Microstructural Behavior of Alumina Aggregate Compacts Prepared by Transient Liquid Phase Sintering

Seung-Jae Lee, Hai-Doo Kim*, Deuk-Yong Lee** and Dae-Joon Kim***

Department of PWR Fuel Development, Korea Nuclear Fuel Co., Ltd., Taejeon 305-353, Korea
*Ceramic Material Group, Korea Institute of Metal & Machine, Changweon 641-010, Korea
**Department of Metallurgical and Materials Engineering, Daelim College of Technology, Anyang 431-715, Korea
***Division of Ceramics, Korea Institute of Science and Technology, Seoul 136-791, Korea
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Although alumina aggregates have been used as refractory aggregates due to the improved mechanical properties of refractories as a result of the low contraction of alumina aggregates, the aggregates have a difficulty in fabrication due to its low sinterability. Two types of alumina aggregates and a fused alumina aggregate containing transient liquid forming additives are prepared to investigate the sintering characteristics of aggregates. Al_2O_3 rich composition in the Al_2O_3-MgO-SiO_2(-TiO_2) system is chosen for the transient liquid phase sintering and the final recrystallized bonding phase between grains inside the fused alumina aggregates is found to be a needle-like mullite phase. The flexural strength of alumina bars, reaction-bonded using the paste having a composition of Al_2O_3-MgO-SiO_2-TiO_2, is about 78 MPa, which is one half value of that of pure alumina.

Key words: Alumina aggregate, Fused alumina, Mullite, Transient liquid phase sintering

I. Introduction

A lthough the sinterability and the densification of alumina, prepared by liquid phase sintering at low temperatures, are enhanced, high temperature properties of
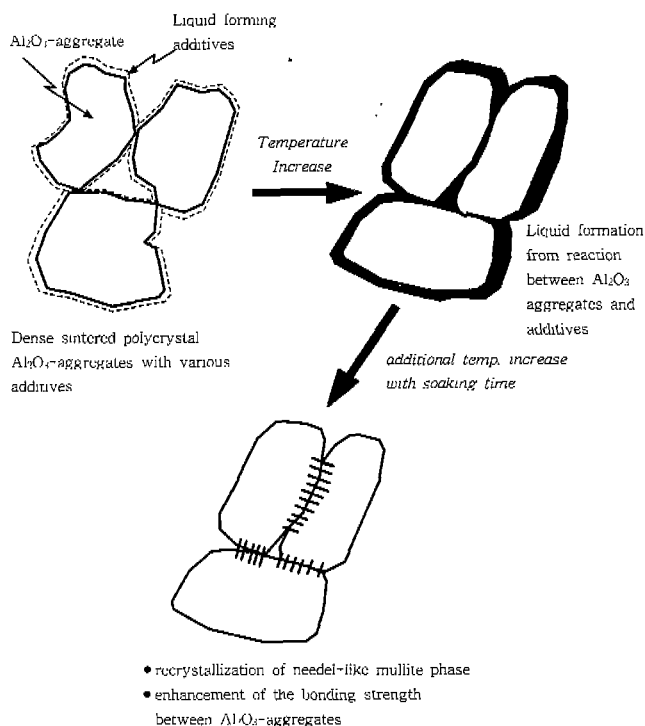

Fig. 1. Schematic representation of the recrystallization of liquid phase between aggregates by transient liquid phase sintering.

alumina are degraded severely due to the existence of liquid phase along the grain boundary. In order to alleviate this problem, a transient liquid phase sintering method is proposed to obtain the special microstructure of ceramics. It is well known that the liquid phase present in the initial stage of the transient sintering is dissipated completely through the recrystallization process during the sintering procedure, resulting in the formation of the needle-like mullite phase and consequently improved high temperature properties, as shown in Fig. 1.[1] In the binary system Fe-Cu,[2] Cu powders are melted to liquid phase at low temperature and then this liquid phase is dissipated into the Fe lattice, consequently resulting in the densification of the alloy iron. In the system Al_2O_3-$MgTiO_3$,[3] liquid phase is formed at 1520°C due to the formation of $MgTiO_3$ and then only Al_2O_3 solid solution remains after sintering at 1650°C. In the ternary system Al_2O_3-MgO-SiO_2, liquid phase begins to occur at 1365°C and then this liquid phase transforms to solid phases, such as mullite, spinel, and forsterite, by the reaction between the solid phase and the reactive liquid phase. Therefore, recrystallization of liquid phase is attributed to final microstructure and bonding phase of the resulting solid phase.[4]

In the Al_2O_3-MgO-SiO_2 (+TiO_2) system, three different types of Al_2O_3 aggregates were prepared, in this study, to investigate the influence of the transient liquid phase sintering on the densification and the high temperature properties of alumina solid solution.

