

## Sintering and Microstructure of Alumina/Mica and Spinel/Mica Composites

Sofia Saori Suzuki, Seiichi Taruta and Nobuo Takusagawa

Department of Chemistry and Material Engineering,  
Faculty of Engineering, Shinshu University, Wakasato 500, Nagano 380-8553, Japan  
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Alumina/mica and spinel/mica composites were fabricated by sintering of compacts containing 20 mass% fluoromica ( $\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$ ) glass and alumina or spinel. In both composites, mica precipitated as plate-like crystals at temperatures lower than 1300°C and melted at 1300°C to 1400°C. In alumina/mica composites, alumina and glass reacted to produce spinel, and the densification progressed by the solution-precipitation of alumina. Consequently, the glass composition changed and the mica did not precipitate at temperatures higher than 1400°C. However, mica precipitated after a reheating process. In spinel/mica composites, the glass composition did not change. After the mica phase melted, it recrystallized during slow cooling. The relative density reached the maximum at 1500°C for alumina/mica and at 1300°C spinel/mica composites, and decreased at further high temperatures.

**Key words :** Fluoromica, Spinel, Alumina, Sintering

### I. Introduction

Recently, ceramics having a controlled and heterogeneous microstructure with high flaw tolerance have received more attention than traditional homogeneous monophasic brittle ceramics.<sup>1</sup> Cai et al.<sup>2</sup> reported that mica glass-ceramics (MGCs) show a higher resistance to strength degradation compared with the base glass. MGCs consist of fine mica grains precipitated in a dense glassy matrix.<sup>3</sup> Cleavage of mica crystal in the basal plane and microcracking in the glass/mica boundary inhibit brittle crack propagation and permit the material to be machined with high-speed tools. Cooper et al.<sup>4</sup> and King et al.<sup>5</sup> showed that it was possible to use fluorophlogopite mica as a fiber-protecting phase in alumina-fiber/alumina-matrix composites to enhance the pullout effect of the fiber by cleavage of mica. On the other hand, it is well known that the presence of a liquid phase may aid the densification of ceramic materials during firing and crystallization in the liquid and/or glass phase increases the fracture toughness. Recently, an alumina/glass composite for dental applications (In-Ceram<sup>®</sup>),<sup>6</sup> which contains 25 vol% glass, showed superior mechanical properties (strength 400 MPa, fracture toughness 3.8 MPam<sup>1/2</sup>) compared to typical dental porcelains. An investigation of the crack path showed that intergranular fracture, deflection and bridging were the major toughening mechanisms.

The aim of this work was to fabricate ceramic/mica composites with fine mica grains dispersed at the grain boundaries of alumina or spinel, which forms a skeleton. It was anticipated that cleavage of the mica phase and/or microcracking in the boundary would lead to high frac-

ture toughness. In the present work, composites were fabricated by sintering of powder mixtures of mica glass and spinel or alumina. The sintering behavior, mica crystallization process, and microstructure were investigated.

### II. Experimental Procedure

#### 1. Synthesis of the Mica Glass

The starting materials of the glass are shown in Table 1 and this batch contained 13.5 mass% excess of fluorine in comparison with the stoichiometric composition of fluorophlogopite ( $\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$ ) owing to the volatilization of fluorine at high temperatures. The reagents were mixed by hand using an alumina mortar and pestle and calcined at 900°C for 1 hour. The batch was melted in a sealed platinum crucible at 1450°C for 4 hours. The melt was cooled rapidly by pouring into water and the visibly devitrified parts were removed. The obtained glass, which is called mica glass in this paper, was pre-milled by hand using an alumina mortar and pestle, passed through a 100-mesh sieve, and mechanically pulverized in ethanol by ball milling for 48 hours using a plastic jar and zirconia balls (3 mm in diameter).

Table 1. Starting Materials of Mica Glass

Reagent	Mass%
$\text{K}_2\text{CO}_3$	15.5
$\text{SiO}_2$	40.4
$\text{MgO}$	16.8
$\text{Al}_2\text{O}_3$	11.4
$\text{MgF}_2$	15.9

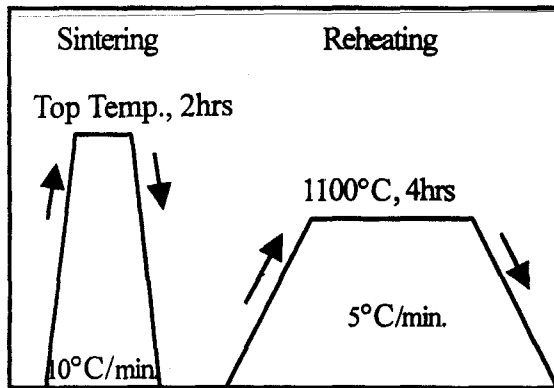


Fig. 1. Heating schedule of alumina/mica composites.

