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Microstructural development and mechanical properties of self-reinforced alumina with CAS addition

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Abstract

In-situ development of platelike alumina grains were obtained by adding CAS glass powder ($CaO–Al_2O_3–SiO_2$) into fine alpha alumina powder sintered in the range from 1550 to 1600°C. The sintering behavior, microstructural development and mechanical properties of self-reinforced alumina ceramics with different amount of additives were investigated. The theoretical densities of the samples sintered at 1550°C reached >97% which appeared to be the optimal sintering temperature and the addition of CAS slightly decreased the densities of samples sintered from 1300 to 1600°C, compared with the samples without CAS additive. The platelike grains were not formed in alumina ceramics without adding CAS, even sintered at 1600°C. When the 0.1∼0.5 wt.% CAS glass powder was added to the starting composition, the platelike grains were formed completely at 1550°C. The formation of platelike grains increased the fracture toughness but decreased the bending strength, the combined action of crack deflection and crack bridging accounted for the observed increase of fracture toughness. The mechanical properties decreased with increasing the sintering temperatures from 1550 to 1660°C. Adding nano γ-Al_2O_3 can enhance the mechanical properties of the samples sintered at 1550 and 1600°C.

Keywords: Al_2O_3; Grain growth; In-situ composite; Microstructure-final; Platelets

1. Introduction

Alumina is the most widely used oxide ceramic as industrial materials because of its high hardness and corrosion resistance, good oxidation resistance and chemical stability. Furthermore, its thermal expansion coefficient is nearer to those of metals than nitrogen ceramics, so it is also an excellent candidate for cermets. Nevertheless, the applications, of Al_2O_3 as structural ceramics are limited due to the low fracture toughness and poor thermal-shock resistance. In order to improve mechanical properties, whiskers, fibers and platelets are dispersed in the alumina matrix because of that they can promote crack defection and grain bridging.[1–3] But incorporation of high-aspect-ratio particles by powder processing leads to the formation of transient stresses during sintering, resulting in densification to be reduced.[4] Therefore, advanced processing techniques such as colloidal processing, hot pressing or isostatic pressing, are required to make the composites to achieve high density and good mechanical properties.[5–7] Moreover, processing and handling of whiskers is associated with severe health hazards. So the relatively high fabricating costs and health hazards have led to a search for alternative fabrication routines. In-situ formation of the elongated grains during sintering is an encouraging concept for high-toughness composites and may represent a comparatively low-cost processing alternative.

A variety of oxides such as MgO, CaO, SiO_2, TiO_2 or Fe_2O_3 are the typical additives that have been commonly used in alumina based ceramics. The presence of small quantities of CaO and SiO_2, which have been often found in the grain boundaries, can affect sintering behavior and play a decisive role in triggering the anisotropic grain growth of alumina in final stage sintering, because at sintering the $CaO–Al_2O_3–SiO_2$ liquid phase can make the distribution of grain boundary-grain boundary dihedral angles wide and make the grains grew discontinuously.[8] So the addition of CaO and SiO_2 creates favorably kinetic conditions for anisotropic grain growth during sintering. About anisotropic grain

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growth, several possible reasons and mechanisms have been proposed for explaining for that, including a wide initial particle size distribution, anisotropic surface energies, twinning, preferential grain boundary mobility, segregation of dopants on specific crystallographic planes, heterogeneous density distribution and others.[9,10]

We have investigated the in-situ formation of elongated Al_2O_3 grains in Al_2O_3 ceramics by adding small amount CAS glass powder and found that CAS glass powder is effective additive for promoting the elongated grains growth. The microstructure features are developed via in-situ formation of platelike grains after densification is first completed and then self-reinforced ceramics can be obtained without the sintering difficulty. This paper describes the process and control of microstructure through in-situ formation of elongated grains with the addition of CAS glass powder and also the relationship between microstructure and mechanical properties.

2. Experimental procedure

2.1. Preparation of CAS glass powder

The calcium aluminosilicate (CAS) glass powder was prepared by milling a mixture of 47.4 wt.% $CaCO_3$, 28.5 wt.% SiO_2 and 24.1 wt.% Al_2O_3 for 24 h, then melting at 1500°C for 6 h and quenching it in cold water. The transparent glass was crushed in a mortar and reduced to <1mm, afterwards milled for 72 h with 5mm diameter high purity Al_2O_3 balls and sieved using a 120 mesh screen. Water was used as the milling dispersant medium for preventing crystallizing. The specific surface area of the CAS glass powder, measured by the BET (Micromeritics Tristar 3000 analyzer) method, is about 2.82 m^2/g and the powder was also characterized by X-ray diffraction (D/max-radiffractometer, Japan) to ensure that it was amorphous. The particle size distribution of CAS glass powder was analyzed using a Mastersizer 2000 Ver. analyzer, with $d_{50}=2.6$ μm, as shown in Fig. 1.