II. Experimental Procedure

MgO (Magnesiumacetate, Merck, Germany), SiO_2 (Type S, Aerosil, Degussa, Germany), TiO_2 (Isoprophytitanat,

Dynamit-Nobel, Germany), Al_2O_3 (A-16 SG, 99.5%, Alcoa, USA), Boehmite (NB 400, VAW, Germany), and fused Al_2O_3 (Mullimil, Germany) were used as the starting powders. An experimental procedure is dipicted in Fig. 2. Three different types of alumina were employed for the preparation of alumina aggregates. Firstly, A-16 Al_2O_3 powders were prepared by adding 300 ppm MgO and 0.3 wt% PEG into A-16 Al_2O_3. The milled powders were sieved to pass a 100 mesh screen and granulated using the clindrical roller. The Al_2O_3 granules were sintered for 2 h at 1600°C. Secondly, 2 wt% of α-Al_2O_3 seed (particle size: 0.5~0.8 μm), that was prepared by the sedimentation method, and 500 ppm MgO were added to Boehmite powders (specific area: 230 m^3, average particle size: 0.008 μm). Then, α-Al_2O_3 was obtained from Boehmite powders by using a sol-gel method.[5-7] These powders were sintered for 1 h at 1450°C. Lastly, fused Al_2O_3 was used for the alumina aggregate.

For the preparation of additives, a mixture of 75 wt% SiO_2(Aerosil) and 25 wt% MgO(Mg-acetate) was mixed using a distilled water. The dried and milled powders were presintered for 3 h at 1350°C, resulting in the formation of cristobalite and enstatite $(MgSiO_3)$. In the system MgO-SiO_2-TiO_2, a 2 wt% TiO_2(Isoprophytitanat), which is a ratio of TiO_2 to the total weight of MgO and SiO_2, was added to the system and presintered for 3 h at 1350°C. Additives were added to three different alumina aggregates by 5, 10,

and 20 wt% and a 0.3 wt% of PVA binder was also added. The powders were milled using a pestle and mortar and sintered in the temperature range of 1400 to 1550°C with different time.

The bar specimens for bending test were fabricated by bonding the two bars using a viscous paste and then dried for 24 h at 60°C. A viscous paste was prepared by adding 12 wt% of PEG binder to the same composition of the additives as above mentioned. The bonded bar specimens were calcined for 3 h at 700°C and then sintered for 1 h at 1500°C. For the mechanical property measurements, the specimens were ground to a size of 43 mm×25 mm×25 mm. The flexural strength was measured using a three-point bending according to DIN 51048.

Thermal linear shrinkage of the small bar specimens(5 mm×5 mm×25 mm) was assessed using a dilatometer(Linseis, Germany) with a heating rate of 5°C/min in the temperature range of room temperature to 1500°C. For the cylindrical specimens, the area change was evaluated to determine the thermal linear shrinkage by using a high-temperature microscopy with a heating rate of 10°C/min in the temperature range of room temperature to 1450°C. The bulk density of the specimens was determined by the Archimedes method. Microstructural behavior of alumina aggregate compacts was investigated using scanning electron microscopy and X-ray diffractometry.

