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Microstructure and Mechanical Properties of Mullite/Zirconia Composites Prepared from Alumina and Zircon under Various Firing Conditions

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Abstract

Zirconia-dispersed mullite composites were prepared by reaction sintering of alumina and zircon powders under various firing conditions. Mullite formed by firing at 1635°C apparently contained > 60 mol% Al_2O_3 and incorporated a small amount of zirconia. This transient mullite composition changed to the normal composition by treatments such as long firing time, annealing, two-step firing and/or seeding. Mullite/zirconia composites at room temperature showed good strength and fracture toughness, but these properties decreased significantly at high temperature because glassy phase in the grain boundaries. Mechanical strength at high temperature could be improved by those firing treatments which reduced the amount of glassy phase, especially by two-step firing and seeding methods.

1 Introduction

As a means to enhance the mechanical properties of mullite ceramics, mullite/zirconia composites have been investigated extensively by many workers.[1-5] Mullite/zirconia composites can be prepared via various methods: (1) sintering of mullite and zirconia, (2) reaction sintering of alumina and zircon, and (3) reaction sintering of alumina, silica and zirconia. We[6] prepared mullite/zirconia composites by these methods and found that composites prepared by method (2) had some unique characteristic features compared with those by the other methods, e.g. higher fracture toughness. We considered that the reason could be attributed to the characteristic microstructure.[6] We also found that the chemical composition of mullite formed in the route (2) composites was richer in alumina than the expected composition of 60 mol%. The reason for these characteristic features of the composites are not clear yet.

In this work, we prepared mullite/zirconia composites from reaction sintering of alumina and zircon under various firing conditions and examined changes of the microstructure, the chemical composition of mullite and their mechanical properties.

2 Experimental Procedure

Fine and high purity alumina (TM-DAR, Taimei Chemicals), zircon (Tosoh) and mullite (MP-20, Chichibu Cement) powders were used for the experiments. The powders were mixed by wet ball milling in ethanol using a polyethylene pot and yttria-stabilized tetragonal zirconia balls of 2 mm in diameter. The mixtures were dried by stirring with a hot stirrer at 80°C. Pellets were compacted by uniaxial pressing at 400 MPa. They were fired under various firing schedules. The firing schedules are shown schematically in Fig. 1 and can be summarized as follows: (1) ordinary firing: fired with a heating rate of 15 K min^{-1}, firing temperature 1570–1635°C for 0–156 h and a cooling rate of 30 K min^{-1}; (2) annealing: fired in two steps, i.e. firing at 1635°C for 12 h and annealing at 1570°C for 12–144 h; (3) re-firing: fired in three steps, i.e. firing at 1635°C for 12–144 h, annealing at 1570°C for 12–144 h and re-firing at 1635°C for 12–144 h; (4) optimized firing: fired by a two-step firing profile at 1570°C for 2 h and subsequently at

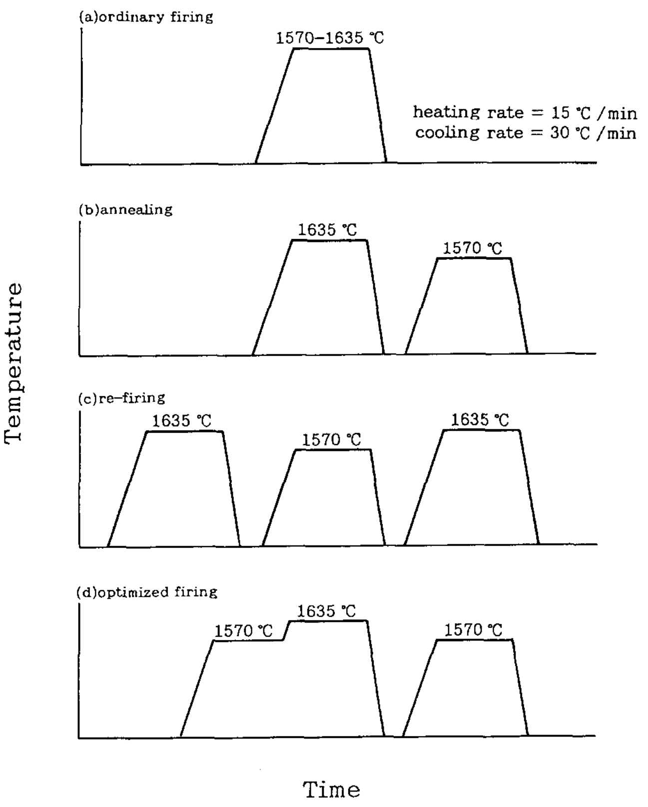

Fig. 1. Scheme of the firing schedules.

