

Microstructure and mechanical properties of 3Y-TZP/Al₂O₃ composites fabricated by liquid phase sintering

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3Y-TZP/Al₂O₃ composites were pressureless sintered with the addition of TiO₂-MnO₂ and CaO-Al₂O₃-SiO₂ glass. The densification, microstructure and mechanical properties of the composites were investigated. It was found that the composites could be densified at a temperature as low as 1400°C by liquid phase sintering. The majority of the grain sizes for both Al₂O₃ and ZrO₂ were below 1 μm because of the lower sintering temperature. A bending strength of 934 ± 28 MPa and fracture toughness of 7.82 ± 0.19 MPam^{1/2} were obtained for 3Y-TZP/Al₂O₃ (20 vol%) composite. Transformation toughening is considered the responsible toughening mechanism. © 2005 Springer Science + Business Media, Inc.

1. Introduction

Transformation toughened zirconia ceramics such as yttria stabilized tetragonal zirconia polycrystal (Y-TZP) are of considerable interest as engineering ceramic materials, exhibiting unusually high values of strength and toughness. The transformation toughening phenomena responsible for these attractive properties mainly arises from volume changes and pseudoplasticity associated with the martensitic tetragonal to monoclinic phase transformation in these materials [1–3].

For structural applications, improved mechanical properties are the usual objective. The addition of one ceramic to another can often produce a composite with more desirable properties than the individual components. Many reports [4–6] have shown that the addition of alumina to yttria-stabilized tetragonal zirconia polycrystals has produced ceramics with improved strength and toughness.

As stated in the previous papers [7–9], the composites were more difficult to densify than the single matrix phase. This is because the second phase usually impedes densification if the particles of the second phase was too large compared to the matrix phase, or if the composite powders were possibly strongly agglomerated. As a result, the sintering must be performed at a higher temperature, or in most cases pressure-aided sintering (hot-pressing or hot-isostatic-pressing) needs to be employed to facilitate the densification of the composites [4, 10–11].

Generally, two approaches were usually employed to enhance sintering kinetics or lower the sintering temperature for ceramics [12]. The first is to improve powder processing, i.e., to use fine starting powders and to eliminate agglomerates in the green bodies, by use of colloidal routes. The second approach is to use sinter-

ing aids or additives. A variety of additives have been found to be effective in the sintering of ZrO₂, such as CuO, B₂O₃, TiO₂ and Mn₂O₃ [13–16]. It has also been found that the densification of Al₂O₃ was greatly enhanced with TiO₂-MnO₂ additions (especially when the weight ratio of TiO₂ and MnO₂ was 1:1), and microstructure development was characterized by their promotion to the grain growth [17–19].

However, few reports have appeared in the literature concerned with the sintering of 3Y-TZP/Al₂O₃ composites at low temperature, and the effects of additives on the microstructure and mechanical properties of the composite remain unknown. The purpose of the present work is to densify 3Y-TZP/Al₂O₃ composite by pressureless sintering with TiO₂-MnO₂ and CaO-Al₂O₃-SiO₂ additives and to investigate the effect of these additives on the microstructure and mechanical properties of the composite.

2. Experimental procedure

Analytical-reagent-grade CaCO₃, Al₂O₃ and SiO₂ were melted to form a ternary glass (CAS) having a composition of 23.0 wt% CaO, 15.0 wt% Al₂O₃ and 62.0 wt% SiO₂. Then the glass was crushed and attrition milled in distilled water using alumina balls as the milling media. After drying, the glass powder was sieved through a 120 mesh. For the final production of the 3Y-TZP/Al₂O₃ composite, high purity commercial 3Y-TZP, α-Al₂O₃, and additives (TiO₂, MnO₂, and CAS glass powder) were weighed and milled according to the compositions listed in Table I. The composite powders were uniaxially dry pressed at 50 MPa, followed by cold isostatic pressing at 200 MPa.

TABLE I Composition for the preparation of 3Y-TZP/Al₂O₃ composites with additives

Samples	Composition				
	3Y-TZP (vol%)	Al ₂ O ₃ (vol%)	TiO ₂ (wt%)	MnO ₂ (wt%)	CaO-Al ₂ O ₃ -SiO ₂ (wt%)
ZA00	100	0	1	1	1
ZA10	90	10	1	1	1
ZA20	80	20	1	1	1
ZA30	70	30	1	1	1
ZA40	60	40	1	1	1
ZA40a	60	40	0	0	0

Samples were heated at 5°C/min to final sintering temperatures of 1300–1450°C, with a holding time of 2 h, and finally furnace cooled. Bulk density was measured using the Archimedes method. The specimens were machined to dimensions of 3 mm by 4 mm. Bending strength was measured by the three-point method with a loading span of 30 mm and a 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 [20]. XRD was performed on the polished surfaces to determine the phase compositions of the sintered materials. The fraction of the monoclinic ZrO₂ was calculated using Garvie and Nicholson's equation [21]. The microstructure of the sintered bodies was observed by examination of polished surface in a scanning electron microscope and transmission electron microscope was used to examine the fine structure.

