

## Effect of composition change on sintering and metallizing of alumina ceramics

Bum-Rae Cho<sup>a,\*</sup>, Jung-Jin Lee<sup>a</sup> and Seung-Kyu Kang<sup>b</sup>

<sup>a</sup>Department of Materials Engineering, Keimyung University, Daegu 704-701, Korea

<sup>b</sup>Department of Transportation Engineering, Keimyung University, Daegu 704-701, Korea

The effects of flux additions on the sintering and metallizing properties of alumina ceramics were investigated. Experimental results showed that the addition of SiO<sub>2</sub>, CaO and MgO as a flux increases the sintering ability of alumina. An increment in the amount of MgO seems to produce a more uniform and finer grain distribution. CaO and MgO addition seemed to promote a glassy state of the SiO<sub>2</sub> easily at a lower temperature. Alumina containing the proper amount of flux additions showed a higher metal-to-bond strength than nearly pure alumina ceramics. This was explained by the fact that the glassy state of SiO<sub>2</sub> migrated into the porous metallizing layer during the metallization process.

**Key words:** Mo-Mn metallization, Flux composition, Reduction sintering.

### Introduction

A metallizing process joining a metal to ceramic has been commonly used in the electronics industry. Metallized ceramics exhibit excellent electrical and mechanical properties to produce many types of electronic assemblies [1, 2]. The most common method is the molybdenum-manganese(Mo-Mn) process. This process is well-established and produces highly reliable joints between metals and ceramics. For the successful application of the Mo-Mn process, the oxidation of manganese and its reaction with a glassy phase in the alumina are principal factors. The presence of a glassy phase in alumina ceramics has an important effect on the metallizing behavior of the ceramics [3]. The bond strength between metals and ceramics decreases with an increase in the purity of the alumina. There are some major problems in joining metal to ceramics. One of the major problems in joining metal to ceramics is the thermal expansion mismatch between them. Generally, ceramic materials have lower thermal expansion coefficients than those of the metallic materials. The difference in the thermal expansion coefficients produces a high stress at the metallized region during cooling from the metallizing temperature to room temperature. The resultant high stress in joining metal to ceramic sometimes makes joints unreliable. Therefore, the thermal stress problems should be overcome to obtain reliable joints between a ceramic and metal [4, 5].

In this study, the effects of SiO<sub>2</sub>, CaO and MgO which were added to alumina ceramics on the sintering and metallizing of alumina ceramics were investigated and

the optimal composition of SiO<sub>2</sub>, CaO and MgO as a flux in the metallization of alumina ceramics was determined.

### Experimental

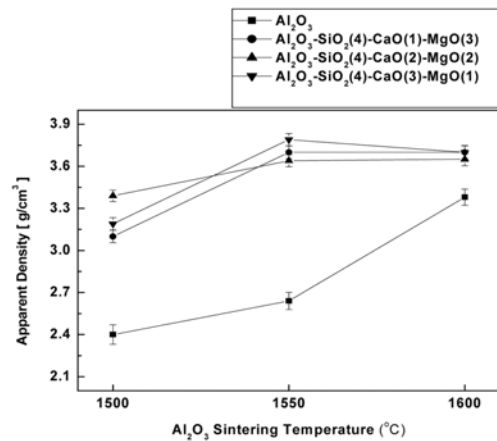
Alumina powders containing different amounts of SiO<sub>2</sub>, CaO and MgO were mixed in an attrition mill at 650 rpm for 2.5 hours. Four different flux compositions are shown in Table 1. Mixed powder was spray-dried and pressed by a Newton press at 20 MPa for 2 minutes to make disk type specimens. The green bodies were sintered at 1,500 °C, 1,550 °C and 1,600 °C for 2 hours in the air. After sintering, the microstructures of the sintered bodies were observed by a scanning electron microscope(Jeol, JSM-5410) and the density and porosity of each specimen were measured to study the sinterability of the specimens. The sintered alumina was cut into samples with dimensions of 36 × 4 × 3 mm and polished for 3-point bend tests. The metal paste was made by mixing together a proper ratio of Mo, Mn and organic additives. The prepared Mo-Mn paste was screen printed on one side of Al<sub>2</sub>O<sub>3</sub> specimen to produce a layer with a thickness of about 30-50 μm. After drying at 180 °C in air for 30 minutes, the alumina specimens were reduction-sintered at 1,250 °C for 1 hour in a H<sub>2</sub> atmosphere with a dew point of 20 °C. Microstructural details of the metallized alumina specimens were observed by the SEM.

