Sintering and Contact Damage of Spinel/Mica Composites Prepared from Alumina, Magnesia and Mica-Composition Glass Powder Mixtures

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アルミナ、マグネシア及びマイカ組成ガラス混合粉体から調製した スピネル/マイカ複合体の焼結挙動と接触損傷

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Conventional alumina and magnesia powders were mixed with a mica-composition glass powder, compacted, and fired. A dense spinel/mica composite was obtained at a low temperature of 1200°C for the specimen of 20% mica-composition glass addition. The sintering was promoted by not only the dissolution of fluorine ion but also the formed liquid phase. The liquid phase allowed the volume expansion caused by the reaction between the alumina and the magnesia to be effective for densification, like a closer packing of particles. Furthermore, the liquid phase caused particle rearrangement and dissolution-precipitation. Numerous flakelike mica crystals of several micrometers separated out in the interparticle regions of the spinel. Both brittle and quasi-plastic damage modes were competitive on the surface and in the subsurface of the specimen. The bending strength was slightly decreased by Hertzian indentation. The fracture site in the post-indented specimen was a cornlike crack. However, the quasi-plasticity prevented catastrophic failure from the cornlike crack. These results indicate that the composite had flaw tolerance.

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1. Introduction

The simplest preparation method for spinel-sintered compacts is the reaction sintering of an alumina and magnesia powder mixture in air. However, dense sintered compacts are difficult to fabricate by this method.¹⁾ Therefore, the fabrication of dense sintered compacts at lower temperatures requires the synthesis of a very fine spinel powder and/or a special firing method.

On the other hand, sintering additives, such as AlF_3 , TiO_2 , $\text{B}_2\text{O}_3 + \text{TiO}_2$, $\text{B}_2\text{O}_3 + \text{LiF}$, or $\text{B}_2\text{O}_3 + \text{CaF}_2$, are reported to be effective for the low-temperature sintering of alumina and magnesia powder mixtures.^{2)–4)} Such sintering behavior is explained by the dissolution of F^- , B^{3+} , and Ti^{4+} into the spinel, which causes lattice defects.^{2)–4)} The addition of CaO also enhances the densification of spinel powder through liquid-phase formation.^{5),6)}

We reported on the fabrication of dense spinel/mica composites by sintering powder mixtures consisting of spinel and mica-composition glass.^{7),8)} The obtained composites exhibited quasi-plastic deformation dependent on the additive amount and composition of the glass powder.⁹⁾

In the present study, in order to fabricate dense spinel/mica composites more simply at lower temperatures, conventional alumina and magnesia powders were used as the spinel raw materials, rather than spinel powder, mixed with mica-composition glass, which contains fluorine, compacted, and fired. The sintering behavior and contact damage of the obtained composites were investigated.

2. Experimental procedure

The preparation method for mica-composition (fluorophlogopite: $\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$) glass powder is given elsewhere.^{7),8)} The starting glass powders of alumina (AES-12,

Sumitomo Chemicals, average particle size of 0.52 μm) and magnesia (MJ-30, Iwatani Chemicals, average particle size of 0.36 μm) were mixed by ball milling. The mixing ratio of the alumina and magnesia powders corresponded to a stoichiometric spinel (MgAl_2O_4) composition, and the additions of glass powder were 0, 5 or 20 mass%. The three specimens are called here the 0% specimen, the 5% specimen and the 20% specimen, respectively. The powder mixtures were calcined at 600°C for 1 h, passed through a 100-mesh sieve, compacted by cold-isostatic pressing at 98 MPa, and fired in a sealed platinum tube at 1150–1500°C for 2 h.

Crystalline phases in the specimens were determined using X-ray diffractometry (XRD). The bulk densities were measured by the Archimedes method. The fracture surfaces of the sintered specimens were observed by scanning electron microscopy (SEM). The polished surfaces of the 20% specimen sintered at 1200°C were indented, using a WC ball with a 3.18 mm radius, at a load of 500 N (Hertzian indentation test), and the specimens were observed by optical microscopy with Nomarski illumination and SEM. The bending strength and post-indentation bending strength of the 20% specimen sintered at 1200°C were measured.

3. Results and discussion

3.1 Sintering and microstructure

The XRD results showed that the alumina and magnesia began to react to form spinel at 900°C in the 5% and 20% specimens and the reaction was completed at 1300°C for the 5% specimen and at 1200°C for the 20% specimen, while in the 0% specimen the reaction started at 1000°C and finished at 1400°C. Thus, the reaction was promoted by the dissolution of fluorine ions into the spinel.^{2),3),10)} Mica crystals ap-

peared at $>800^{\circ}\text{C}$ in the 20% specimen, but not in the 5% specimen. However, by reheating at 1100°C , the mica crystals separated in the 5% specimen.

The bulk densities of the obtained composites are shown in Fig. 1. The 5% and 20% specimens were densified rapidly in the temperature ranges of $1300\text{--}1400^{\circ}\text{C}$ and $1150\text{--}1200^{\circ}\text{C}$, respectively. Dense composites were obtained at 1400°C for the 5% specimen and at 1200°C for the 20% specimen, whereas the 0% specimen was hardly densified, even at 1500°C . Approximate relative densities of both the 5% specimen sintered at 1400°C and the 20% specimen sintered at 1200°C were $>95\%$, as determined from the measured bulk densities and the approximately calculated theoretical densities.