3. Results and discussion

Fig. 1 plots the relative densities against sintering temperature for all the compositions. Calculating of the relative densities was based on the theoretical of 6.08 (3Y-TZP), 3.98 (Al₂O₃), 4.25 (TiO₂), 5.026 (MnO₂) and 2.579 g/cm³ (CAS glass), respectively. According to the CaO-Al₂O₃-SiO₂ and TiO₂-MnO phase diagrams, the melting point was 1170°C for CAS glass,

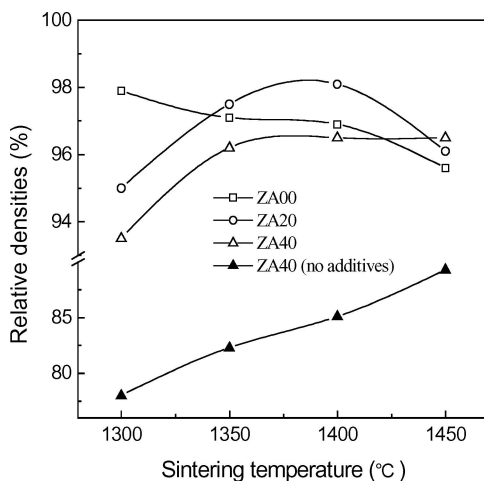


Figure 1 Relative densities versus sintering temperatures for 3Y-TZP/Al₂O₃ composites by liquid phase sintering.

and TiO₂-MnO₂ (1:1 in wt%) had a melting point of 1320°C.

The densification of the composites was greatly improved by the addition of TiO₂-MnO₂ and CAS glass. When sintering was carried out between 1300 and 1450°C, the relative density of ZA40 was much higher than that of ZA40a (no additives). A value of 98% of theoretical was obtained for ZA00 at a temperature as low as 1300°C. ZA20 and ZA40 also reached 98 and 96.5% of theoretical at 1400°C.

The content of Al₂O₃ in the composition had significant influence on the densification. In the range of 1300 to 1450°C, density of ZA00 decreased with sintering temperature, maximum density was obtained at 1300°C. However, maximum densities could only be achieved at 1400°C for ZA20 and ZA40. This result suggests that the composite was more difficult to densify when the Al₂O₃ content increased, which was consistent with the previous research [22, 23].

Fig. 2 shows the microstructure of the composites sintered at 1400°C with the addition of TiO₂-MnO₂ and CAS glass. The dark and bright contrasts in the scanning electron micrographs were Al₂O₃ and ZrO₂ grains, respectively. The mean Al₂O₃ grain size, which increased with the Al₂O₃ content in the composition, was below 1 μm for all samples. Most of the ZrO₂ grains were below 0.5 μm except a few larger grains which exceeded 1 μm. Compared with that by solid state sintering [22, 24, 25], the smaller grain sizes for Al₂O₃ and ZrO₂ were generally considered to be the result of lower sintering temperature by liquid phase sintering.

The SAD and EDS analysis for larger ZrO₂ grains are given in Fig. 3. Small amount of TiO₂ dissolved into the larger ZrO₂ grains, which could act as a stabilizing agent in a similar manner to Y₂O₃ [26]. It was difficult to conclude the larger grains were tetragonal or cubic just from the SAD and EDS patterns, because tetragonal (113) and cubic (310) had the same diffraction exponents. But the XRD analysis revealed the existent of cubic according to Garvie's method [27], which is shown in Fig. 4.

Formation of cubic ZrO₂ was the result of the phase partitioning in the composite. Phase partitioning, namely that Y₂O₃ was not evenly distributed in ZrO₂ grains, was often observed in Y-TZP materials [28, 29]. The grain growth of ZrO₂ strongly depended on the content of Y₂O₃. As a result, the Y₂O₃-poor tetragonal ZrO₂ and the Y₂O₃-rich cubic ZrO₂ had different grain sizes. Cubic ZrO₂ usually had larger grain size. Different explanations still existed about the mechanism leading to phase partitioning in Y-TZP materials [30, 31]. Arguments focused on whether the phase partitioning was caused by grain boundary phase or not. In present research, XRD analysis was also performed for 3Y-TZP/Al₂O₃ composites by solid state sintering at 1400°C, no cubic diffraction peak was observed. It suggests that phase partitioning could be correlated with the grain boundary phase in Y-TZP materials.

