# EFFECT OF ALUMINUM POWDER ON THE SYNTHESIS OF CORUNDUM-MULLITE COMPOSITES

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*Corundum-mullite composites were prepared by reaction sintering from tabular corundum, activated mullite powder, metal aluminum powder and $SiO_2$ micro powder. The effect of aluminum powder content on the synthesis and densification of the corundum-mullite was studied. All raw materials were mixed and pressed into billets with diameters of 20 mm and height of 15 mm. The green-body billets were sintered at temperature from 1100°C to 1500°C in an air atmosphere. Bulk density, apparent porosity, phase composition and microstructure of final sintered products were analyzed. The results indicated that aluminum powder can promote the densification and mullitization of corundum-mullite composites. At the same time, aluminum powder promoted the formation of columnar mullite. Among materials sintered at 1500°C for 3 h, samples with 8 % aluminum powder had the highest bulk density.*

## INTRODUCTION

Alumina ceramics are widely used for structural applications, including for armour, wear resistance applications and some others where they are exposed to severe mechanical stresses often coupled with corrosive and thermal actions [1-3]. One of the directions of modification of alumina ceramics in order to attain desirable properties is creating a secondary crystalline phase. Mullite ($3Al_2O_3 \cdot 2SiO_2$) is a characteristic constituent of all ceramic products made from aluminosilicates, and has become a candidate for a high-temperature structural ceramic, because of its excellent physical properties, such as low dielectric constant, low thermal expansion, high melting point, high resistance to creep and chemical corrosion, high temperature mechanical stability, and thus high thermal shock resistance [4-6]. Thus, mullite is considered a suitable secondary crystalline phase and corundum-mullite composites are made according to appropriate ratio of alumina and mullite [7]. This composite material has better over-all properties than pure corundum or pure mullite and has been considered one of the most promising high temperature structural ceramics for abundant raw materials and high cost-effectiveness [8-9]. At present, it is widely used as kiln furniture materials for producing soft magnetic materials and electrically insulating ceramics [10].

In the case of alumina-mullite materials, the structure and performance of bonding phase mullite directly affects and even determines the performance and application of product [11]. It has been reported that needle-like structure mullite can interleave with corundum phase and improve the strength, toughness and thermal shock resistance of the corundum-mullite composite [12]. At the same time, alumina-mullite materials are difficult to prepare because mullite is not easy sintering [13-14]. Small amounts of liquid phase have been observed to have a significant effect on the densification rate and needle-like mullite formation [15-16]. However, these liquid phases are harmful to the thermal shock resistance and service life of corundum-mullite kiln materials.

The reaction bonding of aluminum oxide (RBAO) was developed by Claussen and his colleagues [17-18]. In this technique, $Al + Al_2O_3$ powder compacts are heat-treated in air to melt and oxidize the Al metal into nano-sized $Al_2O_3$ crystallites, which bond with the originally added $Al_2O_3$ particles and co-sinter to high density. At the same time, this technique did not promote glass phase formation in samples. To a large extent, the RBAO technique has been successfully applied to produce low-shrinkage mullite ceramics by incorporating SiC into the initial $Al + Al_2O_3$ powder mixture [19]. During heat-treatment, SiC is oxidized to $SiO_2$, which reacts with the newly-formed and/or originally-added $Al_2O_3$ to form mullite. In this work, because of the large volume expansion associated with both the oxidation of SiC to $SiO_2$ (108 %), Al to $Al_2O_3$ (28 %) and with the mullite

formation (4.2 %), the sintering shrinkage is effectively compensated. Thus low-to-zero shrinkage mullite composites were prepared. However, no investigations have been made to ascertain the influence of Al content on the mullitization, crystal form and sintering of corundum-mullite composites made by RBAO technique. Therefore, in this paper, we prepared corundum-mullite composites by Al + $Al_2O_3$ + $SiO_2$ + mullite powder and studied the effect of metal aluminum content on the mullitization, crystal form and sintering of these materials.

## EXPERIMENTAL

Tabular corundum (Qingdao Almatis Co., China), activated mullite and metallic aluminum (Zhengzhou Research Institute of Light Metals, China), $SiO_2$ micro powder (Elken international trading company, Norway) were selected as raw materials. Composition and particle size of raw materials are given in Table 1.