## 2. Fabrication of Ceramic/Mica Composites

Mica glass and alumina powder (AES-12, Sumitomo Chemicals, Tokyo, Japan, average grain size 0.48  $\mu\text{m}$ ) were mixed in acetone by ball milling for 24 hours using an alumina pot and alumina balls (10 mm in diameter). Similarly, the mica glass and spinel powder (SP-12, Iwatani Chemicals, Osaka, Japan, average grain size 0.3  $\mu\text{m}$ ) were mixed using a zirconia pot and zirconia balls (3 mm in diameter). Both mixtures contained 20 mass% mica glass. The mixed powders were calcined at 600°C for 1 hour, passed through a 100-mesh sieve, and compacted by cold isostatic pressing at 98 MPa. The powder compacts were approximately 9 mm in diameter, 3 mm in thickness and 0.5 g in weight.

The compacts were then sintered in a sealed platinum tube at 1100° to 1600°C for 2 hours. Both the heating and the cooling rates were 10°C/minute. The alumina/mica composites were further reheated at 1100°C for 4 hours, and in this case, both the heating and the cooling rates were 5°C/minute. The heating schedule is shown in Fig. 1.

For the purpose of investigating the mechanism of mica crystallization, some of the spinel/mica composites were quenched in air after firing at 1300° to 1500°C for 2 hours.

## 3. Characterization of the Composites

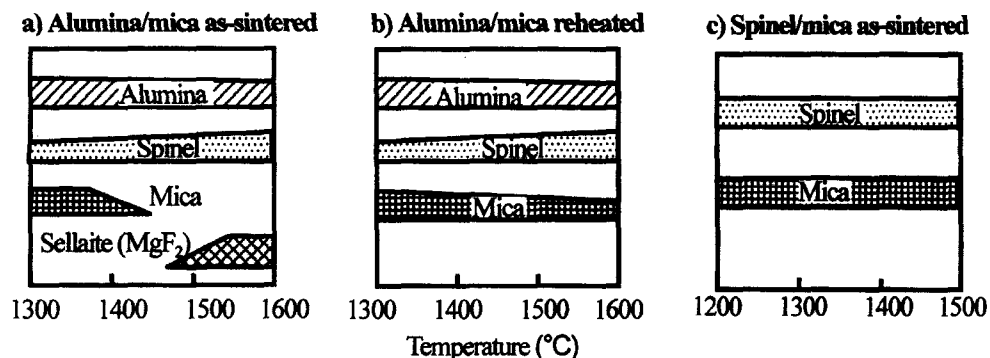


Fig. 2. Crystalline phases of the composites: a) as-sintered alumina/mica composite, b) alumina/mica composite reheated at 1100°C and c) as-sintered spinel/mica composite.

The crystalline phases of the composites were determined using an X-ray diffraction analyzer (XRD)(XRD-6000, Shimadzu, Kyoto, Japan). The relative density of the composite was calculated from the bulk and true densities. The bulk density was measured by the Archimedes' method using water as the medium and pycnometry was used to measure the true density. Fractured surfaces of the composites were observed using a scanning electron microscope (SEM) (JSM-5300, JEOL, Tokyo, Japan). For the quenching experiments, specimens were etched for 5 min with 5% HF, to remove the glass phase.

## III. Results and Discussion

Fig. 2 shows schematically the crystalline phases precipitated in the as-sintered alumina/mica composites, in the same composites reheated at 1100°C and in the as-sintered spinel/mica composites. In the alumina/mica composites sintered at temperatures lower than 1400°C, mica and spinel precipitated. Mica crystallized from the glass and/or liquid phase. Spinel was formed by the reaction between alumina and mica glass. At temperatures

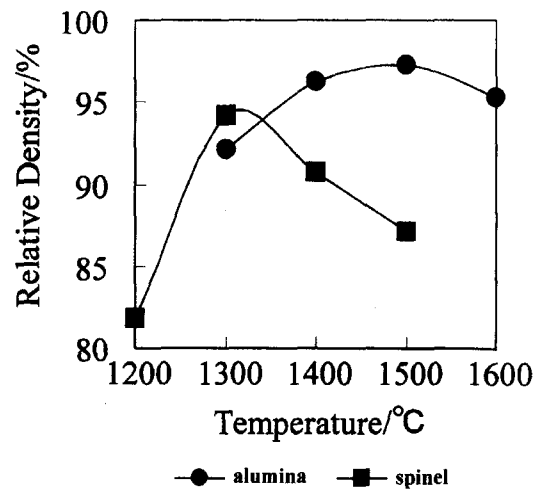


Fig. 3. Relative densities of alumina/mica (●) and spinel/mica (■) composites sintered at various temperatures and reheated.