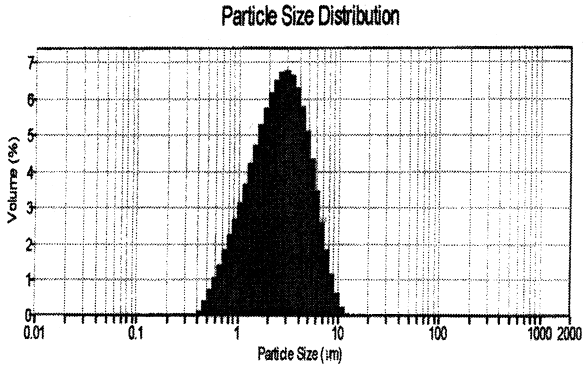

Fig. 1. The particle distribution of CAS glass powder.

2.2. Materials processing

High purity commercial α-Al_2O_3, γ-Al_2O_3 and CAS glass powder were used as the starting powders. The chemical analyses (ICP) are shown in Table 1. The α-Al_2O_3 powder was a monomodal particle size distribution with $d_{50}=2.2$ μm. Table 2 shows the starting nominal compositions for six different materials. The mixed powders were ball-milled in ethanol for 24 h with high-purity Al_2O_3 mediums, then dried and sieved through a 120 mesh screen. After adding PVA and sieving through 40 mesh screen, the mixed powders were uniaxially pressed at 100 MPa and cold isostatically pressed at 250 MPa. The green density of the samples after compactation was 54% of the theoretical density and had no distinct difference with the glass addition. The green compacts were placed in an alumina crucible covered with alumina powder and sintered at 1300, 1400, 1500, 1550 and 1600°C for 3 h in air. The heating rate was 3°C/min and furnace cooling.

2.3. Characterization of materials

Bulk density was measured by the Archimedes method. The sintered samples were polished and chemically etched in boiling 0.3N H_3PO_4 for 3–5 min and/or thermally etched for 10 min at 300°C lower than sintering temperatures. The etched surface was examined by scanning electron microscopy (SEM) (EPMA-8705QHz) to investigate the Al_2O_3 grain size with a lineal intercept method[11] and the distributions of silicon and calcium were analyzed by electron probe micro-analysis (EPMA). Test pieces with dimension of $5\times2.5\times25$ mm^3 for mechanical property measurements were sliced from the sintered specimens, three-point

Table 1
Chemical analyses of starting alumina powders

Starting powder	Element (ppm)						
	Ca	Si	Fe	Mg	Ti	Na	K
α-Al_2O_3	33	30	9	9	<5	–	–
γ-Al_2O_3	0.3	0.6	1.5	0.5	–	0.3	1

Table 2
Nominal compositions of materials

Sample	Composition (wt.%)		
	α-Al_2O_3	γ-Al_2O_3	CAS
A	100	0	0
B	99.9	0	0.1
C	99.5	0	0.5
D	99	1	0
E	98.9	1	0.1
F	98.5	1	0.5

flexural strength measurements were carried out with a span of 20 mm and a crosshead speed of 0.5 mm/min at room temperature by an Instron-1195 Universal Test Machine. Fracture toughness, K_{IC}, was determined using an indentation technique with a Vicker indenter (AKASHI) using 98N load. The formula used for calculating K_{IC} was expressed as $K_{IC} = A(E/H)^{1/2}(P/c^{2/3})$.[12] A minimum of six specimens was tested to obtained a signal datum.