Fig. 5 reveals the composition of the amorphous phase located in grain junctions, which contained Al₂O₃, SiO₂, CaO and MnO₂. TiO₂ was below the

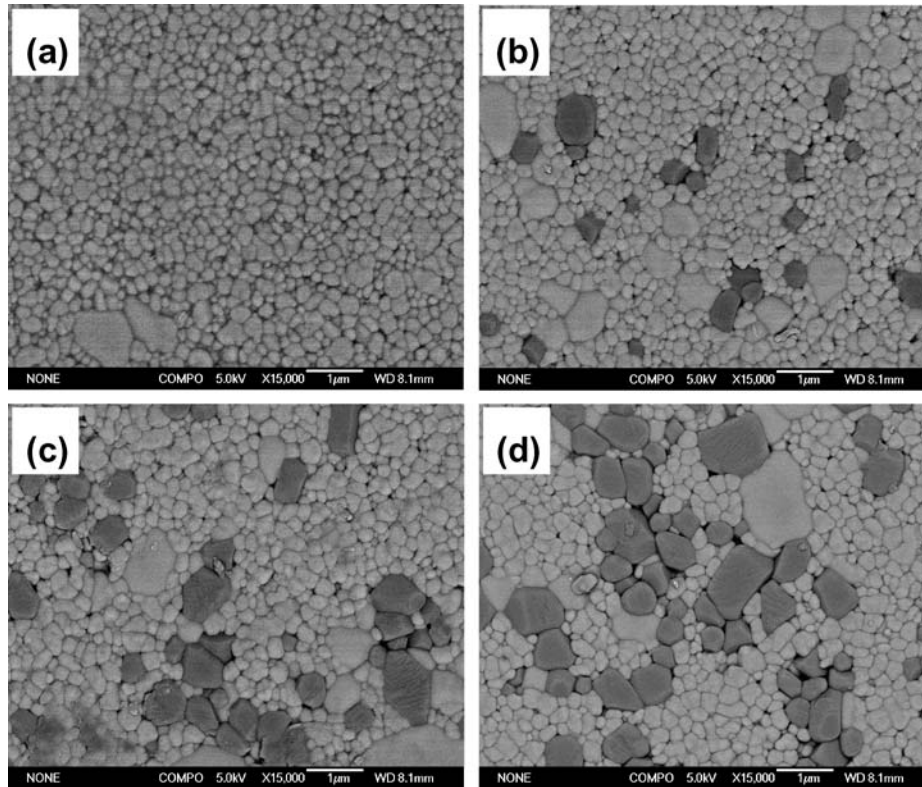


Figure 2 SEM micrographs of 3Y-TZP/ Al_2O_3 composites fabricated by liquid phase sintering at 1400°C : (a) ZA00, (b) ZA10, (c) ZA20, and (d) ZA30.

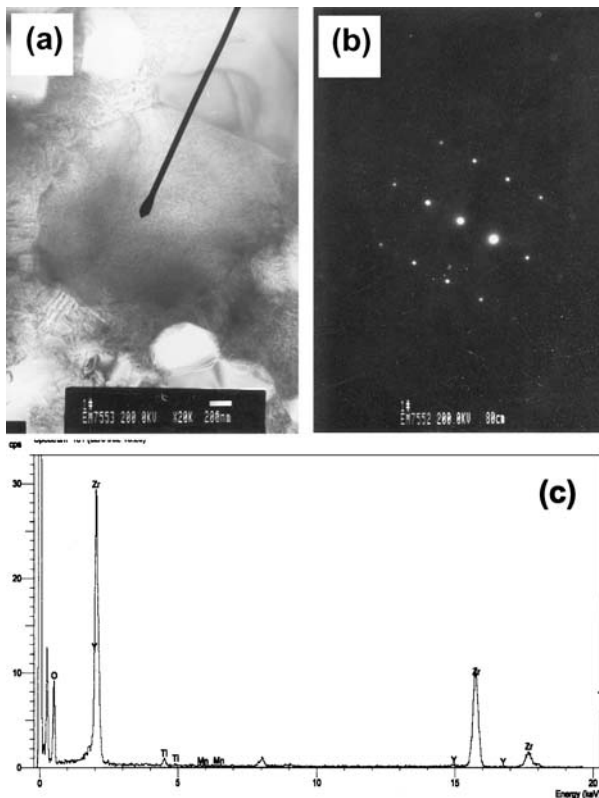


Figure 3 SAD and EDS analysis for larger ZrO_2 grains. (a) and (b) SAD, (c) EDS.

detection limit because it had a solution in ZrO_2 grains. ZrO_2 was also detected in the grain junctions, which came from the dissolve of ZrO_2 grain in the liquid phase, but the influence was not excluded by adjacent ZrO_2 grains to the diffraction.