1635°C for 72 h, and then annealing at 1570°C for 72 h. Additionally, samples seeded with 5 and 20 vol% of mullite particles (average particle size 1·76 μm) were also prepared and fired with the optimized firing schedule.

X-ray diffraction (XRD) patterns of the samples were measured using a powder X-ray diffractometer (Geigerflex, Rigaku) with monochromated CuK_α radiation. Seven mullite reflections in the powdered samples were precisely measured using an internal standard of Si powder. Lattice constants of mullite were calculated by the least-squares method. Microstructure of the fired samples was observed by transmission electron microscopy TEM (JEM 200CX, Jeol) using thin-sectioned samples. Chemical composition of mullite was analysed by EDX (Northern) with the TEM instrument and calculated by the *K*-factor method.

Four-point bending strengths of the samples were measured from room temperature to 1500°C using a testing instrument (Instron 4302) with a crosshead speed of 0·5 mm min^{-1} for a test bar of 3 × 4 × 36 mm^3 (JIS R 1601). The samples used for the measurements were > 98% of relative density and were polished by #800 diamond paste.

Table 1. Lattice parameters of mullite in the variously fired samples

Sample no.	*Temp. (°C)/duration (h)*	*Lattice parameter (nm)*		
		a-*axis*	b-*axis*	c-*axis*
(1) Ordinary firing				
1	1570/12	0·75609(10)	0·76877(14)	0·28853(05)
2	1600/12	0·75640(20)	0·76872(16)	0·28862(01)
3	1635/0	0·75619(13)	0·76890(05)	0·28850(05)
4	1635/6	0·75684(05)	0·76877(16)	0·28852(06)
5	1635/12	0·75701(11)	0·76876(04)	0·28863(01)
6	1635/18	0·75655(11)	0·76882(07)	0·28852(01)
7	1635/24	0·75648(11)	0·76882(12)	0·28861(03)
8	1635/84	0·75636(07)	0·76882(12)	0·28861(03)
(2) Annealing				
9 No. 5 →	1570/12	0·75643(18)	0·76876(05)	0·28853(02)
10 No. 5 →	1570/72	0·75592(07)	0·76879(07)	0·28855(07)
11 No. 5 →	1570/144	0·75533(07)	0·76892(05)	0·28846(02)
(3) Re-firing				
12 No. 9 →	1635/12	0·75622(03)	0·76870(01)	0·28856(04)
13 No. 10 →	1635/72	0·75512(02)	0·76906(05)	0·28850(04)
14 No. 11 →	1635/144	0·75486(11)	0·76907(01)	0·28851(04)
(4) Optimized firing				
15	1570/2,1635/12,1570/72	0·75472(06)	0·76911(04)	0·28839(03)
16	1570/12,1635/12,1570/12	0·75475(28)	0·76909(13)	0·28846(04)
5 Vol% mullite seeded				
17	1570/12	0·75602(07)	0·76909(05)	0·28844(07)
18	1600/12	0·75602(19)	0·76890(13)	0·28851(05)
19	1635/12	0·75607(18)	0·76893(16)	0·28853(04)
20 Vol% mullite seeded				
20	1570/12	0·75512(04)	0·76912(21)	0·28844(03)
21	1600/12	0·75504(08)	0·76910(19)	0·28852(04)
22	1635/12	0·75505(09)	0·76904(14)	0·28847(04)
23	1570/02,1635/12,1570/72	0·75456(09)	0·76911(06)	0·28846(03)

Standard derivations are in parentheses and refer to last decimal place.