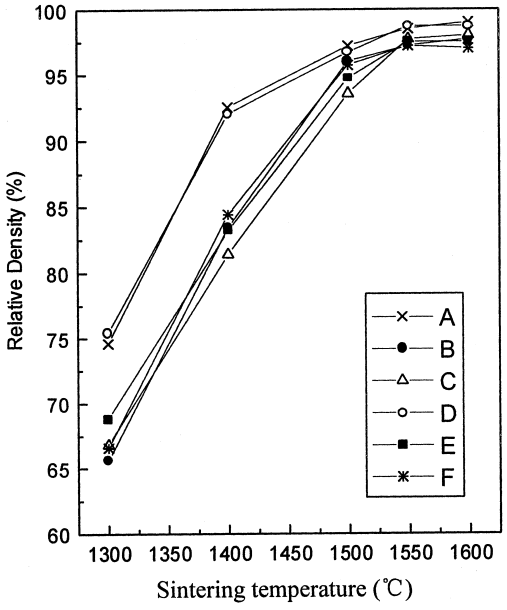

Fig. 2. The relationship of the relative densities and sintering temperatures of samples.

3. Results and discussion

3.1. Sintering characteristic

The percentage of the theoretical densities of the all samples sintered between 1300 and 1600°C are shown in Fig. 2. The sintered densities of the samples were found to be between 66 and 99% of the theoretical densities with significant difference at the sintering temperature from 1300 to 1600°C. The densities of the samples increased with increasing the sintering temperatures, expect for the samples D, E and F from 1550 to 1600°C. At 1300°C, the densification rate of the samples started to increase rapidly. The relative densities of the samples after sintering to 1550°C reached >97%, which appeared to be the optimal sintering temperature, since higher temperature did not increase the densities much. It can be seen from Fig. 2 that the relative densities of the samples without CAS additive were larger than that of the samples with CAS. This was thought to be due to that at low sintering temperatures the viscosity of the CAS liquid phase was too high and played a role as obstacles to densification. At high sintering temperatures

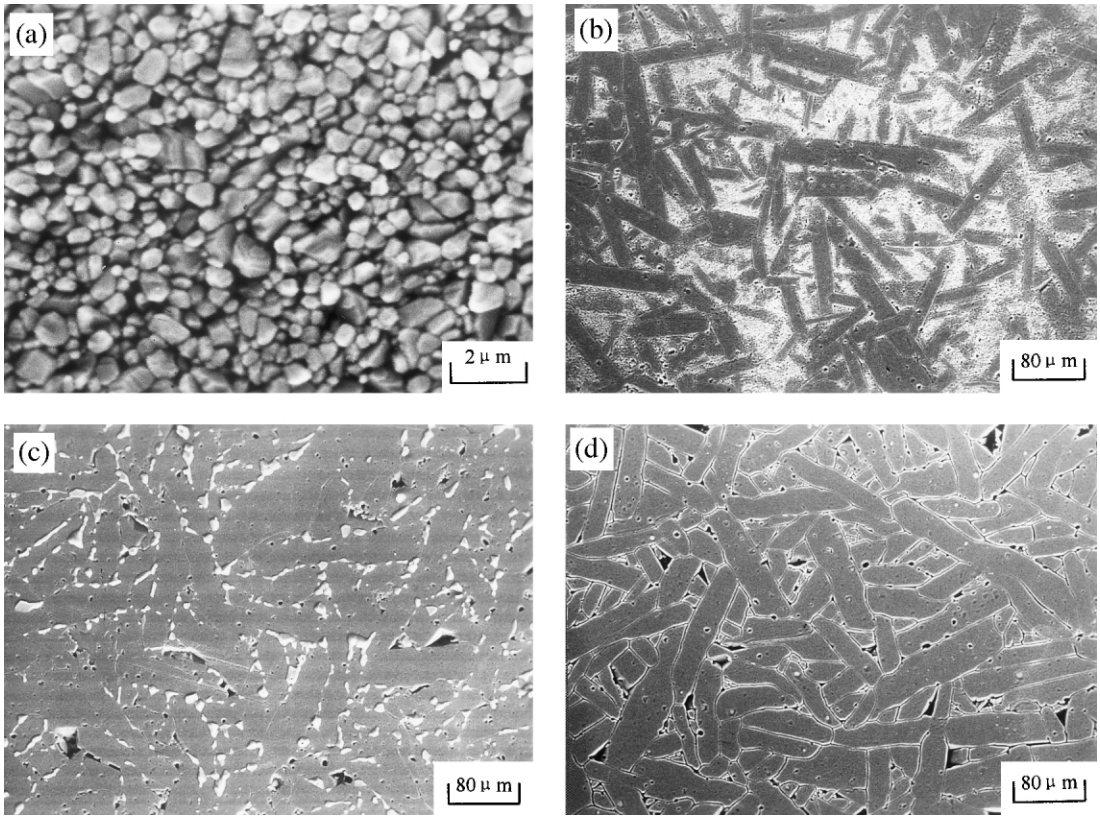

Fig. 3. SEM backscattered image micrographs of Al_2O_3 doped with 0.1 wt.% CAS sintered at: (a) 1400°C; (b) 1500°C; (c) 1550°C; (d) 1600°C.

the CAS liquid phase viscosity decreased and promoted anisotropic grain growth, some pores were retained between the grains or inside the grains. The grains of the samples without CAS additive were equiaxed, only a few pores were retained between grains and there were no significant difference between the densities of samples A and D.