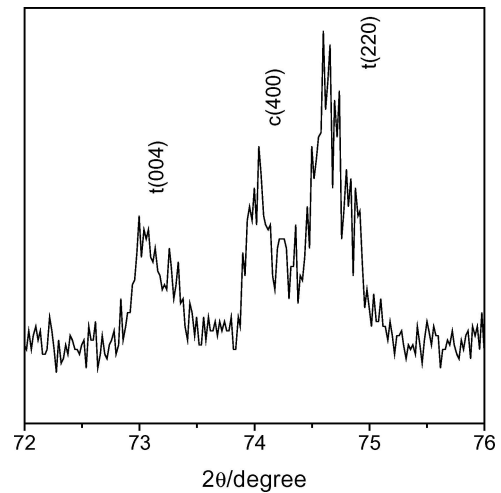


Figure 4 XRD analysis showing cubic ZrO_2 reflection for ZA40 sample sintered at 1400°C .

Measurement of the monoclinic ZrO_2 fraction was performed on the polished surfaces by XRD. Table II summarizes the monoclinic fraction for all samples by liquid phase sintering at 1400°C . Only small amount of monoclinic ZrO_2 was observed in the composites. Fig. 6 shows the XRD pattern for ZA20 sintered at different temperatures. Lower monoclinic fraction was observed when sintered between 1300 – 1400°C . However, a value as high as 35.5% of monoclinic was observed when sintered at 1450°C because of the excessive grain growth. It was well established that the tetragonal \rightarrow monoclinic transformation was correlated with the grain size of ZrO_2 . Tetragonal ZrO_2 would transform to monoclinic ZrO_2 spontaneously if it exceeded

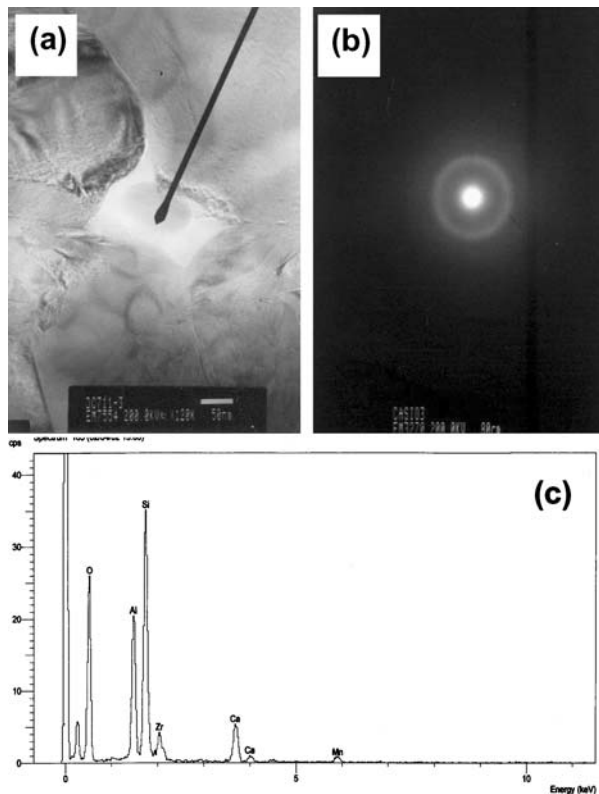


Figure 5 SAD and EDS analysis for grain boundary phase. (a) and (b) SAD, (c) EDS.

the critical grain size. The critical grain size in 3Y-TZP/Al₂O₃ composites was 0.4–0.8 μm which varied somewhat with the powder characteristics, preparation and measurement methods [21]. Lower sintering

TABLE II XRD analysis for 3Y-TZP/Al₂O₃ composites by liquid phase sintering at 1400°C

Samples	Sintering temperature (°C)	Fraction of m-ZrO ₂ on polished surface (%)
ZA00	1400	4.2
ZA10		5.2
ZA20		6.8
ZA30		5.6
ZA40		9.2

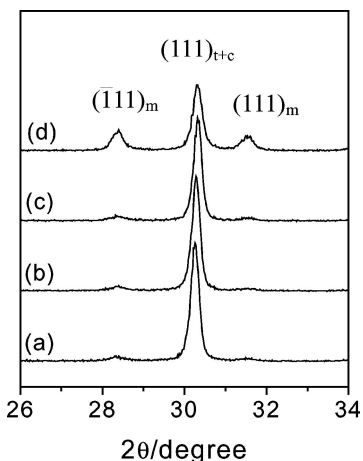


Figure 6 XRD patterns for ZA20 samples sintered at different temperatures: (a) 1300°C, (b) 1350°C, (c) 1400°C, and (d) 1450°C.

