Control of microstructure on multiphase ceramic composites

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Zirconia-toughened alumina (ZTA) ceramics have been studied because of their excellent mechanical properties. By mixing ZrO_2 and Al_2O_3 phases, which have limited solid solubility, the growth of each phase is inhibited. In particular, dual interpenetrating microstructure can be expected in the pure zirconia-alumina composites that have the same volume percentage [1]. Furthermore, it is anticipated that multicomponent ceramic composites, which have small grain size, can be formed due to grain growth retardation by second and third phases [2]. The new multicompositions lead to formation of multiphase composite systems, where some phases were faceted shapes [3, 4]. This improved mechanical properties due to interlocking of grain or lead to textured (or seeded) microstructures.

In this study, three- and four-component composites (Al_2O_3-ZrO_2-Y_2O_3, Al_2O_3-ZrO_2-CeO_2, Al_2O_3-ZrO_2-Y_2O_3-SrO and Al_2O_3-ZrO_2-CeO_2-SrO) are made by chemical solution processing route involving polyethylene glycol polymer as an organic carrier [5–12]. The polymer surrounds and covers the cations or sol particles, which decreases their mobility and constrains the system to reduce premature agglomeration [13, 14]. On the basis of these dual phase composites, which have ZrO_2 and Al_2O_3 in 1:1 mole ratio, multiphase composites which have three or four phases are fabricated, and the novel microstructures and their mechanical behavior are examined.

The transparent precursor sols were prepared from zirconium 2,4-pentanedionate ($Zr(C_5H_7O_2)_4$), which is a source of zirconium, and metal salts of nitrate form (aluminum nitrate, cerium nitrate, yttrium nitrate and strontium nitrate) for other metal sources in proportions of several mole ratios. After dissolving these reagents in ethyl alcohol, the organic carrier, PEG (of M.W.: 2000) was added, and the mixtures were stirred and heated up to 100 °C. The amount of PEG was calculated using a ratio of the total weight of metal ions from cation sources to weight of PEG. In this study, 1:3 ratio was used [12]. As the viscosity increased with the evaporation of ethyl alcohol, the sol turned to a syrup-like gel. Subsequently, a vigorous exothermic reaction occurred which, with continuous heating, converted the gel into an expanded, porous solid. Finally, the porous precursors were calcined at 800 °C for 2 hrs

TABLE I Observed phases and average grain sizes of two- and three-component composites, pressureless sintered at 1500 °C for 1 hr

Components	Mole ratio	Observed phases	Avg. grain size (μm)
Al_2O_3:ZrO_2:Y_2O_3	1:1:0.5	t-ZrO_2, YAG	0.4
Al_2O_3:ZrO_2:CeO_2	1:1:0.5	t-ZrO_2, Al_2O_3, CeO_2	0.7
Al_2O_3:ZrO_2	1:1	Al_2O_3, t-ZrO_2, m-ZrO_2	0.8