3.2. Microstructure development

The microstructure development of the alumina with 0.1 wt.% of CAS glass powder sintered from 1400 to 1600°C for 3 h are shown in Fig. 3. At 1400°C, the microstructure showed equiaxed Al_2O_3 grains with average grain size of 1.5 μm. The platelike grains can be observed in the samples with 0.1 wt.% of CAS additive sintered at 1500°C, but there are only a few platelike grains in equiaxed fine Al_2O_3 matrix, the average length and width of platelike grains was about 150 and 25 μm respectively. At 1550°C, the grains all formed platelike grains with average length and width size of 250 and 50 μm, respectively, because the sintering temperatures can affect the grain size at the critical densities through the change in the ratio of densification to coarsening rate, the platelike grains can only grow in the regions where the local density reaches the critical density.[13] So the platelike grains, which were uniform in size, appeared quite suddenly when the compacts reached final densities. This is easy to understand since the platelike grain growth need mass transportation. It can be seen from the Figs. 3(c) and (d) and 4(b) and (d) that the CAS amount from 0.1 to 0.5 wt.% had no significant effect on the size of platelike grains, however the samples with 0.5 wt.% CAS have fewer pores than those with 0.1 wt.% CAS. It was due to that more liquid phase made the pores disappear easier. The samples almost have the same grain size sintered at 1550 and 1600°C. The temperatures seemed to have no influence on the microstructure of samples from 1550 to 1600°C, except for sample A which is more dense. The average grain size was about 5.5 μm at 1550°C and 5.8 μm at 1600°C, respectively, as shown in Fig. 4(a) and (c). According to the Al_2O_3–SiO_2–CaO phase diagram, the possible crystalline phases in equilibrium with Al_2O_3 in alumina ceramics with 0.1 or 0.5 wt.% CAS were $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$ and $2CaO{\cdot}Al_2O_3{\cdot}SiO_2$, but crystallization was thought to be very difficult due to the short cooling time.[14] Post-sintering annealing was usually needed to devitrity the glass and produce crystalline boundary phases, Bryoson et al.[15] pointed that even in this case, some residual glass phase remained and the presence of glass phase was expected ultimately to control both grain morphology and many mechanical properties of ceramics.

