Hardness and Fracture Toughness of Alumina-Based Particulate Composites with Zirconia and Strontia Additives

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Abstract

This project aims to study characteristics and mechanical properties i.e. hardness and fracture toughness of alumina matrix composite materials containing zirconia and strontium oxide. Two groups of composite specimen were fabricated: (i) Al_2O_3 matrix with 3 mol% Y_2O_3- ZrO_2, varied from 10, 20, 30 and 40 vol%, and (ii) Al_2O_3 matrix with 2, 5, 10 and 15 vol% SrO added in the form of $SrCO_3$. The powders were blended and then pressed into pellets. The compacts were pressureless sintered at 1600 $^{\circ}$C for 2 hours in air. Density measurement of the sintered composites was carried out using liquid immersion. Hardness and fracture toughness were carried out using the Vickers indentation. Microstructure was observed using scanning electron microscopy and phase content was detected by mean of X- ray diffraction. The Al_2O_3 containing ZrO_2 forms finer alumina grains along with phase transformation, leading to higher toughness. Meanwhile, the Al_2O_3 containing SrO forms elongated grains, enhancing toughness due to crack deflection. Then, the blend between Al_2O_3-ZrO_2-SrO composites was assumed whether a combination of them both may improve the mechanical properties. It was found that an addition of SrO and ZrO_2 in the same Al_2O_3 matrix could not provide better hardness, but could improve fracture toughness compared to the two-component composites.

Introduction

Alumina is one of the ceramic materials that have been successfully used in structural applications due to several desirable properties, e.g. high mechanical strength, thermal stability, excellent corrosion and wear resistance. However, its poor fracture toughness or brittleness is still the main issue. There are many ways to overcome such weakness, including making it as composite materials. The reinforcement in alumina can be particulates, whiskers, short and long fibers, which provide several approaches to enhance fracture toughness, i.e. particle strengthening, phase transformation and crack deflection. These mechanisms can incorporate and promote superior mechanical properties. The commonly and widely used particulate reinforcement in alumina matrix is zirconia. The mechanical properties significantly depend on the tetragonal-to-monoclinic transformation, according to service conditions such as temperature or applied loads. Therefore, zirconia needs dopants like yttria or ceria in order to stabilize tetragonal phase at room temperature, which could later turn to monoclinic, and provide volume expansion along with compressive strain in the structure. Moreover, fine zirconia particles inhibit crack propagation of the matrix during sintering that promotes fracture toughness for a certain extent, as reported elsewhere [1-2, 6]. In fact, not only zirconia, any particles can offer toughening by inhibiting abnormal grain growth. Particles can be in the forms of both isotropic and anisotropic grains, such as rod-like or platelet. Apart from isotropic phase, elongated grains of alkali earth hexaluminates comprising alumina and alkali earth oxides, like calcia strontia, are of interest.

There are many methods to prepare such alkali earth hexaluminates, including solid state reaction and sol-gel techniques. As far as a sintering technique is concerned, the plate-like calcium or strontium hexaluminates could be obtained from a mixture of 1 mol of calcia or strontia and 6 mol of alumina and sintered at the temperatures up to 1600°C.[3-4] However, a difficulty to synthesize

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using high temperatures is still a problem. Lower sintering temperatures could be possible when some sintering aids are used, which the chemical stability as well as mechanical properties could be affected form glassy phase at grain boundaries.[7] Additionally, the properties and morphology of the platelets may sensitively alter with impurities attached in the starting powders and tend to have grain growth along with poor density.[5-6] Alternatively, sol-gel process can offer higher quality fine hexaluminate powders even the starting precursors, catalyst and process parameters need to be strictly controlled.[8-9]

There have been many studies reporting the ability to improve strength in alumina matrix as a presence of the hexaluminate phases.[5-10] Cutler et al.(1991) demonstrated that an addition of strontia in the form of $SrZrO_3$ into Ce-TZP/Al_2O_3 composites provided higher flexural strength and fracture toughness. The finding agreed with studies done by Maschio et al.(1999) which also presented superior toughness in Al_2O_3-Cr_2O_3/ZrO_2 composites with a small amount of strontia additive. Schmid et al.(1999) proposed that a new preparation route of hexaluminate reinforced toughened alumina from a reaction between $Ca(NO_3)_2$, $Sr(NO_3)_2$ and $Al(NO_3)_3$ and the enhanced properties was similarly introduced. Thus, it is possible to combine zirconia and strontium hexaluminate in alumina matrix in order to get toughened alumina-based composites.