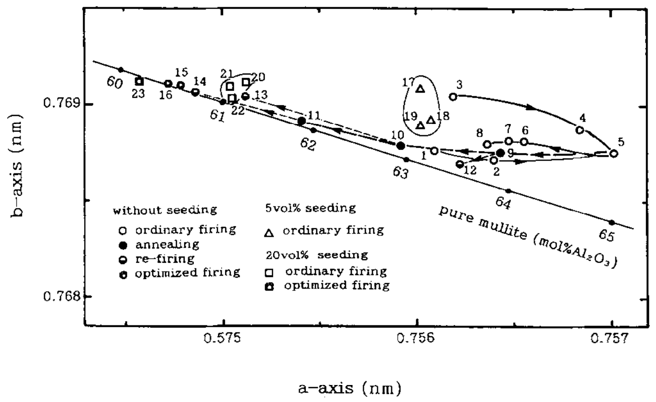

Fig. 2. Relation between the lengths of the *a*- and *b*-axes of mullite in the samples prepared under various conditions (see text and Table 1 for details).

Edges were chamfered with a diamond disc. Fracture toughness was determined using an indentation microcrack method[7] with a load of 49 N.

3 Results and Discussion

3.1 Ordinary firing

In these experiments, the samples were prepared with two series of firing conditions. In the first series, the samples were fired for a constant duration of 12 h with firing temperatures from 1570 to 1635°C. In the second series, the samples were fired at a constant temperature of 1635°C with duration varying from 0 to 156 h. Lattice constants of mullite in these samples are listed in Table 1. The correlation between the lengths of the *a*- and *b*-axes is shown in Fig. 2. In the first series, the length of the *a*-axis of mullite increased with higher firing temperature while the lengths of the *b*- and *c*-axes did not change significantly (samples 1, 2, 5). The change was especially large between the mullite fired at 1600°C and that at 1635°C (samples 3–8). Due to this increase of the length of the *a*-axis, the lattice constant data of the mullite fired at 1635°C deviated from the relation reported for pure mullite, which is also depicted in Fig. 2. This deviation of the data suggests incorporation of ZrO_2 into the mullite structure. A second series of experiments was, therefore, made in order to elucidate this phenomenon.

Table 2. Chemical analysis of mullite by EDX

Sample no.	*Chemical composition (mol %)*			
	Al_2O_3	SiO_2	ZrO_2	Al_2O_3/SiO_2
3	61·3(13)	37·5(13)	1·2(04)	1·63
5	63·4(09)	35·5(09)	1·1(05)	1·79
8	63·8(10)	36·1(07)	1·1(04)	1·77
11	62·9(09)	36·5(09)	0·6(02)	1·73
21	60·7(07)	38·8(07)	0·5(02)	1·56

Standard derivations are in parentheses and refer to last decimal place.

The lengths of the *a*- and *b*-axes for the second series samples (3–8) are also shown in Fig. 2. With longer firing time, the cell edges changed on a line parallel to the composition line of pure mullite, indicating increasing Al_2O_3 contents. This trend continued up to 12 h. Since this line runs parallel