III. Results and Discussion

The linear shrinkage variation of the A-16 specimen doped with 5 wt% MgO-SiO_2 is plotted in Fig. 3 as a function of temperature with high-temperature microscopy. In Fig. 3, the highest shrinkage of the specimen is observed at temperatures between 1420°C and 1460°C, which is higher than 1355°C of the eutectic point in the system Al_2O_3-MgO-
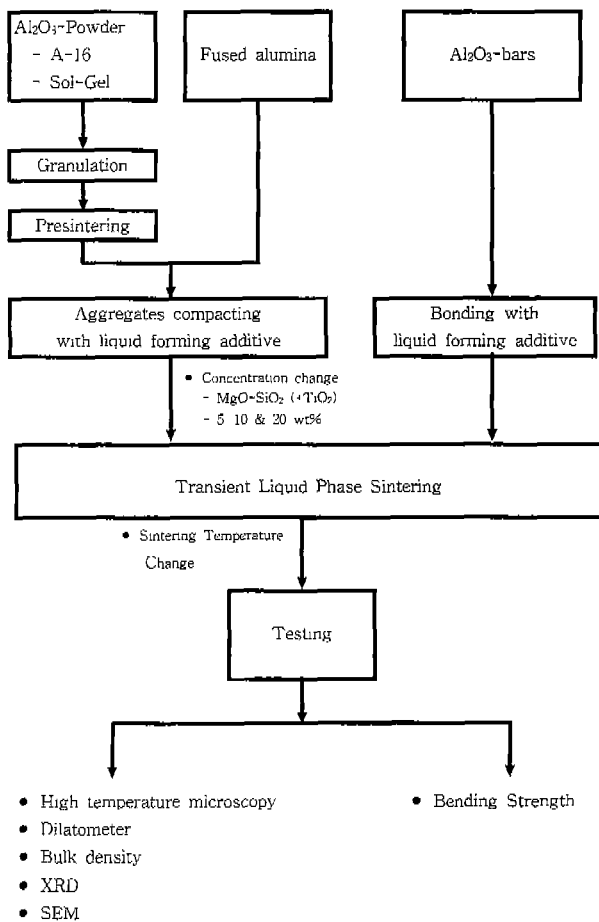

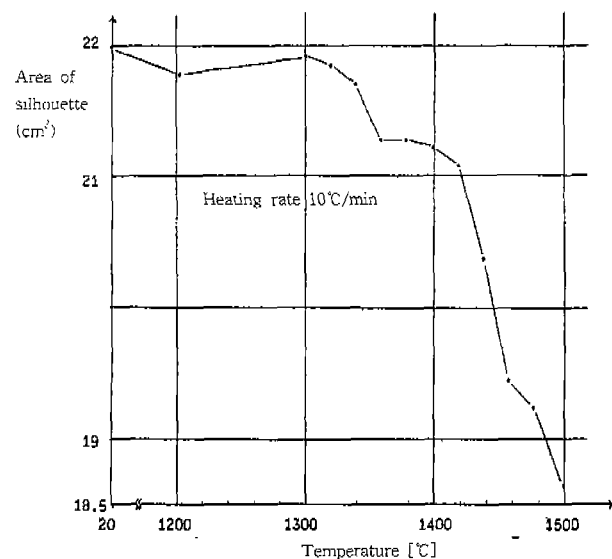Fig. 2. Flow chart for the experimental procedure.

Fig. 3. Shrinkage variation of the A16 alumina aggregates doped with 5 wt% MgO-SiO_2 as a function of temperature. The shrinkage of the specimen is obserbed by using a high temperature microscopy.
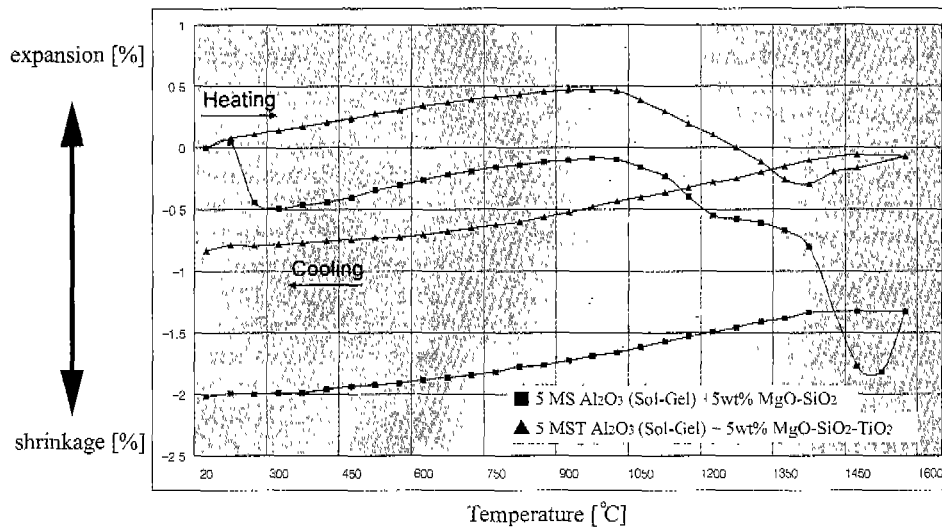
Fig. 4. Linear shrinkage variation of the aggregates having two different types of additives, prepared by sol-gel method, as a function of temperature.