This work focuses on the characteristics of alumina, particularly a change in hardness and fracture toughness, as a function of zirconia and the in situ strontium hexaluminate. The alumina-based composites were prepared from conventional powder processing straightforward. Zirconia was deliberately added into the in situ mixture of strontia and alumina which the strontium hexaluminates was obtained from solid state sintering. Vickers indentation technique was employed in order to evaluate hardness and toughness of the composites.

Materials and Experimental Procedures

The experimental works were divided into three main parts: (1) alumina-strontia (2) alumina-zirconia and (3) alumina-strontia-zirconia systems. Three Lab-grade starting powders were employed. Alumina powder (Al_2O_3, AES-11, Sumitomo, Japan) was used as a matrix material while 98% purity strontium carbonate ($SrCO_3$, Sigma-Aldrich Inc., USA) and 3 mol% yttria-stabilized zirconia (Y_2O_3-ZrO_2, TZ-3YSB, TOSOH Cooperation,

Japan) were used as additives using a 5wt% PVA solution as a binder. The first parts covered the formation of strontium hexaluminates in alumina matrix composites. Strontia, in the form of carbonate compounds, was added into alumina from 0, 2, 5, 10 and 15 vol%. In the second part, the mixture contained yttria-zirconia from 0, 10, 20, 30 to 40 vol%. No sintering aids were employed in these powder mixtures. The powder mixtures were separately wet-mixed in ethanol using alumina balls, dried and screened. The dried blend was unidirectionally pressed into pellets at 30 MPa. Then, the pellets were sintered at 1600°C for 2 hours in an air atmosphere. Phase content was analyzed by X-ray diffractometry. Density of the sintered pellets was measured using liquid immersion technique whereas relative density values were determined based on the theoretical densities of the sintered products, i.e., 3.97 g cm^{-3} for Al_2O_3, 3.95 g cm^{-3} for $SrAl_{12}O_{19}$ and 6.15 g cm^{-3} for zirconia. Theoretical density of the composites was obtained from the rule of mixture. Volume fraction of each constituent phase in the sintered composites was semi-quantitatively estimated from the strongest XRD peaks and compared to the calculation of stoichiometry, assuming the complete reaction of the hexaluminate was achieved. Microstructure observation was also carried out using scanning electron microscopy. The polished surfaces were thermally etched at 1500 °C for 20 minutes. Hardness and fracture toughness of the composites were measured by Vickers indentation and computed from equation 1 and 2, respectively.[12-13]

$$H_V = 1.8544 \left(\frac{P}{(\overline{d})^2} \right) \tag{1}$$

$$K_C = 0.0726 \left(\frac{P}{(\overline{c})^{3/2}} \right) \tag{2}$$

Then, the best three formulations of each part compromising both hardness and fracture toughness were ranked and combined, on the basis of the same alumina content. The effective properties as a combination of strontia and zirconia in alumina matrix were evaluated and discussed. Where H_V and K_C stand for Vickers' hardness and fracture toughness, respectively. The P is an applied load in kgf (10 kg) over the as-polished surface for 15 seconds while $\overline{d}$ and $\overline{c}$ represent the mean length of diagonal and the mean crack length of the indented marks, in unit of mm.

Results and Discussion

Alumina-Strontia System

According to XRD pattern shown in Figure 1, corundum (alumina), strontium hexaluminate ($SrAl_{12}O_{19}$) in the samples containing SrO from 2 to 10vol%. It was also found strontium dialuminate ($SrAl_2O_4$) with both phases mentioned earlier in the composition of 15vol% SrO. From the phase diagram of alumina-strontia system (Vishista et al., 2009), the stoichiometric strontium hexaluminate can be occurred when the ratio of alumina to strontia is 1:6 by mol. The volume contents of strontium hexaluminate were approximately 15.3, 37.3 and 82.8% in the composites with 2, 5 and 10vol% SrO, respectively. There were very few amount of alumina existed in the composites with 15vol% SrO. The amount of the hexaluminate phase strongly affected the density of the sintered samples, that is, it reduced density. This was caused by the decomposition of carbonate while sintering. Carbon dioxide gas is emitted from strontium carbonate and some gas pores are trapped in the structure. The production of carbon dioxide depends on the amount of the carbonate and tends to give porous structure, according to up to 8% loss of ignition. The generation of strontium hexaluminate compound is also accompanied by volume expansion.