According to the composition shown in Table 2, all raw materials were weighed and then were ball-milled in absolute ethyl alcohol for 5 h, with highly pure $Al_2O_3$ balls as a milling media. After drying at 60°C for 24 h, the powders were sieved through a 100 μm screen to break up agglomerates. The powders were then pressed at 200 MPa in a stainless-steel die into billets with a diameter of 20 mm and a height of 15 mm. The billets then were heated at 1100°C, 1300°C and 1500°C for 3 h, respectively in an air atmosphere.

Table 2. Starting mixture composition (mass %).

| Type | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Tabular corundum | 75 | 73 | 71 | 69 | 67 |
| Activated mullite | 18 | 18 | 18 | 18 | 18 |
| $SiO_2$ micro powder | 7 | 7 | 7 | 7 | 7 |
| Metallic aluminum | 0 | 2 | 4 | 6 | 8 |

Phase analysis was performed by X-ray diffractometer (D/MAX2500PC model, Rigaku Co., Japan) using Ni filtered Cu $K_\alpha$ under the following conditions: scanning speed of 2°$min^{-1}$ and temperature of 16°C. The density and porosity of the sintered specimens was measured by the Archimedes method in kerosene to avoid hydration of unreacted metal alumina powder. The microstructure was observed by scanning electron microscopy (SEM) (KYKY-2800B). Linear changes were obtained by comparing the diameter of the specimens before and after sintering. Particle size was measured by a laser diffraction method (Mastersizer 2000E, Malvern Instruments Ltd., England).

## RESULTS AND DISCUSSION

### Densification

The bulk density and apparent porosity of samples containing different content of aluminum powder are shown in Figure 1 and Figure 2, respectively. It is found that when the content of aluminum powder is less than

Table 1. Compositions (mass %) of raw materials.

| Type | $Al_2O_3$ | $SiO_2$ | $Fe_2O_3$ | $K_2O$ | $Na_2O$ | C | Al | Fe | Si | Particle size (μm) |
|---|---|---|---|---|---|---|---|---|---|---|
| Tabular corundum | 99.6 | 0.03 | 0.05 | – | 0.02 | – | – | – | – | 19.6 |
| Activated mullite | 75.24 | 22.76 | 0.36 | 0.41 | 0.1 | – | – | – | – | 3.0 |
| $SiO_2$ micro powder | 0.34 | 98.3 | – | 0.04 | 0.2 | 0.38 | – | – | – | 2.0 |
| Metallic aluminum | 0.83 | – | – | – | – | – | 98.44 | 0.06 | 0.3 | 18.5 |

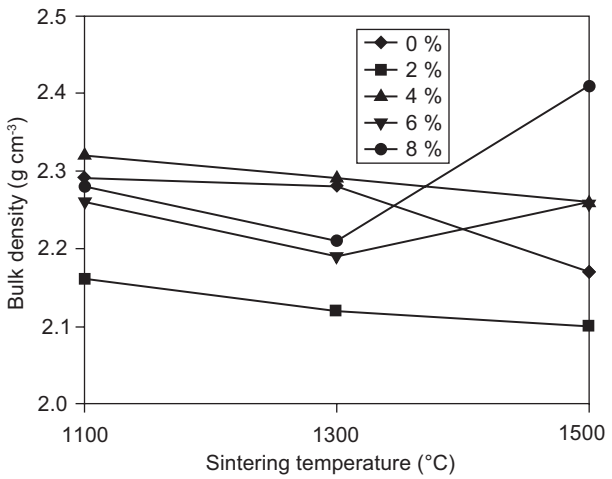



Figure 1. Bulk density of samples as a function of sintering temperature.

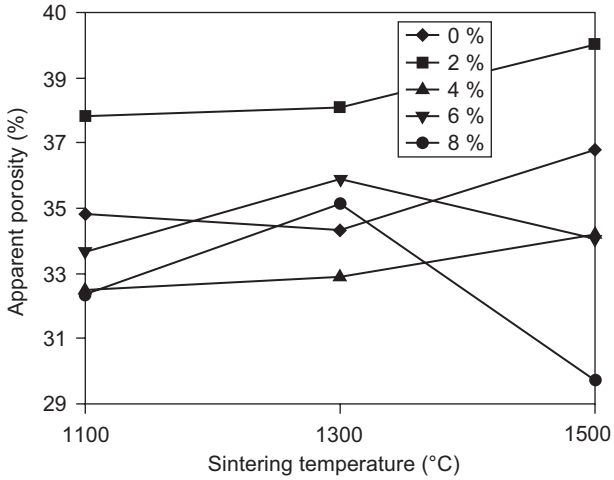



Figure 2. Apparent porosity of samples as a function of sintering temperature.

