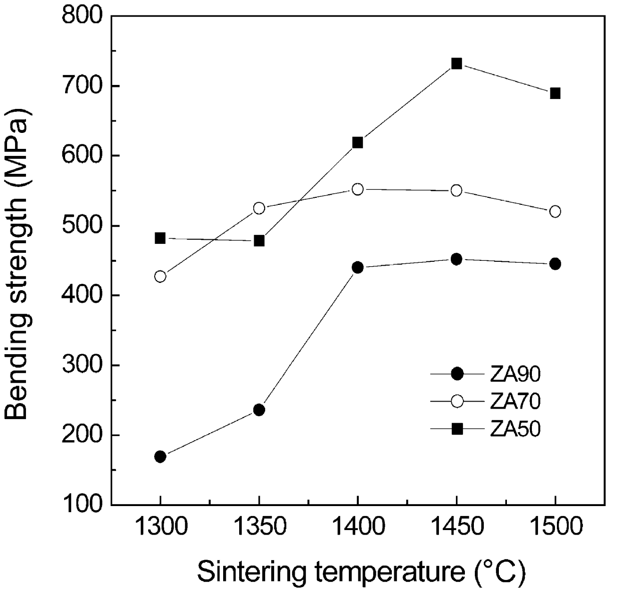

Fig. 5. Bending strength as a function of sintering temperature of ZTA samples.

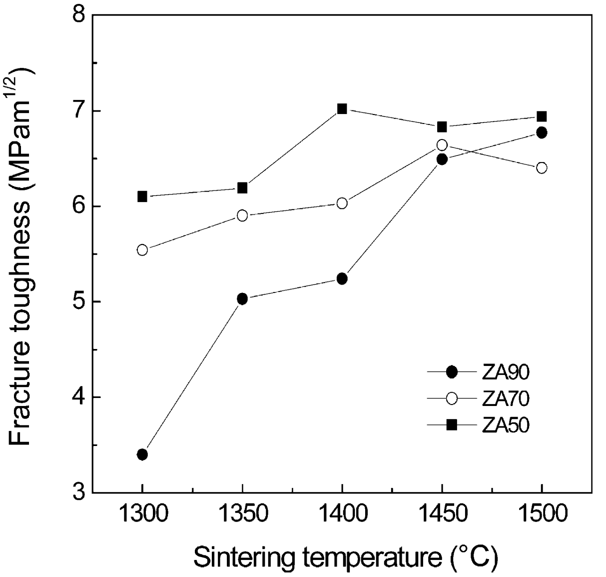

Fig. 6. Fracture toughness as a function of sintering temperature of ZTA samples.

sintering temperatures up to 1500 °C, which suggests the microcrack toughening is in operation.

4. Conclusion

Al_2O_3/3Y-TZP (up to 50 vol.%) composite could be densified at a temperature as low as 1400 °C by codoping with small amount of TiO_2–MnO_2 and CaO–Al_2O_3–SiO_2 glass. It was found that platelike Al_2O_3 grains could form even at 1400 °C because of the TM-CAS codoping. Compared with solid-state sintering, finer grains composite could be obtained by liquid-phase sintering because of the lower sintering temperature. Better mechanical properties were also obtained.

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