Figure 2 displays a series of backscattered electron micrographs of the composites showing the morphology of alumina and the hexaluminate. Alumina grains were comparatively isotropic while the hexaluminate grains were needle-like. Hardness and fracture toughness of the composite reflected the effects of the hexaluminate. Hardness massively reduced with increasing strontia content while there was a variation in fracture toughness, it slightly increased until 5vol% SrO and then continuously decreased. This can be explained by their structures. A drop in hardness was as a result of porous microstructure generated by a formation of the hexaluminate. A Fformation of the phase was always accompanied by poor density. In contrast, fracture toughness of the systems rose in the samples of 2 and 5vol% SrO. This was possibly come from optimum strontium hexaluminate phase. Anisotropic grains of the hexaluminates in alumina deflected crack propagation direction along grain boundaries. However, in the sample with 10vol% SrO or more, the fraction of the hexaluminate phase was expected to rise, along with volume expansion and CO_2 decomposition which led to porosity. Once the microstructure become porous, the resistance against the applied load was poorer but such those pores and cracks due to volume expansion and gas removal could obstruct the crack propagation. When the crack tips meet other crack lines or pores, stress concentration around the tips was released and could stop crack growth. Therefore, the amount of needle-like hexaluminate grains, pores and volume expansion should have to be compromised.
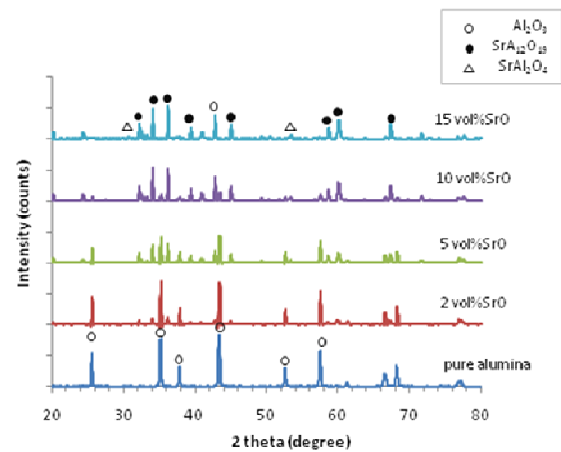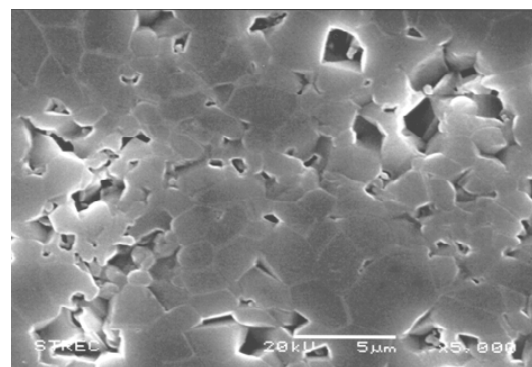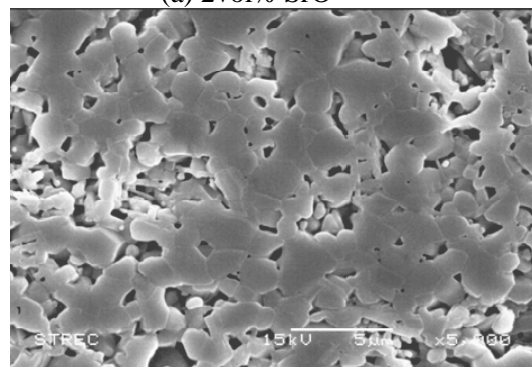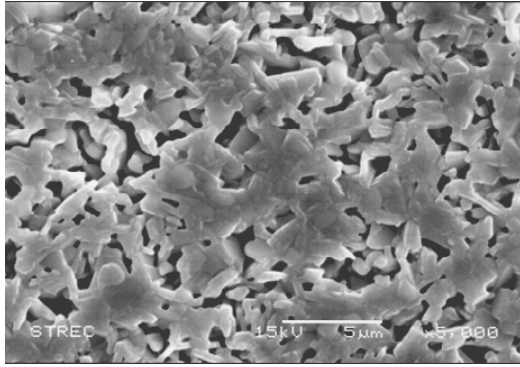