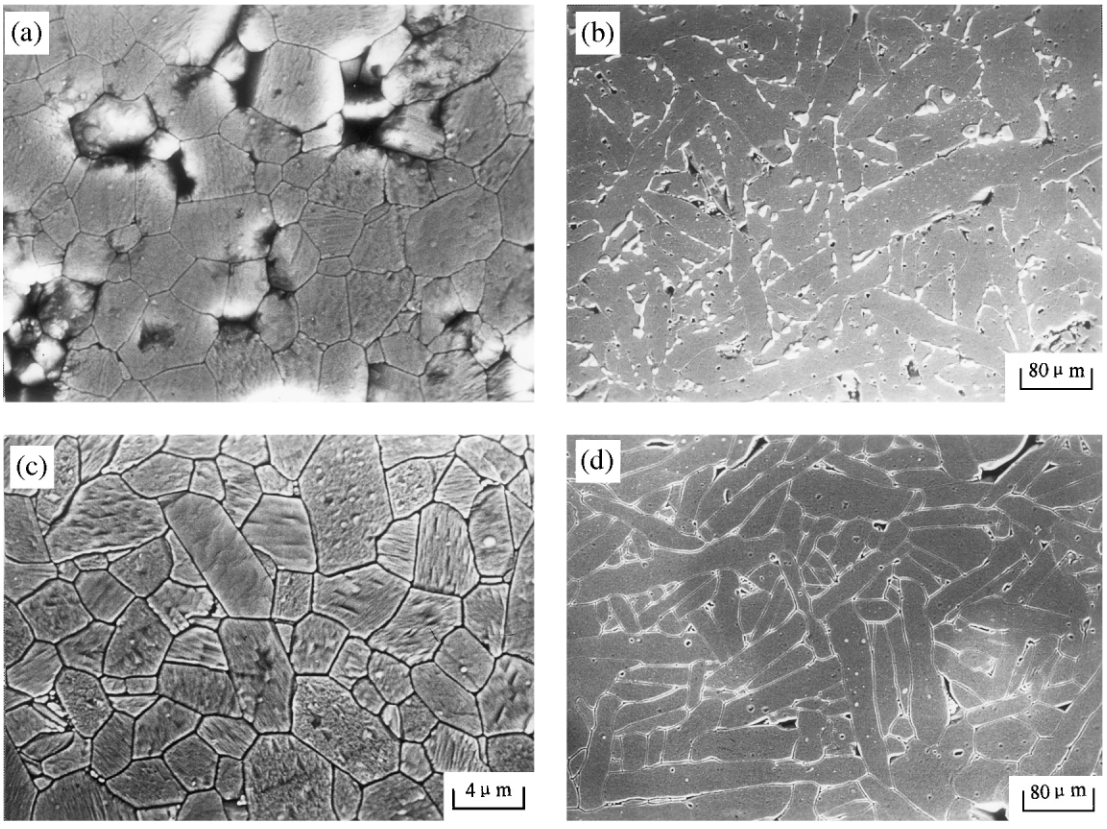

Fig. 4. SEM backscattered image micrographs of Al_2O_3 samples: (a) with 0 wt.% CAS sintered at 1550°C; (b) with 0.5 wt.% CAS sintered at 1550°C; (c) with 0 wt.% CAS sintered at l600°C; (d) with 0.5 wt.% CAS sintered at 1600°C.

Chou et al.[16] studied the formation of the [0001]-oriented α-Al_2O_3 from γ-Al_2O_3 films and found anisotropic grain growth of α-Al_2O_3 during phase transformation. However, in this experiment, only adding γ-Al_2O_3 cannot trigger the anisotropic grain growth and the average grain size was about 5.7 μm, as shown in Fig. 5, but CAS powder can, because it can form a liquid phase in grain boundaries at sintering temperatures and the formation of liquid phase along grain boundaries makes an interfacial energy difference between the basal planes and other planes, which makes the growth rate different and forms platelike grains.[17] In liquid sintering, the platelike grains can occur only in the condition that the grain growth is controlled by an interfacial reaction, not by a diffusion process. This happens because diffusion control will make the planes have enough time to absorb the dopants selectively and all planes will have the same interfacial energy and growth rate, generating an equiaxial grains microstructure.

The growth rate of grains, dG/dt, in the case where diffusion through the liquid layer or controlled by the surface reaction is rate limiting, may be expressed by Eqs. (1) and (2), respectively:[18]

$$\frac{dG}{dt} = \frac{2\vec{\gamma}vDc}{\delta RTr} \quad (1)$$

$$\frac{dG}{dt} = \frac{2\vec{\gamma}vk}{RTr} \quad (2)$$

where $\vec{\gamma}$ is the surface tension, v the molar volume of liquid phase, D diffusion coefficient, c the saturation solubility, δ the thickness of liquid layer, r the radius of matrix grains, k the reaction constant. Song et al.[13] estimated that the Al_2O_3 grain growth for long- and short-axis directions controlled by surface reaction rate should meet the necessary component diffusivity of the order of 10^{-8} and 10^{-9} cm^2/s in $CaO–Al_2O_3–SiO_2$ systems at 1650°C, respectively. In fact, the diffusivities of components in the systems are at least on the order of 10^{-6} cm^2/s at 1650°C. So it is considered that the grain growth of alumina with CAS liquid phase is controlled by an interfacial reaction. The interfacial reaction rate is expected to be different in the direction of both axes, because grain growth in the long-axis direction seems to occur by the continuous growth mechanism. However, the grain growth in short-axis direction would require the two-dimension nucleation mechanism.

It can be observed from Fig. 6 that the second phase spread along the Al_2O_3 grain boundary and made it easy to identify the elongated grains and to make out the distribution of elements Ca and Si by EPMA.