higher than 1500°C, sellaite ( $MgF_2$ ) precipitated instead of mica. However, mica precipitated by reheating the specimens at 1100°C. On the other hand, mica precipitated in all of the spinel/mica composites sintered at 1100° to 1600°C.

Fig. 3 shows the relative densities of the composites sintered and reheated. The maximal relative density was achieved at 1500°C (97.4%) for alumina/mica composite and at 1300°C (94.2%) for spinel/mica composites. The densification progressed mainly by solution-precipitation, and the solution-precipitation of alumina progressed at higher temperatures compared with the densification of spinel. The relative density of both compacts decreased at further high temperatures. This behavior will be explained later.

Fig. 4 shows SEM photographs of the fractured surfaces of the alumina/mica composites at lower and higher magnifications. In the composite sintered at 1400°C and reheated, most of the alumina grains were smaller than 5  $\mu m$ , spinel precipitated as submicron-sized rhombic grains. Mica precipitated as plate-like crystals embedded in glass phase, even before the reheating process. In the composite sintered at 1500°C and reheated, most of the alumina grains grew to 7  $\mu m$  and faceting occurred. In the composite sintered at 1600°C and reheated, the alumina grain size was from 5 to 20  $\mu m$  and excessive grain growth was observed. Some alumina grains were

elongated owing to the anisotropic grain growth. Plate-like mica crystals grew to a size similar to that of the alumina grains with increase in temperature.

Fig. 5 shows SEM photographs of the fractured surfaces of spinel/mica composites at lower and higher magnifications. At 1300°C, the microstructure was dense with pores smaller than 1  $\mu m$ . Mica precipitated as plate-like crystals <5  $\mu m$  in size. Spinel showed a typical rhombic geometry and Particle size <5  $\mu m$ . At 1400°C, spherical pores ranging from 5 to 10  $\mu m$  appeared. Most of spinel grains were in the range from 2 to 4  $\mu m$ . At 1500°C, the spherical pores grew to ~15  $\mu m$  and the spinel grains grew slightly to ~5  $\mu m$ . In the composites sintered at 1400°C to 1500°C, mica precipitated as plate-like crystals, and grew slightly to size of <10  $\mu m$ .

Fig. 6 shows the results of quenching experiments for spinel/mica composites. In the composite quenched from 1300°C, mica precipitated, which indicates that mica grew from preexisting nuclei during heating. In the composite quenched from 1400°C, mica was not present, which indicates that mica melted at 1300° to 1400°C and reprecipitated during the slow cooling process. Therefore, the mechanism of mica precipitation occurring below 1300°C was different from that occurring above 1400°C.

In the alumina/mica composites, alumina and glass reacted to produce spinel and the amount of the spinel increased at higher temperatures. In addition, solution-