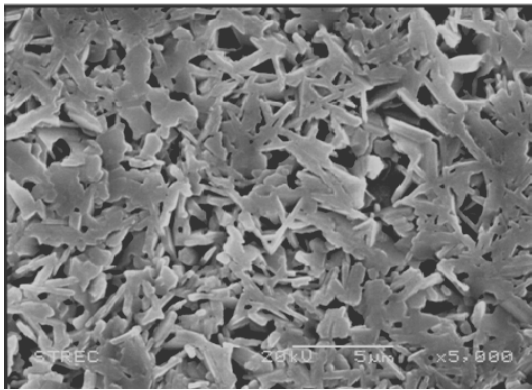**Figure 1.** XRD patterns of alumina and strontia system sintered at 1600°C.

(a) 2vol% SrO

(b) 5vol% SrO

(c) 10vol% SrO

(d) 15vol% SrO

Figure 2. Backscattered electron micrographs of alumina and strontium hexaluminate phases.

Alumina-Zirconia

There were three phases found in all of samples sintered at 1600°C, i.e., corundum, tetragonal and monoclinic zirconia, as shown in Figure 3. It was shown that no reactions between alumina and the zirconia. Tetragonal phase was still partially occupied in alumina due to yttria, which inhibits phase transformation to monoclinic when cooling down. A presence of zirconia resulted in a continuous increase in density and denser structure. This can be described in the term of the density of each component. The density of zirconia is around 6.15 g cm^{-3} whereas that of alumina is 3.97 g cm^{-3}, therefore the effective density values of the alumina-zirconia rise with increasing zirconia content. For the microstructure, Figure 4 illustrates finer alumina grains compared to that of the monolithic alumina. Zirconia had quite small grain of 0.5 micron, approximately. When being accompanied with alumina, evenly distributed fine zirconia grains acted as grain refiner and led to smaller alumina grains, which was possibly enhanced mechanical properties, particularly fracture toughness. As far as hardness and fracture toughness were concerned, it can be seen that both values altered in opposite manner. Hardness of the composites slightly dropped but fracture toughness obviously improved. Partially stabilized zirconia can enhance toughness via phase transformation mechanism. Once the cracks travels, the stress concentration at crack tips can change zirconia from tetragonal to monoclinic. The phase change resulted in volume expansion around the crack tip and neighbouring grains become in compression and impede crack propagation. To overcome such compressive stress, more energy is required to make cracks move further. A combination of grain reduction and phase transformation could toughen alumina matrix.

Table 1. Density, hardness and toughness of the derived composites.