One reason for this low-temperature sintering was the dissolution of fluorine ions into the spinel.^{(2)–(4)} The differential thermal analysis (DTA) of the mica-composition glass showed that mica crystals separated out at $\sim 900^{\circ}\text{C}$ and that

Fig. 1. Bulk densities of sintered 0% (◆), 5% (▲) and 20% (●) specimens.

the residual glass melted at $\sim 1050^{\circ}\text{C}$. This result indicates that the formation of a liquid phase at $>1050^{\circ}\text{C}$ played an important role in the densification. The liquid phase is necessary for the dissolution of fluorine.⁽¹⁰⁾ In addition, rearrangement of the particles and dissolution-precipitation through the liquid phase promoted densification. The viscosity of the liquid phase must be sufficiently lowered at higher temperatures to allow the liquid to spread throughout the entire specimen by capillary force. Therefore, as the amount of additive glass decreased, the composites were densified at higher temperatures than the liquid-phase formation temperature of $\sim 1050^{\circ}\text{C}$.

A comparison of the spinel/mica composites obtained in this study with those obtained in the previous one⁽⁹⁾ is shown in Table 1. The 20% specimen of the present study was densified at a lower temperature than that of the previous study⁽⁹⁾ in which the spinel powder was used as raw materials. The densification is generally impeded when volume expansion, which is caused by the reaction between raw materials, occurs during sintering. Although, in the 20% specimen of the present study, the volume expansion was caused by reaction between the alumina and the magnesia in the temperature range from 900 to 1200°C , the densification was promoted. In such a temperature range, the liquid phase was formed as well as the volume expansion. The liquid phase allows the particles to rearrange and pack more closely. Such a rearrangement occurred in both the present study and the previous one. Moreover, the microstructure to be shown later in Fig. 2(c) demonstrates that the particle size of spinel formed in the present study was almost the same as that ($0.3\text{ }\mu\text{m}$) of spinel powder used in the previous study. Additionally, the preparation method was the same for both studies, except for the raw materials of spinel used. Therefore, the low-temperature sintering of the present study resulted from volume expansion under the existence of the liquid phase. Probably, under the existence of the liquid phase the volume expansion (i.e., volume increase)

Fig. 2. SEM micrographs of fracture surfaces of 5% specimen sintered at (a) 1300°C and (b) 1400°C , and 20% specimen sintered at (c) 1150°C and (d) 1200°C .

Table 1. Comparison of Spinel/Mica Composites Obtained in This Study with Those Obtained in a Previous Study⁹⁾

Spinel raw materials	Specimen	Densification temperature / °C	Relative density / %	Bending strength / MPa	Post-indentation bending strength / MPa
Spinel ⁹⁾	5%	1400	96.8	278 ± 9	176 ± 26
	20%	1300	94.5	266 ± 15	206 ± 10
Alumina and Magnesia	5%	1400	96.7	—	—
	20%	1200	95.4	200 ± 12	188 ± 9

prompted the particle rearrangement and/or filled space (pores). Consequently, the volume expansion acted effectively for the densification, like a closer packing of particles, through the liquid phase. On the other hand, the densification temperatures of the 5% specimens showed the same value in the present and the previous studies. Because the 5% specimens did not have a sufficient amount of liquid, closer packing of particles under the existence of the liquid phase, which was mentioned above, did not occur efficiently.

SEM micrographs of the fracture surfaces of the 5% and the 20% specimens are shown in Fig. 2. Extended growth of some spinel grains was observed in the 5% specimen sintered at 1300°C. Because a small amount of liquid phase was distributed nonuniformly at lower temperatures in the 5% specimen, some spinel grains grew rapidly in areas with much liquid-phase. In both the 5% specimen sintered at 1400°C and the 20% specimen sintered at 1200°C, the spinel grains grew to several micrometers. These microstructures indicate that dissolution-precipitation through the liquid phase highly promoted sintering. In the 20% specimen, numerous flakelike mica crystals with several micrometers, separated out in the interparticle regions of the spinel. On the other hand, little solid sintering of spinel occurred at 1200°C. As these results indicate, contact among spinel grains in the 20% specimen was less than that in the dense spinel/mica composites obtained in previous studies.^{7)–9)}

3.2 Contact damage

The bending strength of the 20% specimen was lower than that of the spinel/mica composites obtained in the previous study⁹⁾ (Table 1). This difference resulted from less contact among spinel grains in the 20% specimen of this study, as just mentioned. The strength was slightly decreased by Hertzian indentation. This small deterioration implies that the 20% specimen had flaw tolerance.

Optical micrographs of Hertzian indentation damage and the failure origin site of the post-indentated 20% specimen are shown in Fig. 3. Although a small crack, which was part of the ring crack, and an undeveloped cornlike crack, were observed at the surface and in the fracture surface, a residual depression was formed at the surface. This Hertzian indentation damage shows that both brittle and quasi-plastic damage modes were competing in the 20% specimen, according to the reports^{11)–16)} on the contact damage by the Hertzian indentation test. The fracture site in the post-indentated specimen was the cornlike crack. However, quasi-plasticity prevented catastrophic failure from the cornlike crack.

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Fig. 3. (a) Optical micrograph of post-indentated surface and (b) SEM micrograph of post-indentated fracture surface of 20% specimen sintered at 1200°C.