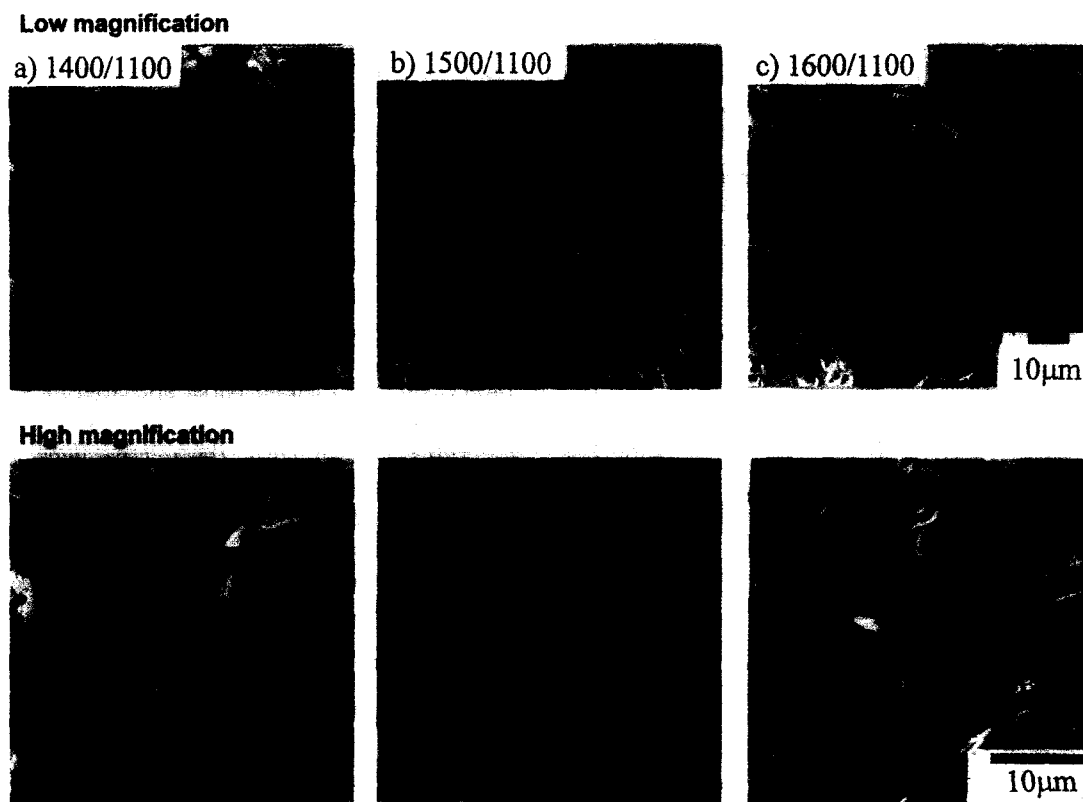
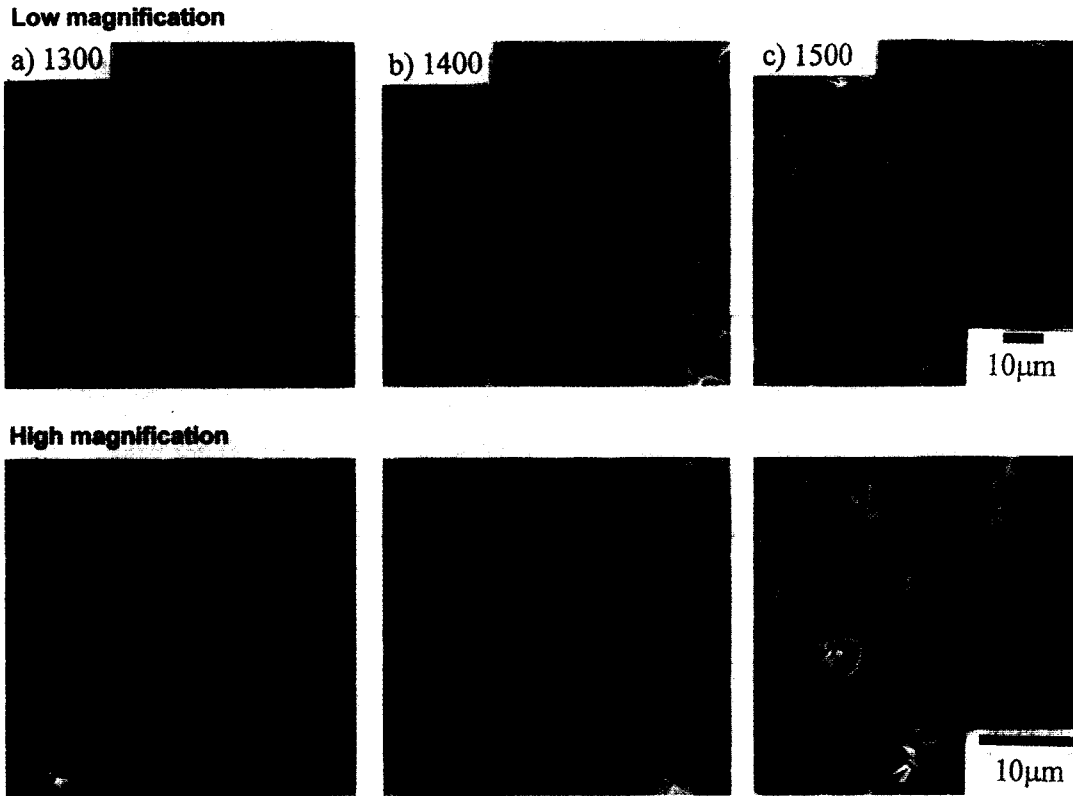
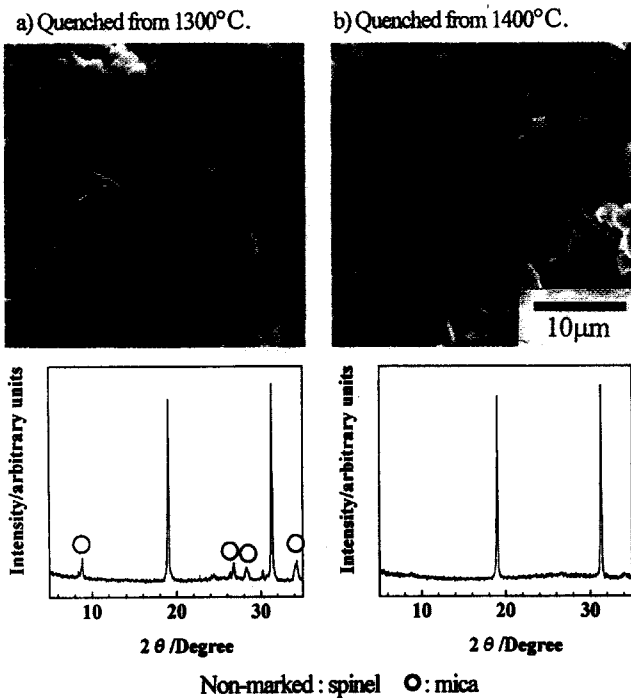