4 %, the bulk density of samples decreased and apparent porosity increased with increasing sintering temperature. However when the content of aluminum powder is higher than 4 %, the bulk density of samples first decreased and then increased with increasing sintering temperature. At the same time the apparent porosity first increased and then decreased with increasing sintering temperature. This is because the aluminum melting point is low (660°C) and alumina formed by oxidation of aluminum has higher activity. Liquid phase and high activity alumina promote mullitization at lower temperature. Thus when the content of aluminum powder is higher than 4 %, a high degree of mullitization is observed at 1300°C. The volume expansion (see Figure 3) caused by mullite reaction led to the highest apparent porosity and the lowest bulk density of samples sintered at 1300°C. As the sintering temperature increased to 1500°C, the volume shrinkage and degree of sintering increased. Thus these samples had the lowest apparent porosity and the highest bulk density at 1500°C. For the samples with the content of aluminum powder less than 4 %, mullitization moved to higher temperature ranges (1300-1500°C) due to the low content of liquid phase and of high activity alumina from oxidized aluminum powder. Thus these samples had the lowest bulk density and the highest apparent porosity at 1500°C.

From Figure 1 and Figure 2 we also found that the aluminum content 2 % led to low densification. When the content of aluminum powder is higher than 2 %, the densification of samples increased with increasing of Al powder at 1500°C. However, the densification of samples had a downward trend with the increasing of Al powder at 1100°C and 1300°C. This is also because the Al powders promote mullitization at lower temperature.

## Phase analysis

X-ray diffraction patterns of samples with different content of aluminum powder and sintering temperature are shown in Figure 4. It was found that when the sintering temperature was 1100°C, $Al_2O_3$, $SiO_2$, and mullite

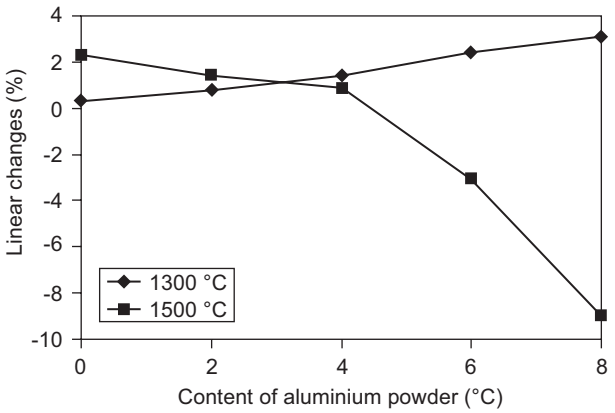



Figure 3. Linear changes in samples as a function of sintering temperature.