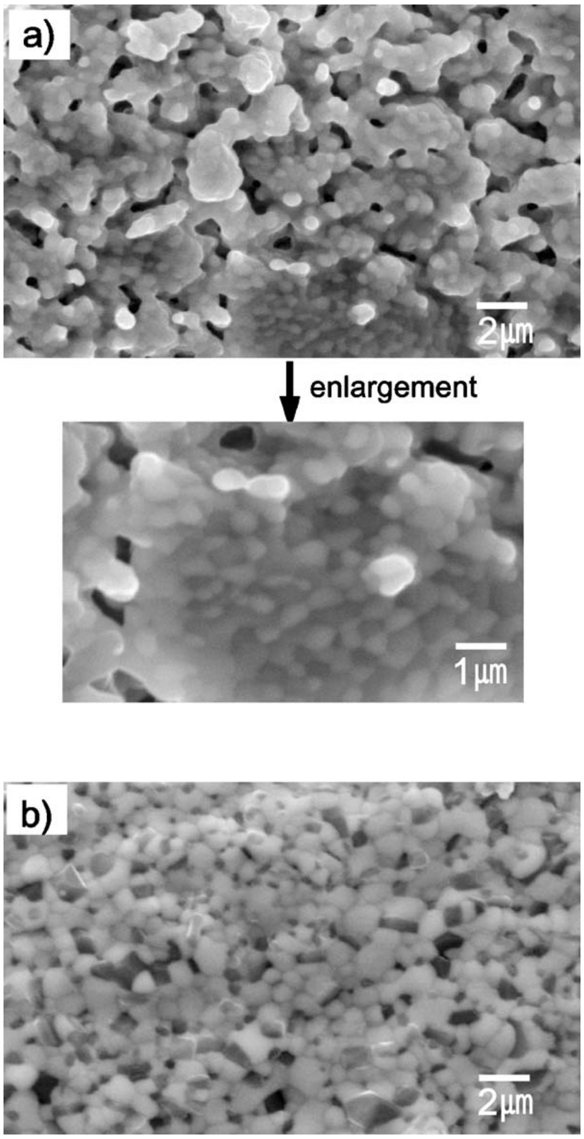

Figure 1 SEM micrographs of sintered (a) Al_2O_3-ZrO_2-Y_2O_3 and (b) Al_2O_3-ZrO_2-CeO_2 composites at 1:1:0.5 mole ratio.

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and then subjected to attrition milling at 240 rpm for 5 hrs with zirconia (3Y-TZP) balls as the milling media. The calcined and attrition-milled powders were uniaxially pressed at 10 MPa. The pellet-shaped green compacts were sintered in an air atmosphere at 1500 °C for 1 hr.

The final phases present in the sintered composites were determined with an X-ray diffractometer (Dmax automated powder diffractometer, Rigaku/USA, Danvers, MA) using Cu K_α radiation (40 kV, 40 mA). The measurements were made with a scanning speed of 10 °C/min and a sampling interval of 0.02 °C at room temperature. The surface microstructures of the sintered pellets were examined by scanning electron microscopy (SEM, Hitachi S530, Hitachi, Japan). The specimens were mounted on an aluminum stub and Au-Pd sputtered on 15 mA for 40 s. The average grain sizes of sintered microstructures were analyzed according to the Jeffries-Saltykov method [15]. Flexural strength was measured by a three point bending test using a 20.0 ± 0.1 mm support span, at a crosshead speed of 0.1 mm/min, using an universal testing machine (model 4502, Instron Corp., Canton, MA). Flexural bars of dimensions 30 mm × 4 mm × 3 mm were surface polished using #1200 SiC paper. Vickers indenter (model 4204, Buehler, USA) was also used for measurement of fracture toughness.

Table I presents observed final phases and average grain sizes of two- and three-component systems. In the ZrO_2-Al_2O_3 composite, m-ZrO_2 and t-ZrO_2 coexisted with α-Al_2O_3 phase, showing an average grain size of 0.8 μm. In the Al_2O_3-ZrO_2-Y_2O_3 system, zirconia existed only as tetragonal phase and a new phase of YAG was observed. In the 1:1:0.5 mixing ratio, the grain size was smaller than that of the zirconia-alumina, 1:1 mole ratio composite. In the Al_2O_3-ZrO_2-CeO_2 system, obvious three phases of t-ZrO_2, Al_2O_3 and CeO_2 were observed at the 1:1:0.5 mole ratio. In the composite, the microstructure showed an average grain size of 0.7 μm. Fig. 1 shows the SEM micrographs of the sintered Al_2O_3-ZrO_2-Y_2O_3 and Al_2O_3-ZrO_2-CeO_2 composites. The smallest grain size was

TABLE II Observed phases and average grain sizes of four-component composites, pressureless sintered at 1500 °C for 1 hr at different mole ratio