Fig. 4. SEM photographs of fractured surfaces of alumina/mica composites sintered at a) 1400°C/1100°C, b) 1500°C/1100°C and c) 1600°C/1100°C.



**Fig. 5.** SEM photographs of fractured surfaces of spinel/mica composites sintered at a) 1300°C, b) 1400°C/1100°C and c) 1500°C/1100°C.



**Fig. 6.** SEM photographs and XRD patterns of spinel/mica composites quenched from a) 1300°C and b) 1400°C. (SEM: fractured surfaces were etched with 5% HF, 5 min.).

precipitation of alumina progressed, causing the glass to become rich in aluminum and poor in magnesium. Con-

sequently, mica did not precipitate in the composites sintered at 1500° and 1600°C. However, the reheating process promoted diffusion in the glass and thus mica precipitation. Densification and grain growth progressed by solution-precipitation of alumina as the temperature increased. The relative density achieved maximum at 1500 °C and decreased at 1600°C owing to the excessive grain growth.

In contrast to the alumina/mica composite, in the spinel/mica composite, mica precipitated even at high temperatures because the glass composition did not change. In specimens sintered at temperatures higher than 1400°C spherical closed pores appeared as shown in Fig. 5 (b). Such spherical pores became larger at higher temperatures. Consequently, the relative density achieved a maximum at 1300°C and decreased at further high temperatures owing to the formation and growth of the spherical pores.

The probable cause of the spherical pore formation are the evolution of fluorine gas and the processing parameter described as follows, but it is not clear. In an additional experiment, spherical closed pores of ~20 to 50 µm in size were observed not only in spinel/mica composites but also in alumina/mica composites sintered at temperatures higher than 1500°C. In these composites, the powders were mixed in a plastic ball mill and the mica glass powder contained agglomerates which were three to five times larger than alumina particles. In the present work, the

mixing of the powders with alumina media reduced agglomeration and permitted the liquid to distribute more uniformly during sintering. Therefore, it is important to mix the powders uniformly and reduce the grain size mismatch among the powders in order to achieve a uniform liquid distribution and consequently, an increase in densification.

#### IV. Conclusions

Alumina/mica composites and spinel/mica composites were fabricated by the sintering of mixtures of mica glass and alumina or spinel powder. The results were as follows:

(1) In both composites, mica precipitated as plate-like crystals embedded in a glass phase at temperature lower than 1300°C and melted at 1300°C to 1400°C.

(2) In alumina/mica composites, as alumina and glass reacted to produce spinel, and the densification progressed by the solution-precipitation of alumina, so the glass composition changed. Consequently, mica did not precipitate at temperatures higher than 1400°C. However, a reheating process promoted diffusion in the glass and mica precipitated as plate-like crystals at the alumina grain boundaries.

(3) In spinel/mica composites, the glass composition did not change even at high temperatures. After mica melted, it recrystallized during cooling as plate-like crystals.

(4) Densification by solution-precipitation of alumina progressed at higher temperatures compared with spinel densification. Consequently, the relative density of alumina/

mica composites achieved the maximum at 1500°C and decreased at 1600°C owing to excessive grain growth. The relative density of spinel/mica composites achieved the maximum at 1300°C, and decreased at further high temperatures owing to the formation and growth of spherical pores.

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