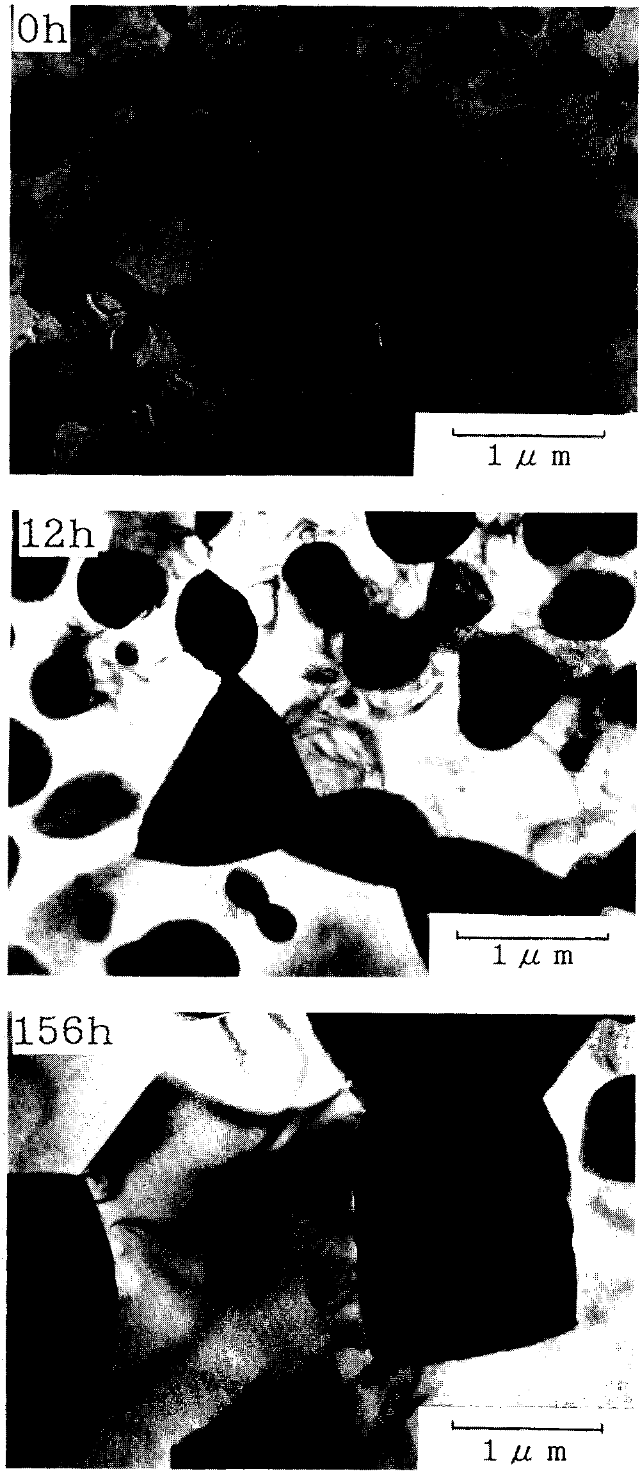

Fig. 3. TEM photographs of the 'ordinary firing' samples with various firing times.

to the pure mullite line, it is suggested that a small amount of zirconia is incorporated in these mullites. With firing times longer than 12 h, the a-axis became shorter again. This new trend approached the pure mullite line but stopped at a certain stage intermediate between pure mullite and the line given by samples 3, 4 and 5. Chemical compositions of some mullites were analysed by EDX and are listed in Table 2. From these data, it is confirmed that a small amount of zirconia was incorporated in the mullites (samples 3 and 5).

Figure 3 shows the microstructural changes in the samples fired at 1635°C for different times. With longer firing time, the grain size of the zirconia drastically increased and the thickness of a glassy grain boundary phase also increased. As the XRD and EDX results indicated, the mullites were richer in alumina than the expected composition of 60 mol%. Therefore, some excess silica should be exsolved and be present in the samples. Indeed, a thick amorphous film was observed in the grain boundaries as shown in Fig. 4. This amorphous film totally covered the mullite grains. The amorphous film was, therefore, considered to be silica-rich in composition. The liquid phase from which this amorphous film was formed is considered to have evolved transiently at high temperature because of the peculiar mullite formation reaction in this system, i.e. silica formed by the decomposition of zircon reacted with alumina to form mullite at high temperature. With higher firing temperature, the amount of the liquid phase apparently increased. Therefore, the chemical composition of mullite changed transiently towards the $2Al_2O_3{\cdot}SiO_2$ composition and incorporated some amount of zirconia due to the rapid mullitization in the presence of the liquid phase. However, this transit state then gradually changed to the apparently stable state at that temperature with longer firing time and the transiently formed mullite changed its chemical composition towards the apparently stable state and exsolved zirconia as a result. (This apparently stable state does not mean really equilibrium stable state.) Similar transient zirconia incorporation in mullite was also reported in the crystallization of mullite in rapidly quenched mullite/zirconia composites by Yoshimura *et al.*[8]

3.2 Annealing and re-firing

With longer firing times up to 156 h at 1635°C in the ordinary firing method described above, the chemical composition of mullite became almost constant at some intermediate state as reported in the previous section. Although the sample (5) showed a very high fracture toughness of 6·9 MPa $m^{1/2}$ and good four-point bending strength of 310 MPa at room temperature, the existence of a silica-rich amorphous phase in the grain boundaries was anticipated to be detrimental for high temperature mechanical properties of the composites. Hence, an annealing treatment was attempted at 1570°C in order to crystallize the grain boundary phase by a reaction between the amorphous phase and the alumina-rich mullite. This reaction should also