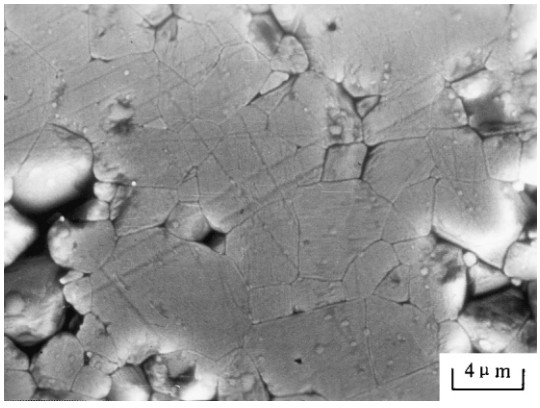

Fig. 5. SEM backscattered image micrograph of Al_2O_3 doped with 1 wt.% γ-Al_2O_3 sintered at 1550°C.

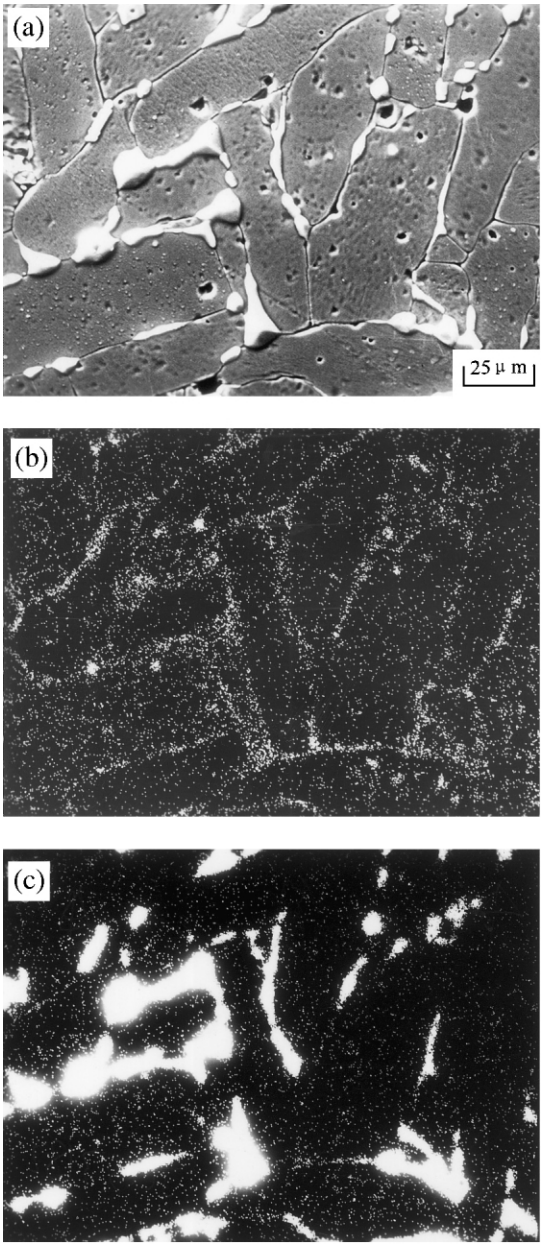

Fig. 6. EPMA of Al_2O_3 doped with 0.5 wt.% CAS: (a) SEM backscattered image micrograph; (b) the distribution of silicon; (c) the distribution of calcium.

Table 3
The bending strength and fracture toughness of samples sintered at 1550 and 1600°C

Sample		A	B	C	D	E	F
Bending strength (MPa)	1550°C	343±32	206±28	183±20	425± 18	248±25	218±46
	1600°C	338±25	201±40	180±30	359±22	249±35	213±27
Fracture toughness (MPa $m^{1/2}$)	1550°C	3.52±0.5	4.35±0.2	4.08±0.5	3.75±0.7	4.93±0.4	4.49±0.2
	1600°C	3.47±0.4	4.28±0.6	3.81±0.1	3.60±0.4	4.20±0.8	4.05±0.6

EPMA analysis revealed this phase mainly contained Ca and P, the existence of P was due to the reaction of H_3PO_4, which was used in chemical etching, with CAS liquid phase. A combined chemical and thermal etching procedure was used to achieve rapid etching with the minimum of surface microstructure alteration.[19] The distribution of Si was in the grain boundaries. It could be concluded that CAS liquid phase segregated in grain boundaries at sintering temperatures.