SiO_2. It indicates that the formation of liquid phase in this system is retarded due to the loss of reactivity as a result of presintering of the aggregates.

The alumina aggregates, prepared by the sol-gel method, show different shrinkage behavior as depicted in Fig. 4. The specimen alloyed with 5 wt% MgO-SiO_2 (5MS) shows the highest linear shrinkage at 1473°C and then its shrinkage decreases due to the formation of mullite and spinel. However, the aggregate (5MST), doped with TiO_2 in addition to 5 wt% MgO-SiO_2, shows relatively low linear shrinkage at temperatures from 1400 and 1450°C. From the above test results, it is concluded that the liquid phase in MgO-SiO_2 system is strongly formed in temperature range of 1400 to 1450°C and in MgO-SiO_2-TiO_2 system slowly formed under 1400°C.

Bulk density of three types of alumina aggregates specimens is depicted in Figs. 5 and 6 as a function of the amount of additives and sintering conditions, respectively. In Fig. 5, as the additive content increases, the density decreases

since the density of newly formed phases, such as mullite, spinel and cordierite, is lower than that of alumina and the extent of these phases increases. The highest density is observed for the specimen having 5 wt% additives, and warping phenomenon is found for the specimen containing 20 wt% additives. Both the fused alumina and the alumina prepared by sol-gel method, doped with MgO-SiO_2-TiO_2, shows better density than those doped with MgO-SiO_2 probably due to the difference in viscosity of formed liquid phase. In Fig. 6, the bulk density of the fused alumina specimens is higher than that of the aggregates prepared by sol-gel method due to the enhancement of the liquid phase sintering effect through no grain boundary of fused alumina aggregate.

From the observation of XRD, four types of phases, corundum, spinel, cordierite and cristobalite, exist at 1400°C, but
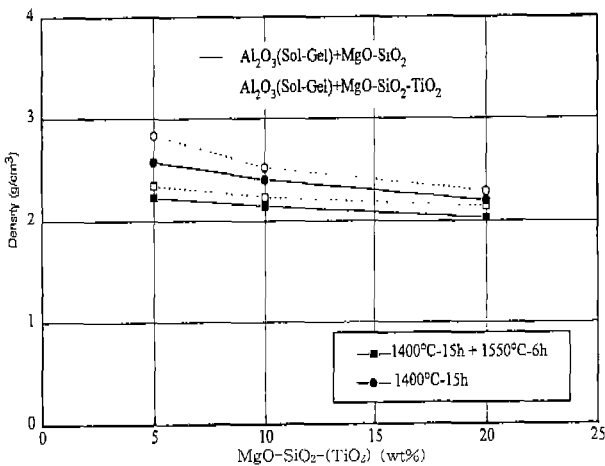

Fig. 5. Bulk density of the alumina aggregates having two types of additives, prepared by sol-gel method, doped with 5 wt% MgO-SiO_2-(TiO_2) as a function of sintering condition.

□ 5MS : sol-gel-Al_2O_3+5wt% MgO-SiO_2

▤ 5MST : sol-gel-Al_2O_3+5wt% MgO-SiO_2-TiO_2

▨ 5MS1 : fused Al_2O_3+5wt% MgO-SiO_2

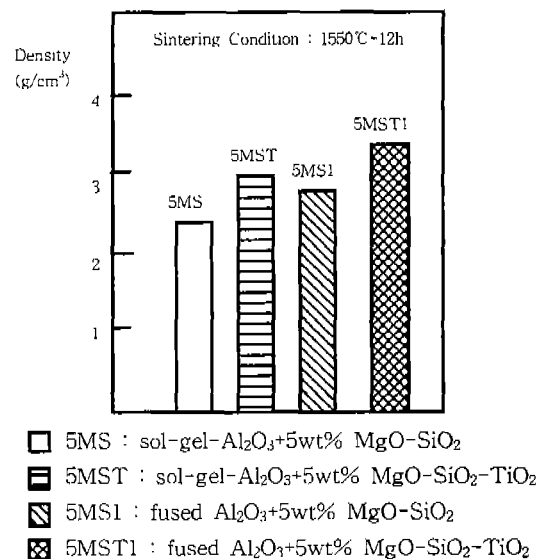▩ 5MST1 : fused Al_2O_3+5wt% MgO-SiO_2-TiO_2