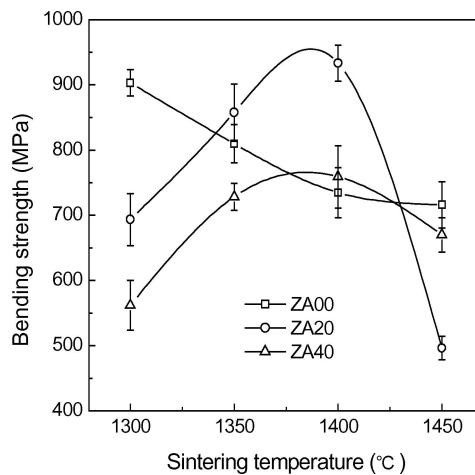


Figure 7 Bending strength as function of sintering temperature for 3Y-TZP/Al₂O₃ composites by liquid phase sintering.

temperature resulted in smaller ZrO₂ grain size, which was beneficial to the retention of tetragonal ZrO₂ at room temperature.

Bending strength of the composites was plotted as a function of sintering temperature, which is shown in Fig. 7. In the range of 1300 to 1450°C, Strength for ZA00 decreased with the sintering temperature. A maximum strength of 903 ± 20 MPa was obtained when sintered at 1300°C. Relative densities could be a good explanation for this result. ZA00 reached its maximum density at 1300°C (see Fig. 1). Beyond 1300°C, a reduction in density occurred due to the formation and evolution of gaseous species caused by pore coarsening, as evinced by bloating and blistering in some of the materials. As a result, the strength decreased when sintering was carried out at higher temperatures. Maximum strength for ZA20 (934 ± 28 MPa) and ZA40 (759 ± 48 MPa) were obtained when sintered at 1400°C.

Fracture toughness of the composites was plotted against sintering temperature in Fig. 8. All samples reached their maximum toughness when sintered at 1400°C. A value of 7.82 ± 0.19 MPam^{1/2} was obtained for ZA20. When the sintering temperature raised to 1450°C, monoclinic ZrO₂ fraction increased drastically, and the toughness decreased. This result suggests

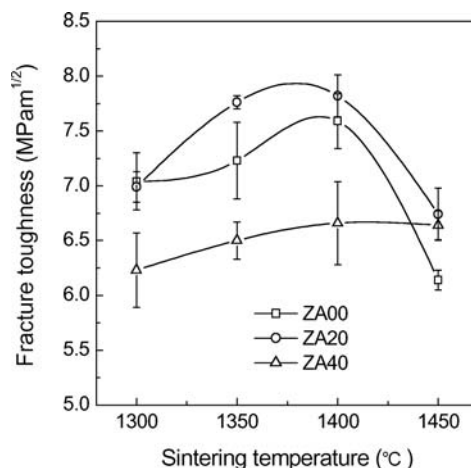


Figure 8 Fracture toughness as a function of sintering temperature for 3Y-TZP/Al₂O₃ composites by liquid phase sintering.

that the main contribution to toughness was tetragonal → monoclinic transformation toughness.

4. Conclusions

1. 3Y-TZP/Al₂O₃ composites were densified by pressureless sintering at a temperature as low as 1400°C with the addition of small amount of TiO₂-MnO₂ and CaO-Al₂O₃-SiO₂ glass.

2. Compared with solid state sintering, liquid phase sintering led to smaller grain sizes (<1 μm) for both Al₂O₃ and ZrO₂ grains because of the lower sintering temperature. A few larger cubic ZrO₂ grains were also observed only in the samples by liquid phase sintering, which suggests that the phase partitioning of Y₂O₃ was correlated with the grain boundary liquid phase.

3. Lower sintering temperature was beneficial to the retention of tetragonal ZrO₂ phase at room temperature, and higher mechanical properties were also achieved. Bending Strength of 934 ± 28 MPa and fracture toughness of 7.82 ± 0.19 MPam^{1/2} were obtained for 3Y-TZP/Al₂O₃ (20 vol%) composite when sintered at 1400°C. The results indicate that liquid phase sintering has a potential advantage in the fabrication cost and room temperature mechanical properties.

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