| Chemical composition	Density (g cm^{-3})	Relative density	LOI (%)	Hardness (GPa)	Toughness (MPa m$^{1/2}$)
Pure alumina	3.85 ± 0.02	1	1.46 ± 0.01	15.67 ± 0.74	3.10 ± 0.19
2 vol% SrO	3.47 ± 0.01	0.87	2.48 ± 0.02	10.02 ± 0.58	3.70 ± 0.33
5 vol% SrO	2.86 ± 0.03	0.72	3.69 ± 0.15	3.47 ± 0.21	3.57 ± 0.39
10 vol% SrO	2.30 ± 0.01	0.58	5.16 ± 0.03	0.87 ± 0.08	1.55 ± 0.16
15 vol% SrO	2.36 ± 0.02	0.59	8.34 ± 0.03	1.03 ± 0.03	1.54 ± 0.15
10 vol% ZrO$_2$	4.07 ± 0.01	0.97	-	16.21 ± 0.39	3.50 ± 0.28
20 vol% ZrO$_2$	4.28 ± 0.01	0.97	-	15.95 ± 0.69	3.70 ± 0.33
30 vol% ZrO$_2$	4.49 ± 0.01	0.96	-	15.60 ± 0.41	4.24 ± 0.34
40 vol% ZrO$_2$	4.60 ± 0.41	0.95	-	15.17 ± 0.38	4.55 ± 0.13
Pure zirconia	5.97 ± 0.03	1	-	12.28 ± 0.09	5.08 ± 0.55
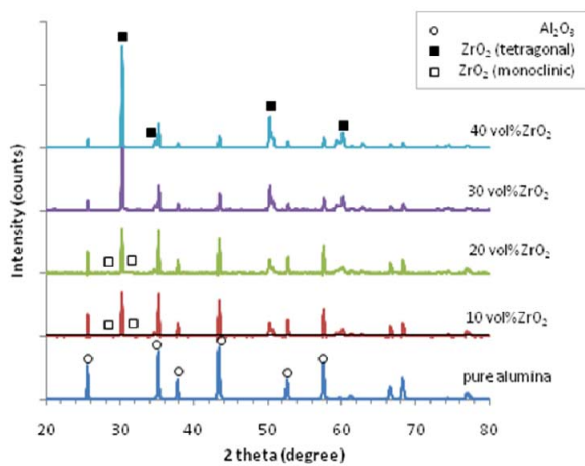
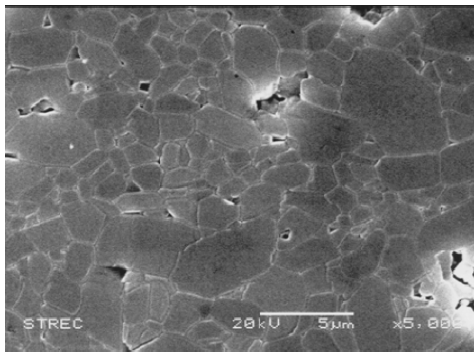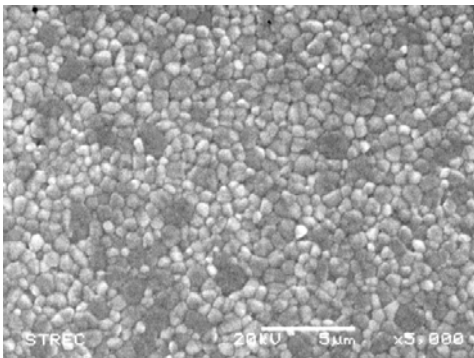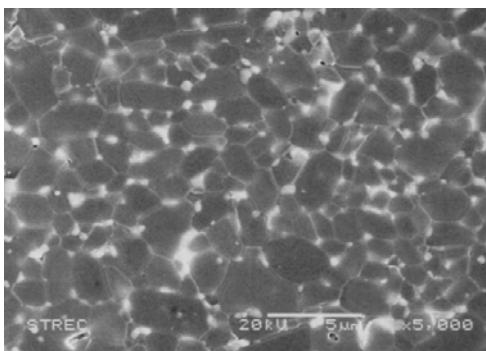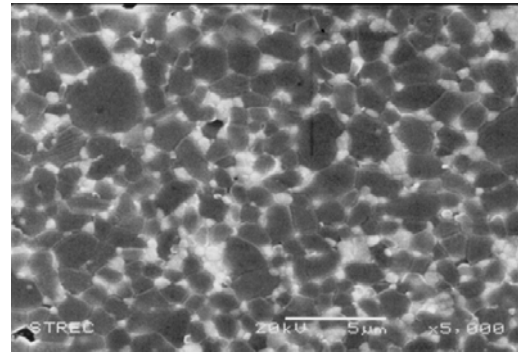**Figure 3**. XRD patterns of alumina and zirconia system sintered at 1600°C.
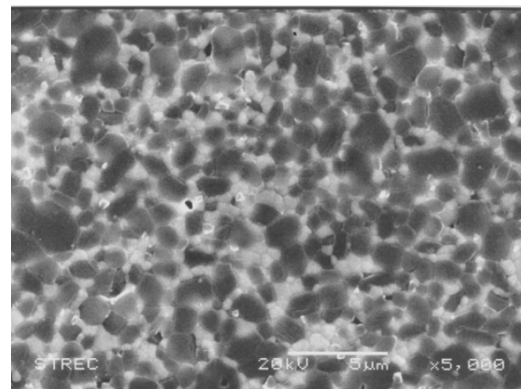

(a) pure alumina
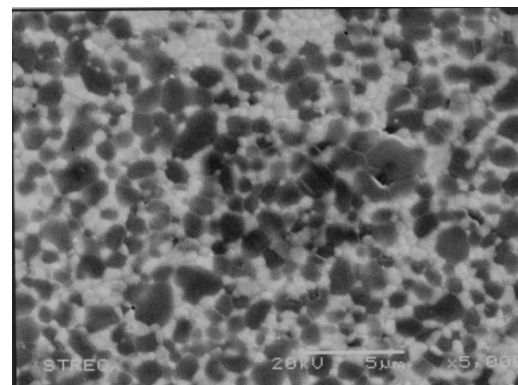

(b) pure zirconia

(c) 10vol% ZrO_2

(d) 20vol% ZrO_2

(e) 30vol% ZrO_2

(f) 40vol% ZrO_2

Figure 4. Backscattered electron micrographs of the zirconia-toughened alumina at various zirconia contents.