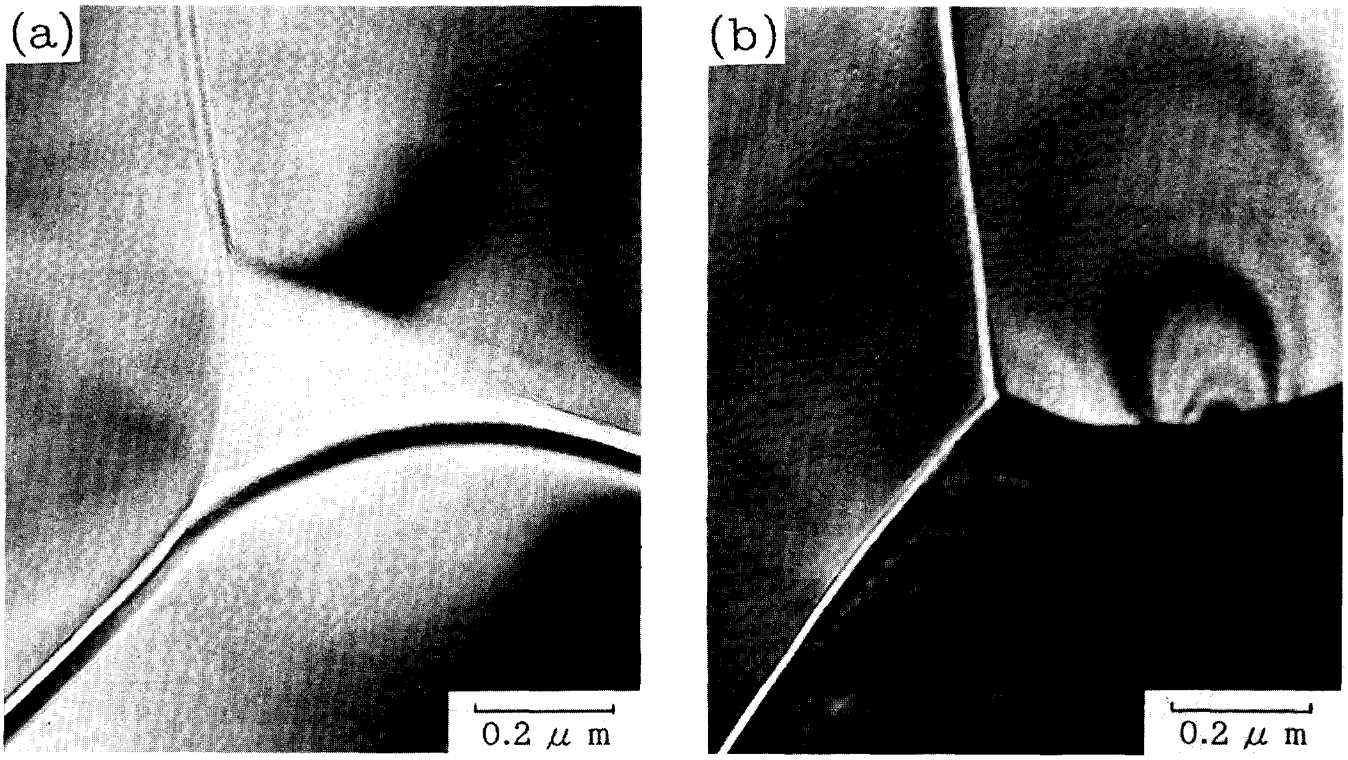

Fig. 4. TEM photographs of the grain boundaries of the 'ordinary firing' samples: (a) fired at 1635°C for 1 h; (b) for 156 h.

change the chemical composition of mullite to 60 mol% Al_2O_3. The lattice parameter changes resulting from the annealing treatment are also shown in Fig. 2 (samples 9–11). With longer annealing time at 1570°C, the chemical composition of mullite indeed shifted and approached the expected value of 60 mol% Al_2O_3. As is evident from Fig. 2, zirconia was mostly expelled from mullite by this treatment. This was also confirmed by EDX analysis listed in Table 2. The annealing treatment at 1570°C was found to be effective to change the chemical composition of mullite to the expected value. Further, annealing experiments were performed at 1520 and 1450°C but they were found to be less effective than those at 1570°C.