3.3. Mechanical properties

Table 3 summarizes the strength and fracture toughness of the samples sintered at 1550 and 1600°C. It can be seen from the table that samples A and D exhibit a relatively high strength and low fracture toughness and the others exhibit a relatively high fracture toughness and low strength. This was attributed to the effects of the CAS liquid phase and the elongated grains, which can result in crack deflection and crack bridging. The combined action of crack deflection and crack bridging took place with a significant increase in the toughness, microscopy observation of the self-reinforced alumina revealed that cracks deflected along the interface between elongated grains. The strength decreased when increasing the amount of CAS additive, but the fracture toughness increased first and then decreased when increasing the amount of CAS. It was considered that more CAS liquid phases in the grain boundaries had some effect on the mechanical properties. The samples, except for D, had almost the same strength, however the fracture toughness decreased slightly with increasing sintering temperatures from 1550 to 1600°C. It was difficult to explain the mechanism of the slight decrease in the fracture toughness definitely, the possibility was that the sintering temperatures had some effects on the grain boundary characteristic of the platelike grains. The samples A and D had lower mechanical properties sintered at 1600 than at 1550°C because at 1600°C recrystallization occurred and formed exaggerated platelike grains which affected the properties, as shown in Fig. 7. It was interesting that adding the nano γ-Al_2O_3 can enhance the fracture toughness and strength to some extent. This was thought to be due to that the nano γ-Al_2O_3 modified the characteristic of CAS liquid phase and improved the bond between alumina grains. The microstructure of the sample with 0.1 wt.% of CAS and 1 wt.% of γ-Al_2O_3 additives sintered at 1550°C is shown in Fig. 8, the average length and width of grains was 200 and 37 μm, respectively. However, in self-reinforced ceramics the existence of large elongated grains usually is associated with a decrease in strength, so the size and morphology of the elongated grains must be carefully controlled to optimize the strength and toughness. This requires attention to those parameters including interfacial structure and properties, reinforcement strength, morphology, size and mismatch between matrix and intergranular phases that control the toughening contribution.[20] In fact, when high strength is not needed but excellent thermal-shock resistance is needed, the

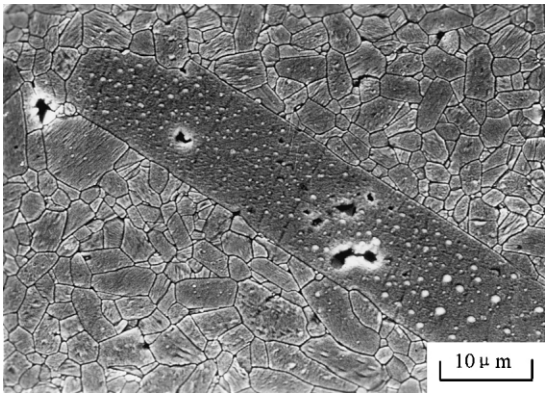

Fig. 7. SEM backscattered image micrograph of exaggerated platelike grain growth in sample A sintered at 1600°C.

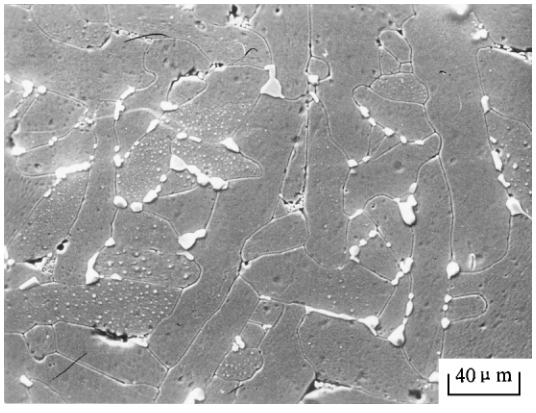

Fig. 8. SEM backscattered image micrograph of the sample with 0.1 wt.% CAS and 1 wt.% γ-Al_2O_3 additives sintered at 1550°C.

self-reinforced alumina ceramics could readily meet the service requirements.

4. Conclusion

Self-reinforced Al_2O_3 ceramics with high fracture toughness had been developed by adding CAS glass powder, which trigger the anisotropic grain growth. The results demonstrated that the necessary condition for platelike grain growth was the existence of liquid phase, which provided kinetic and thermodynamic conditions favorable to anisotropic grain growth. The theoretical densities of the samples sintered at 1550°C reached >97%. The temperature at which the platelike alumina grains were observed was about 1500°C. However, the platelike grains were formed completely at 1550°C. The platelike grains improved the fracture toughness and decreased the bending strength. The increase in toughness was ascribed principally to the combined action of crack deflection and crack bridging.

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