Components	Mole ratio	Observed phases	Avg. grain size (μm)
Al_2O_3:ZrO_2:Y_2O_3:SrO	1:1:0.5:0.2	t-ZrO_2, SrO, (YAG), (SrY_2O_4)	0.5
	1:1:0.5:0.4	t-ZrO_2, SrO, (YAG), SrY_2O_4	0.4
Al_2O_3:ZrO_2:CeO_2:SrO	1:1:0.5:0.2	t-ZrO_2, CeO_2, SrO, $SrAl_{12}O_{19}$	0.4
	1:1:0.5:0.4	t-ZrO_2, CeO_2, SrO, ($SrAl_{12}O_{19}$)	0.5
	1:1:0.5:0.6	t-ZrO_2, CeO_2, SrO	0.5

( ): minor phase.

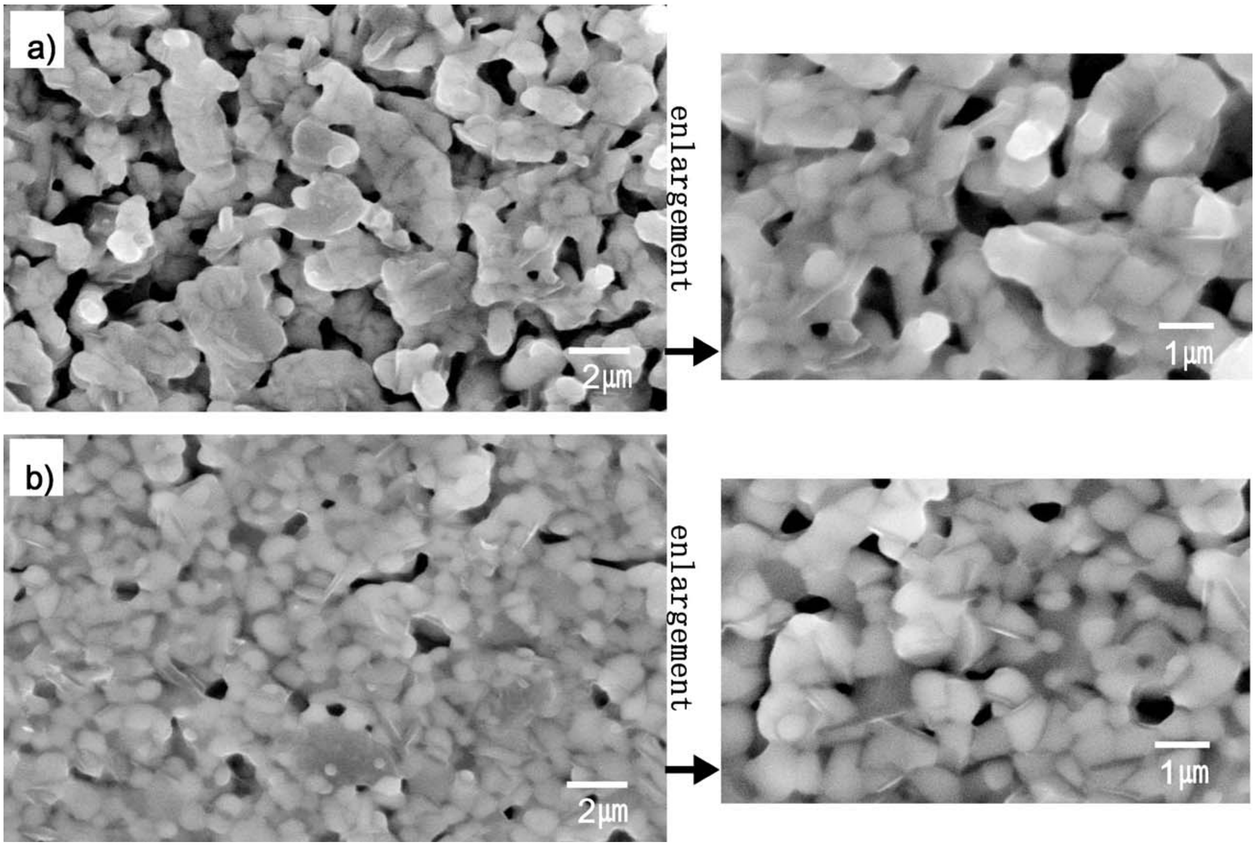

Figure 2 SEM micrographs of sintered Al_2O_3-ZrO_2-Y_2O_3-SrO composites at (a) 1:1:0.5:0.2 and (b) 1:1:0.5:0.4 mole ratio.

observed in the 1:1:0.5 mole ratio of Al_2O_3-ZrO_2-Y_2O_3 composite.

Table II lists observed final phases and average grain sizes of four-component composites. SrO was added to each system for the four-component systems. In the Al_2O_3-ZrO_2-Y_2O_3-SrO system, four phases were observed. However, YAG phase, which was a major phase in the three-component composite, was minor and new phases of SrO and SrY_2O_4 were observed. Fig. 2 shows the SEM micrographs of the sintered Al_2O_3-ZrO_2-Y_2O_3-SrO composites. The grains had no change in size in comparison with the microstructure of three-component composites. However, some needle-like particles were newly observed as the SrO content increased. It may be speculated that the needle-like phase was SrY_2O_4 as a result of phase development. In the Al_2O_3-ZrO_2-CeO_2-SrO system, four obvious phases were observed in the 1:1:0.5:0.2 mole ratio. And the $SrAl_{12}O_{19}$ phase was gradually decreased as the SrO content increased. Fig. 3 shows the SEM micrographs of the sintered Al_2O_3-ZrO_2-CeO_2-SrO composites. The grain sizes were more decreased in comparison with the three-component composites. It means that the effect of grain growth retardation worked in