### Results and Discussions

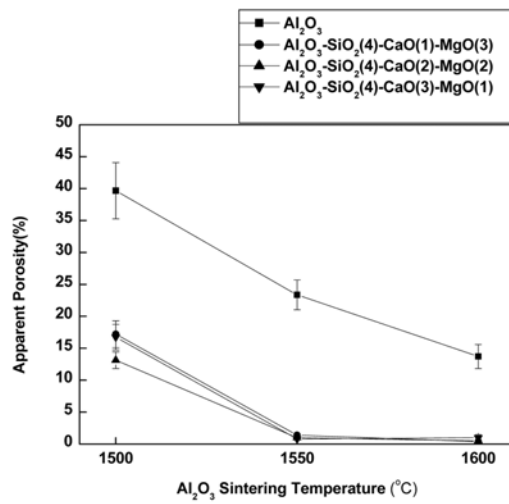
**Table 1.** Flux compositions of alumina specimens [wt%].

	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MgO
S1	99.9	-	-	-
S2	92	4	1	3
S3	92	4	2	2
S4	92	4	3	1

\*Corresponding author:  
Tel : +82-53-580-5359  
Fax: +82-53-580-5359  
E-mail: chobr@kmu.ac.kr



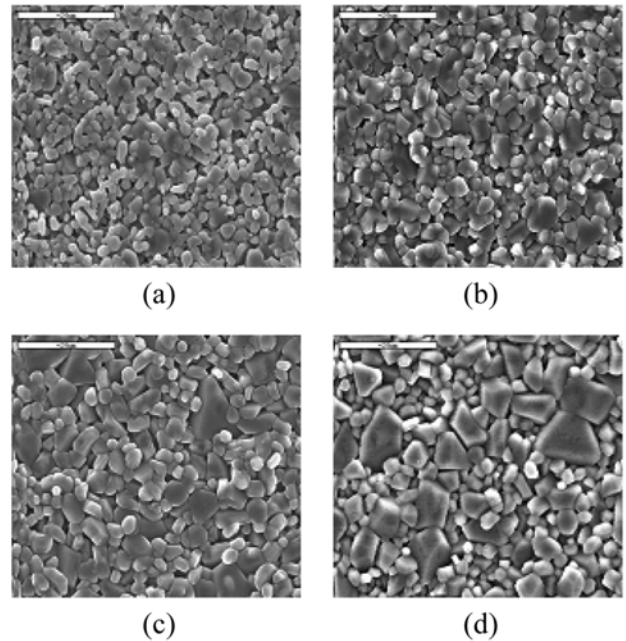
(a)



(b)

**Fig. 1.** Measurement of (a) density and (b) porosity of S1, S2, S3 and S4 sintered at various temperatures.

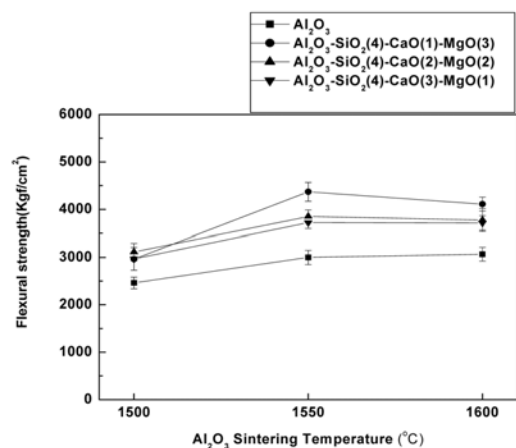
In order to examine the effect of flux additions on the sinterability of alumina ceramics, three different sintering temperatures of 1,500 °C, 1,550 °C and 1,600 °C were selected. After sintering, the resultant density and porosity of each specimen were measured and compared. As shown in Fig. 1(a), the S1 containing no flux shows the lowest density values at all sintering temperatures compared to the others. Even though the density of S1 gradually increased with an increase in the sintering temperature, the highest density value of S1 obtained at 1,600 °C was still lower than the lowest values of others obtained at 1,500 °C. The S2, S3 and S4 specimens showed similar density values at all sintering temperatures and they already approached the highest value at 1,550 °C. Fig. 1(b) shows that the porosity values of the specimens have a similar tendency to the density variation in Fig. 1(a). The S1 sintered at 1,600 °C still had a porosity of more than 15%, while the others had lower porosities. This result was explained by the theory that the added flux melts into a glass