In the next step, we re-fired the annealed samples again at 1635°C. The lattice constants of mullite changed again upon this treatment, indicating that the chemical composition further approached 60 mol% Al_2O_3. This implies that no liquid phase was formed during this re-firing even though it was fired at the same firing temperature as that of the 'ordinary firing', where a transient metastable liquid phase had formed. The reaction that occurred in the re-firing treatment was, therefore, considered to approach stable state at this temperature. In the case of the ordinary firing at 1635°C, the change of the lattice constants showed limitation and stopped at some intermediate stage even after long firing times. Comparing with this result, the change of the lattice constants of mullite was accelerated in the annealing and re-firing treatments. The driving force for this change is, however, uncertain at present.

3.3 Optimized firing

From the previous results, we found that the chemical composition of mullite formed by the ordinary firing was alumina-rich and yielded a silica-rich amorphous film in the grain boundaries. This type of microstructure is anticipated to lead to degradation of mechanical properties at high temperature. In order to avoid the formation of alumina-rich mullite, we considered two counterplans.

The first counterplan was firing the samples by a two-step firing schedule, which was first proposed by Claussen and Jahn.[2] The concept of this process was to separate the densification stage and the reaction stage. In the present study, we attempted to form mullite at a temperature lower than 1635°C to avoid alumina-rich mullite formation. Therefore, mullitization was done by holding at 1570°C for 2–12 h and then the samples were sintered at the higher temperature of 1635°C. Indeed, mullite formed by this firing schedule was much closer in composition to 60 mol% Al_2O_3 than in the samples made by the 'ordinary firing'. The samples were then further annealed at 1570°C as shown in Fig. 1. By this firing schedule (d), the chemical composition of mullite in the composites became very close to the expected composition of 60 mol% Al_2O_3 as shown in samples 15 and 16 of Fig. 2. The difference between the results of this firing schedule (samples 15 and 16) and the annealing schedule (samples 13 and 12) was quite considerable. This is attributed to the difference of their mullitization temperature. Apparently the chemical composition of firstly formed mullite is very important for the ability of the mullite to reach the final equilibrium composition close to 60 mol% Al_2O_3.

Our second counterplan was the seeding method. Composites seeded with 5 and 20 vol% of mullite particles were prepared. As is apparent from the data of samples 17–22 in Fig. 2, the chemical composition of the mullite formed depended on the amount of seeding but was almost independent of the firing temperatures. Therefore, we combined the two counterplans of two-step firing and seeding methods and found that the mullite thus formed (sample 23 in Fig. 2) showed a composition very close to 60 mol% Al_2O_3.

3.4 Temperature dependence of bending strength

Figure 5 shows the four-point bending strength of the mullite/zirconia composites from room temperature to 1500°C. The bending strength of the 'ordinary firing' sample (5) was fairly high (310

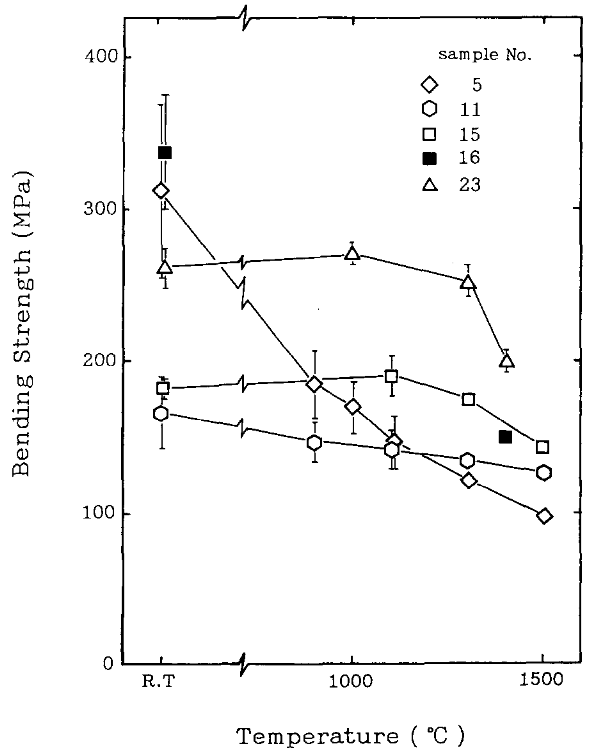

Fig. 5. Temperature dependence of the four-point bending strength different samples (see Table 1 for processing details).