the multiphase system consisted of Al_2O_3-ZrO_2-CeO_2-SrO. In particular, needle-like particles were also observed in the 1:1:0.5:0.2 mole ratio. As the SrO content increased, the $SrAl_{12}O_{19}$ phase gradually disappeared with decreasing needle-like grains. From the result, the needle-shape phase should be $SrAl_{12}O_{19}$.

The results of the mechanical test for the Al_2O_3-ZrO_2-CeO_2-SrO composites as a function of SrO content are listed in Table III. The highest flexural strength and fracture toughness were observed in the 1:1:0.5:0.2 ratio. The four-component composites had almost the same grains in size, however, the composite of 1:1:0.5:0.2 ratio showed more improved mechanical behavior than the other two cases. It can be speculated that the needle-shape phase, $SrAl_{12}O_{19}$, had an influence on the increase of strength and toughness. The four-component composites showed almost two times higher strength in comparison with the three-component composite. It is certain that the improved strengh is due to the decreased grain size by grain growth retardation in the multiphase composite.

TABLE III Mechanical behavior of Al_2O_3-ZrO_2-CeO_2-SrO composites, pressureless sintered at 1500 °C for 1 hr at different mole ratio

Mole ratio	Flexural strength (MPa)	Fracture toughness (MPa·$m^{1/2}$)
1:1:0.5:0.2	490	6.99
1:1:0.5:0.4	383	5.58
1:1:0.5:0.6	358	5.11
cf) Al_2O_3:ZrO_2:0.5CeO_2	270	4.41

Finally, Al_2O_3-ZrO_2-Y_2O_3-SrO and Al_2O_3-ZrO_2-CeO_2-SrO compositions made multiphase composites, in which grain growth was inhibited by the constraint effect. Some phases were faceted shapes, and needle-like grains were observed in the composites involving SrO. The new textured microstructures showed improved mechanical properties.