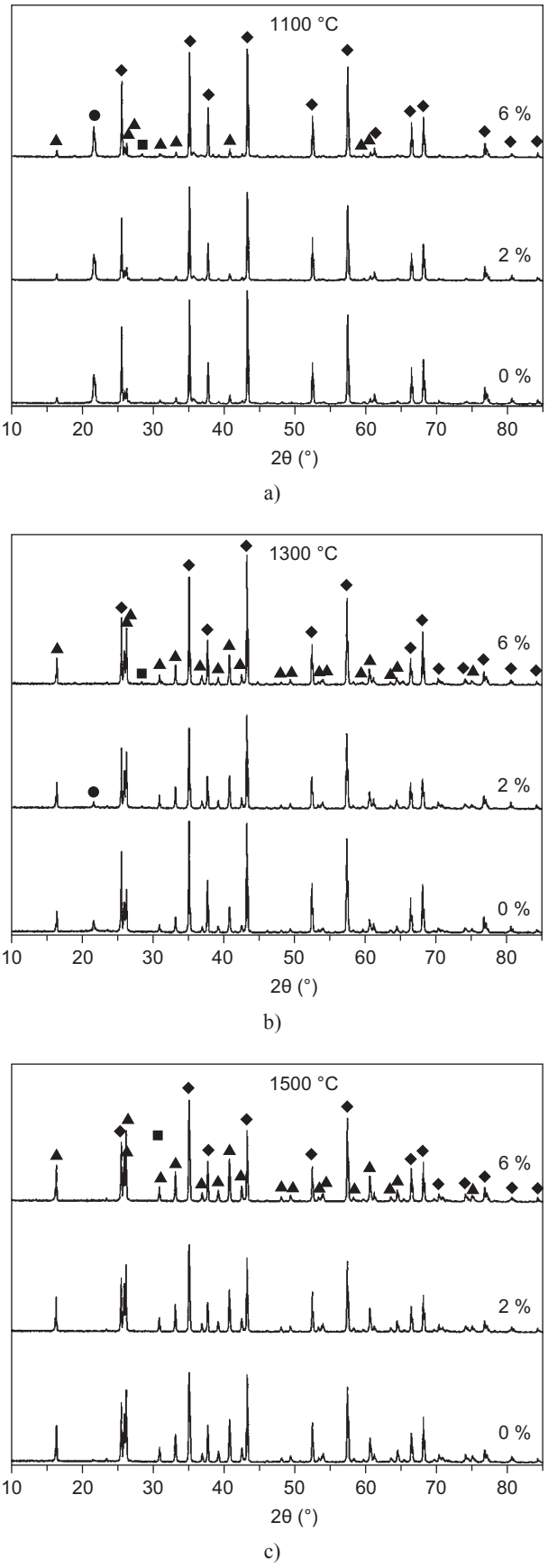
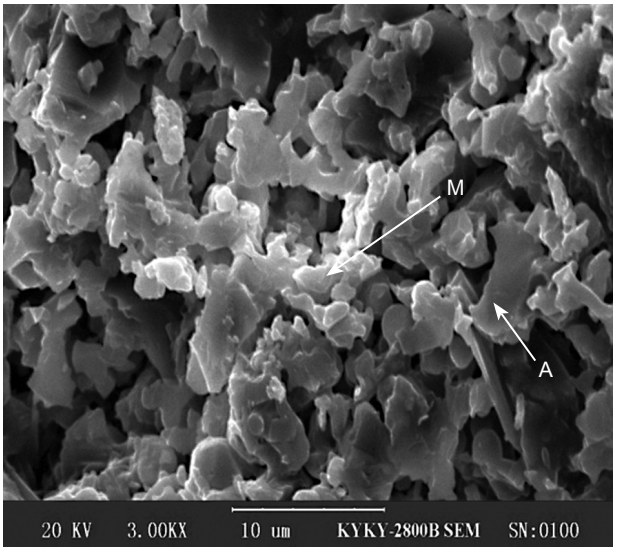
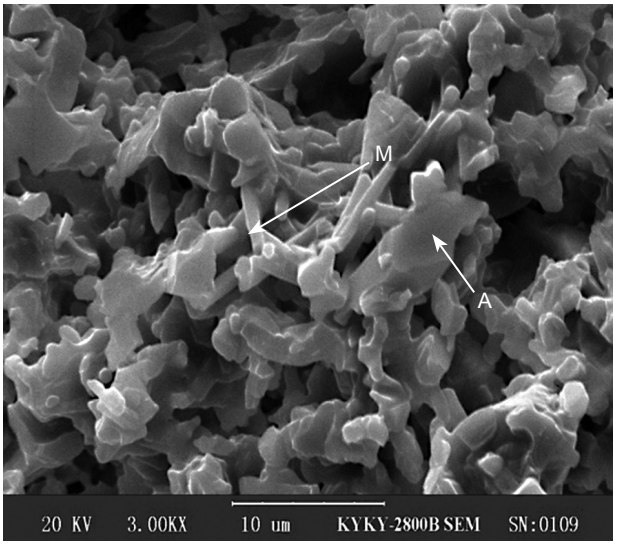