Alumina-Strontia-Zirconia

According to the experimental results reported previously, the data from both alumina-containing binary systems providing the best selected hardness and fracture toughness as well as other characteristics could be ranked. Using fracture toughness as a criterion, from highest to lowest, they were grouped as follows:

Group (I)   alumina with 40vol% zirconia (A40Z)
                    and alumina with 2vol% strontia (A2S)

Group (II) alumina with 30vol% zirconia (A30Z)
and alumina with 5vol% strontia (A5S)
Group (III) alumina with 20vol% zirconia (A20Z)
and alumina with 15vol% strontia (A15S)

In order to investigate characteristics of the three-component systems as a function of a combination of zirconia and strontium hexaluminate, all mixtures needed reformulation on the basis on alumina content. It meant that amount of the additives were applied relative to the amount of alumina matrix, not to the whole volume of powder mixtures. It was noted that the values of relative density, hardness and fracture toughness of the samples with 10 and 15vol% SrO were comparatively close, so they were assumed to be similar.

Phase composition of each mixture in Figure 5 shows alumina, zirconia and both of strontium aluminate compounds as expected. The density values of the three groups increased with increasing zirconia and decreasing strontia content. This related to the dense microstructure illustrating in Figure 6. Microstructure of the samples in group(I) and group(II) had less pores compared to that of the group(III) which contained higher pore fraction together with the needle-like phase could be obviously noticed. As far as the mechanical properties of these groups were concerned, a combination of zirconia and strontia additives offered an improvement of fracture toughness even hardness values fell in between their original blends, as shown in Figure 7. All effective hardness of the grouped samples were enhanced relative to its alumina-strontia mixture and tended to alter dominantly with strontia content. This resulted from the modified density and microstructure. The availability of 40 vol% zirconia provided higher density and fine alumina grains meanwhile the formation of strontium hexaluminate occurred from only 2vol% strontia, in other words, it came from very small amount of strontium carbonate. The reaction between alumina and strontia did not disturb the whole structure. When the amount of strontia added into the mixture increased, more porous microstructure was obtained even zirconia was available. As for the fracture toughness, it was shown that the toughness was enhanced by the two additives. This may be caused by phase transformation from zirconia and crack deflection for strontium hexaluminate toughened the materials. However, it was noted that the improved fracture toughness was possibly related to small amount of porosity attached in microstructure, which could end crack propagation.
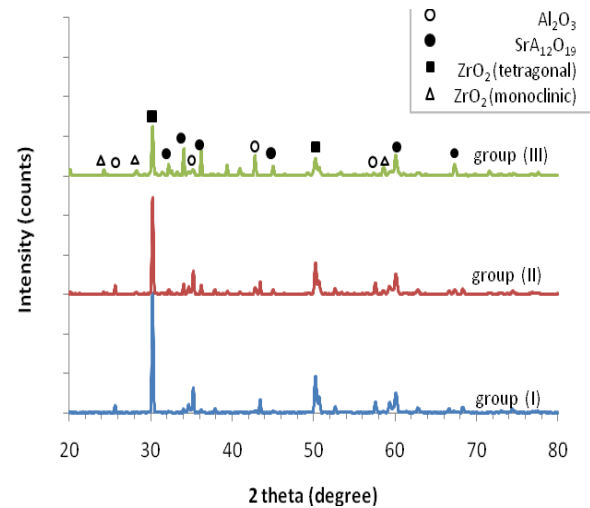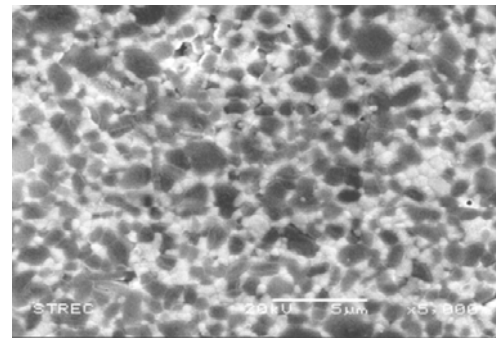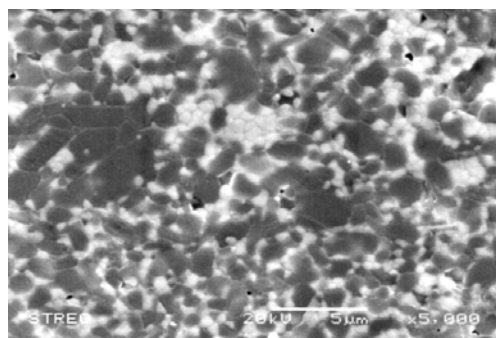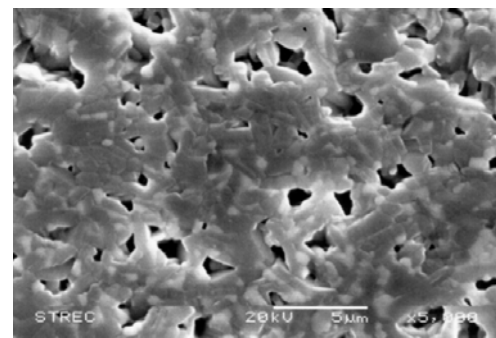