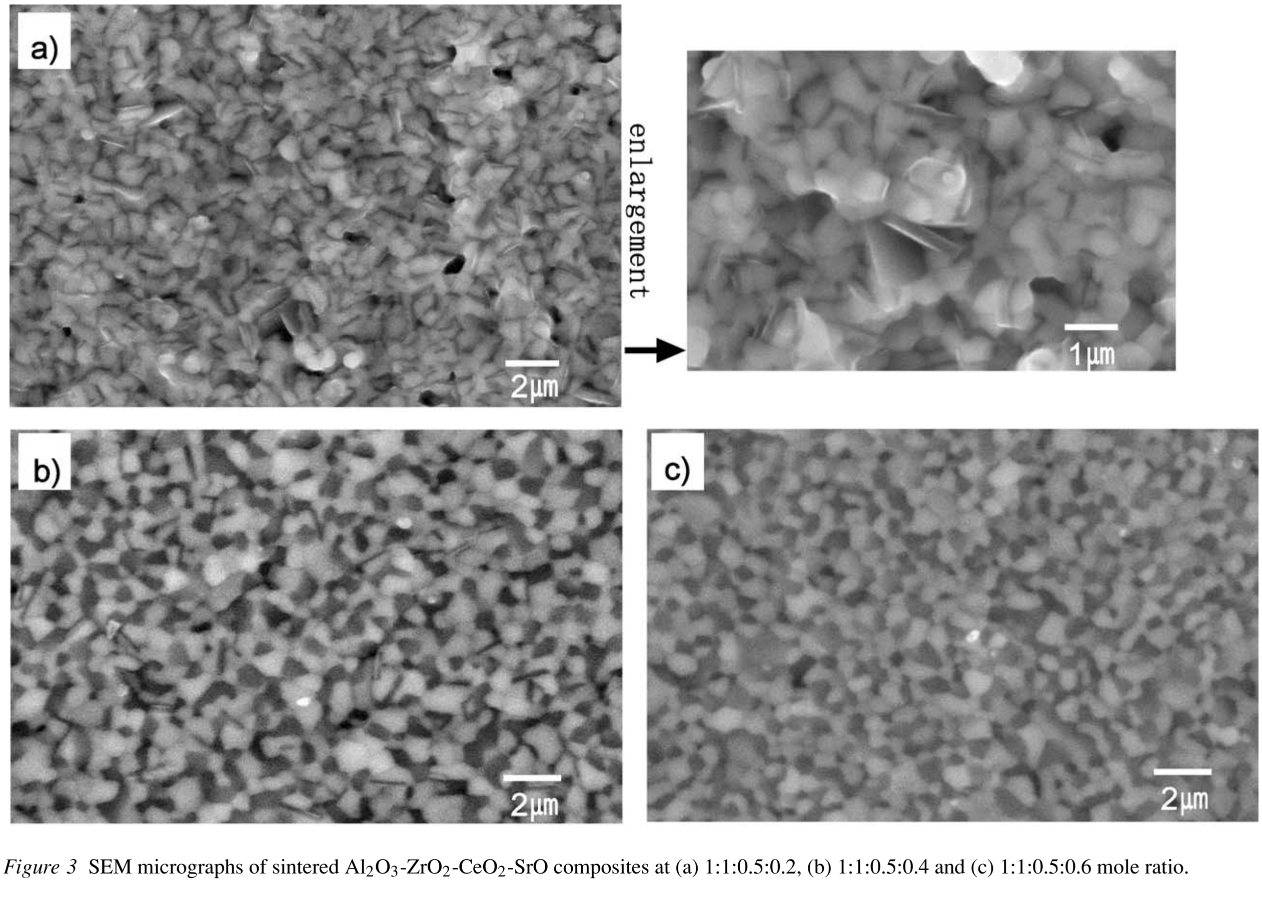

Figure 3 SEM micrographs of sintered Al_2O_3-ZrO_2-CeO_2-SrO composites at (a) 1:1:0.5:0.2, (b) 1:1:0.5:0.4 and (c) 1:1:0.5:0.6 mole ratio.

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