MPa) at room temperature. However, it decreased linearly with temperature and was only 100 MPa at 1500°C. This large degradation of the strength was considered to be due to the presence of a thick and continuous silica-rich amorphous film in the grain boundaries as shown in Fig. 4. To avoid this degradation of strength at high temperature, the amorphous phase was crystallized by annealing at 1570°C for 144 h. The bending strength of the annealed sample (11) was, however, very low at room temperature. Since a jagged pattern was observed in the stress–strain curve of this sample, microcracking in the annealed sample was considered to be the main reason for the low bending strength. Many cracks along the grain boundaries were indeed observed by TEM. The cracks were considered to occur by the crystallization of mullite from the reaction of alumina-rich mullite and silica-rich amorphous phase in the grain boundaries. Therefore, crystallization of the grain boundaries was found not to be effective in these composites although this technique was reported to be effective to enhance the mechanical properties of silicon nitride.[9]

To avoid the formation of glassy phase and microcracks in the samples, we adopted the two-step firing and annealing treatments. Sample (15) showed a fair enhancement of the bending strength for the whole temperature range compared with the annealed sample (11). This enhancement of bending strength was considered to be due to the shorter firing time, that is, decreased grain size. However, the grain size of this sample was still much larger than that of the 'ordinary firing' and the bending strength at room temperature was also lower. With shorter annealing time, the bending strength (sample 16) was found to increase to around 340 MPa at room temperature but it was not improved at high temperature because of the residual glassy phase. On the other hand, the seeded sample (23) showed an improvement of high temperature strength compared with the previous sample (16). Since the firing schedule was the same for these two samples, the seeding with mullite particles was found to be effective to improve high temperature strength. This also confirms that seeding is very effective to control the chemical composition of mullite formed in the reaction sintering of alumina and zircon.

Torrecilas *et al.*[10] and Kubota *et al.*[11] examined the high temperature mechanical properties of zirconia-dispersed mullite composites and also zirconia- and alumina-dispersed mullite composites prepared by reaction sintering of alumina and zircon. Torrecilas *et al.*[10] considered the formation of liquid phase at high temperature. Recently, Ebinuma *et al.*[12] showed direct evidence of liquid phase formation at high temperature in the reaction sintering of alumina and zircon. Torrecilas *et al.*[10] and Kubota *et al.*[11] shifted the bulk chemical composition towards an alumina-rich composition to avoid the liquid phase formation. These composites showed little degradation of high temperature strength because of almost glass-free grain boundaries, but lowering of creep properties was inevitable due to co-existence of alumina. Comparing with their data, the bending strengths of the seeded sample in the present study were similar or a little higher for all temperatures from room temperature to high temperature.

4 Summary

Zircon-dispersed mullite composites were prepared via reaction sintering of alumina and zircon with various firing schedules. The following results were obtained.

In the 'ordinary firing' schedule, the chemical composition of the mullite formed was extraordinarily alumina-rich and a small amount of zirconia was incorporated. This caused continuous thick glassy films in the grain boundaries. Incorporation of zirconia was transient and expelled by longer firing time. By long duration of annealing at 1570°C, zirconia was also exsolved from mullite and some change was observed in the chemical composition of mullite by the crystallization of the glassy grain boundaries. However, it was insufficient for complete crystallizing of the glassy grain boundaries. Further progress was made by the re-firing treatment but this treatment was still insufficient for complete crystallization. The two-step firing treatment to form mullite at 1570°C was effective to avoid the formation of alumina-rich mullite. Seeding with 20 vol% of mullite particles accelerated the mullitization at that temperature. The 'ordinary firing' samples showed good four-point bending strength and fracture toughness at room temperature but showed degradation of the mechanical properties at high temperature. This was attributed to the continuous and thick glassy phase in the grain boundaries.

Four-point bending strength of the samples could not be improved when they were prepared by long firing time at high temperature because grain growth and microcracking occurred by these treatments. High temperature strength was improved, however, by reducing the silica-rich amorphous glassy phase in the grain boundaries. Seeding with mullite particles combined with two-step firing were most effective to obtain high strength from room temperature up to 1500°C.

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