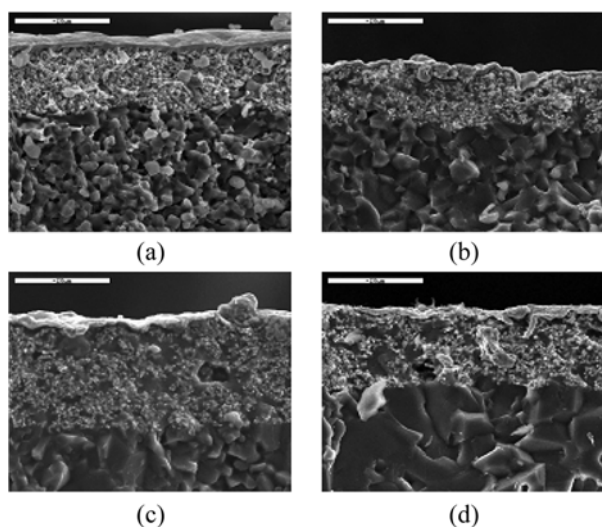
**Fig. 2.** SEM micrographs of (a) S1, (b) S2, (c) S3 and (d) S4 sintered at 1,550 °C

and the sintering process is intensified by solution and recrystallization of the alumina [6].

Fig. 2 shows SEM micrographs of alumina specimens sintered at 1,550 °C for 2 hours. It was observed that the S1 containing no flux still includes numerous voids after sintering as shown in Fig. 2(a). This fact indicated that the sintering at 1,550 °C for 2 hours was not sufficient for densification and grain growth to occur in the S1. Fig. 2(b) through (d) show the well-sintered microstructures due to the flux additions. Fig. 2(b) shows a microstructure of the MgO-rich specimen with fine grains uniformly distributed in the whole area. Fig. 2(c) and (d) indicate that the number of much larger grains increased as the amount of CaO added was increased. This result is not clearly explained yet, but it showed that a proper flux



**Fig. 3.** Measurement of bending strength of S1, S2, S3 and S4 sintered at various temperatures.



**Fig. 4.** SEM micrographs of the metallized interfaces of (a) S1, (b) S2, (c) S3 and (d) S4.

composition of MgO and CaO is important to obtain better mechanical properties of alumina ceramics.

The mechanical strength of the specimens was measured using 3-point bending tests and the resultant bend strengths are shown in Fig. 3. As expected, the S1 sample containing no flux shows the lowest strength values at all points. The other specimens containing flux show similar strength values and the S2 sample having a wholly uniform distribution of fine grains shows the highest values.

Fig. 4 shows SEM micrographs around the interfaces of specimens metallized by the Mo-Mn process. Generally, a reaction zone resulting from the flowing of glassy phases into the voids of the sintered layer is formed between the sintered metal and ceramic to obtain an excellent bond strength after metallizing [7]. Fig. 4(a) shows that the interface of the metallized S1 specimen is imperfect and numerous voids are found at the interface between layers. However, as shown in Fig. 4(b), (c) and (d), strong metal-to-ceramic joints are achieved by the capillary action where the voids in the metal layer are filled with glassy phases.

## Conclusions

The effects of composition changes of SiO<sub>2</sub>, CaO and MgO which were added to alumina ceramics on the sintering and metallizing of alumina ceramics were investigated. SEM observation revealed that the microstructures obtained at various conditions varied with the sintering temperature and flux composition. The sinterability of the alumina ceramics was enhanced by the SiO<sub>2</sub> which melted into a glassy state during the sintering process. 3-point bend tests showed the tendency that specimens containing proper amounts of flux showed higher bend strengths than nearly pure alumina ceramics. The addition of CaO and MgO seems to promote the production of a glassy state of SiO<sub>2</sub> at a lower temperature. A MgO-rich specimen showed a more uniform and finer grain distribution. The resultant interfacial microstructure of the SiO<sub>2</sub>-rich metallized alumina ceramics also showed good metallizing properties with no defects between layers. This was explained by the fact that the glassy state of the flux migrated from the ceramic base into the porous metallizing layer by capillary action.

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