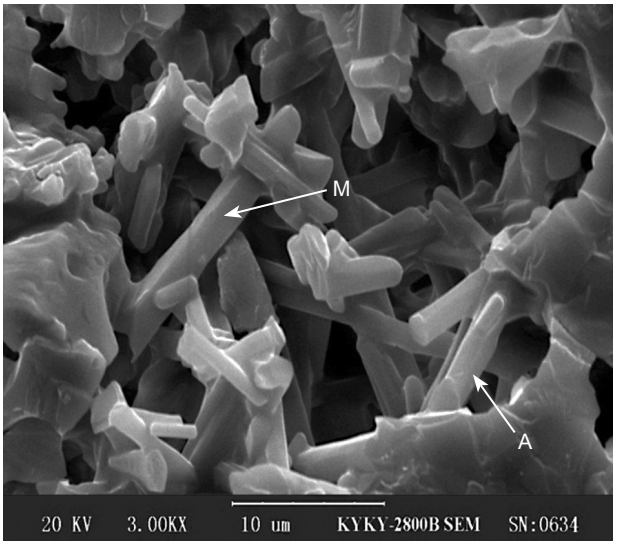

Figure 4. XRD patterns of specimens with different content of aluminum powder sintered at different temperature (● - $SiO_2$, ♦ - $Al_2O_3$, ■ - Si, ▲ - mullite).




a) 0 %




b) 2 %




c) 6%

Figure 5. SEM photographs of the samples sintered at 1500°C for 3 h (M: mullite, A: alumina).

were detected in all samples. And small amounts of Si produced by reduction of $SiO_2$ by aluminum were found in samples with 2 % and 6 % aluminum powder. After processing at 1300°C, mullite and $Al_2O_3$ were the main crystalline phases in all samples and a small amount of Si was also found in samples with 2 % and 6 % aluminum powder. Comparing X-ray diffraction patterns of the samples with different content of aluminum powder it was found that peak intensity of $SiO_2$ gradually decreased with the increasing content of aluminum powder and disappeared in case of sample with 6 % aluminum powder. This means that aluminum supports the reaction of $SiO_2$ with $Al_2O_3$ to form mullite and that all $SiO_2$ reacted to mullite at 1300°C in the sample with 6 % aluminum powder. When the sintering temperature is 1500°C, $SiO_2$ and Si are not detected, mullite and alumina are the only crystalline phases in all samples. This indicated that $SiO_2$ in sample with 2 % and 0 % also converted to mullite.

## Microstructure

Scanning electron micrographs of the samples with different content of aluminum powder sintered at 1500°C for 3 h are shown in Figure 5. Figure 5 shows that at the same sintering temperature, the grain size and morphology of mullite in the sample change with different content of aluminum. In the sample without aluminum powder, grain size of mullite and corundum is small. At the same time, mullite crystals were found in granular and poorly developed columnar form. The grain size of samples with 2 % aluminum powder is larger than that of the sample without aluminum powder, and a small amount of shorter length, needle-like mullite particles can been observed. As for the samples with 6 % aluminum powder, grains of corundum and mullite developed large and intertwined. Most of mullite developed needle-like structure and grew together. Clearly, aluminum powder promoted the formation of columnar mullite. This is because molten aluminum wets some mullite and $SiO_2$ grains. According to the two dimensional nucleation theories [20-21], the interface wetted by molten aluminum has small nucleation potential barrier, large nucleation rate and fast moving rate. This supports the growth of columnar crystals on the wetting interfaces. Therefore, columnar mullite content in corundum-mullite material increased with the increasing content of aluminum powder. This is consistent with the reports in the literature that liquid phase is advantageous in forming the columnar mullite [22].

## CONCLUSION

The results above lead to the following conclusions:

- Aluminum powder can promote the densification of corundum-mullite composites. When the content of aluminum powder is less than 4 %, samples have the

lowest bulk density at 1500°C. At the same time, when the content of aluminum powder is more than 4 %, samples have the lowest bulk density at 1300°C.

- Aluminum powder is beneficial to mullitization of samples. $SiO_2$ of sample with 2 % aluminum powder completely converted to mullite at 1500°C. However, $SiO_2$ in sample with 6 % aluminum powder completely converted to mullite already at 1300°C.
- At the same sintering temperature, the grain size and morphology of mullite in the samples varied with the change of aluminum powder content. The grain size of samples with 6 % aluminum powder was larger than that of samples with 2 % and 0 % aluminum powder. At the same time, aluminum powder promoted the formation of columnar mullite. Columnar mullite content in corundum-mullite material increased with increasing content of aluminum powder.

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