Figure 5. XRD patterns of alumina and zirconia system sintered at 1600°C.

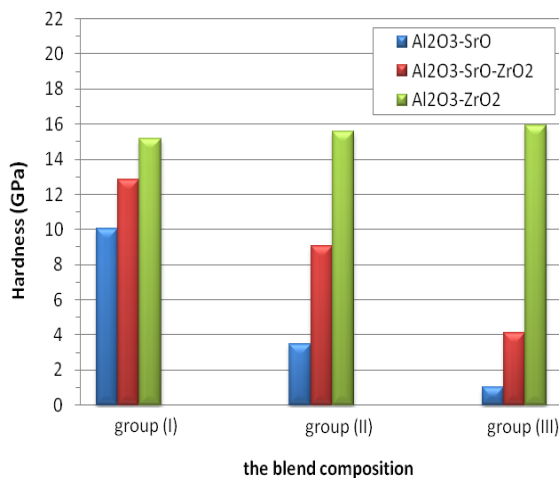
(a) group I (40 vol% ZrO_2 and 2 vol% SrO)

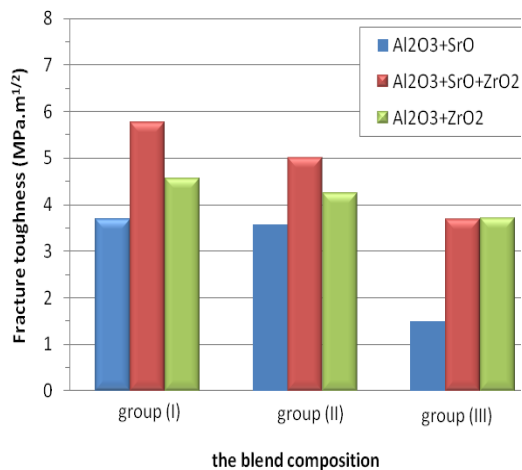(b) group II (30 vol% ZrO_2 and 5 vol% SrO)

(c) group III (20 vol% ZrO_2 and 15 vol% SrO)

Figure 6. Backscattered electron micrographs of the toughened alumina with zirconia and hexaluminates.

(a) hardness

(b) fracture toughness

Figure 7. A comparison of (a) hardness and (b) fracture toughness of the blend determined from Vickers indentation method.

Conclusions

A variation in hardness and fracture toughness of alumina as a presence of partially stabilized zirconia and strontium aluminate compounds has been focused. Zirconia mainly toughens alumina matrix and reduces alumina grain size while the hexaluminate phase, derived from the in situ mixture of alumina and strontium carbonate via solid state reaction, provides needle-like phase accompanied by porosity. The availability of both additives offers an improvement in fracture toughness but not for hardness. They both are likely to be able to enhance fracture toughness due to a combination of phase transformation from zirconia and crack deflection caused by anisotropic hexaluminate grains if the microstructure contains less pore content. Dense structures of alumina with zirconia and hexaluminate phase are to be further investigated.

Acknowledgements

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