Fig. 6. Bulk density of the specimen, prepared by sol-gel method and fused alumina. The specimens were sintered for 12 h at 1550°C.
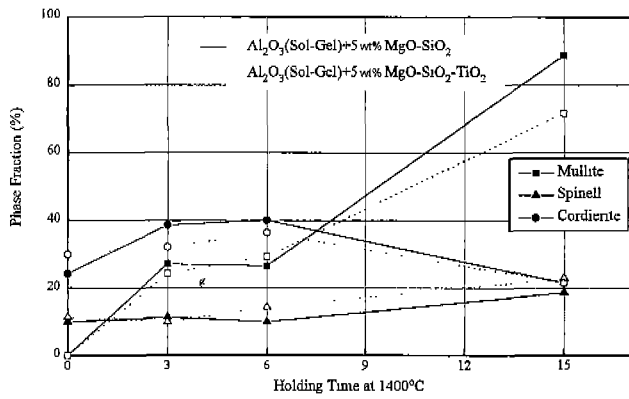
Fig. 7. Fraction of phases of the alumina aggregates as a function of sintering time. The specimens were sintered at 1400°C.
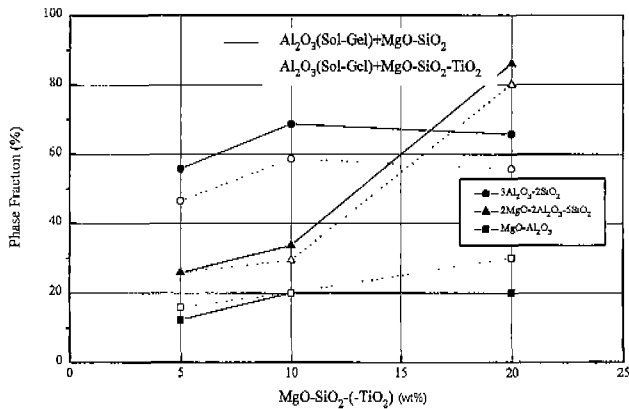

Fig. 8. Fraction of phases of the alumina aggregates, prepared by sol-gel method, as a function of amount of additives. The specimens were sintered for 15 h at 1400°C.

Fig. 9. Scanning electron micrographs of the A-16 alumina aggregates doped with 5 wt% $MgO-SiO_2$. The specimens were sintered for 12 h at 1550°C.

Fig. 10. Scanning electron micrographs of the alumina aggregates, prepared by sol-gel method, doped with 5 wt% $MgO-SiO_2$. The specimens were sintered for 12 h at 1550°C.

Fig. 11. Scanning electron micrographs of the fused alumina aggregates doped with 5 wt% $MgO-SiO_2-TiO_2$. The specimens were sintered for 12 h at 1550°C.

the mullite phase begins to form as the sintering time increases, as shown in Fig. 7. The mullite content increases sharply with the increase of sintering time as shown in Fig. 7. On the other hand, the cordierite phase starts to decrease after sintering for 6 h at 1400°C and then disappears after sintering above 1500°C. In Fig. 8, although the phase difference of aggregates doped with 5MS and 5MST is indistinguishable, the amount of cordierite increases when the specimens are doped with more than 10 wt% additives, but the fraction of spinel and mullite remains to be almost constant.

The liquid phase was visible along the grain boundary inside the A-16 aggregates as a result of the reaction between the liquid phase and the aggregate grains, as depicted in Fig. 9. It was reported that the alumina aggregates prepared by sol-gel method, sintered for 1 h at 1450°C, show 99% of relative density and dense microstructure,[7] but the liquid phase is still observed along the grain boundary inside aggregates, as shown in Fig. 10. Microstructure of fused alumina aggregates doped with $MgO-SiO_2(+TiO_2)$ is shown in Fig. 11. In Fig. 11, fused alumina aggregates are bonded by the liquid phase due to the reaction between the fused alumina and the additives, showing the typical round grain shape by liquid phase sintering. The 5MS and 5MST
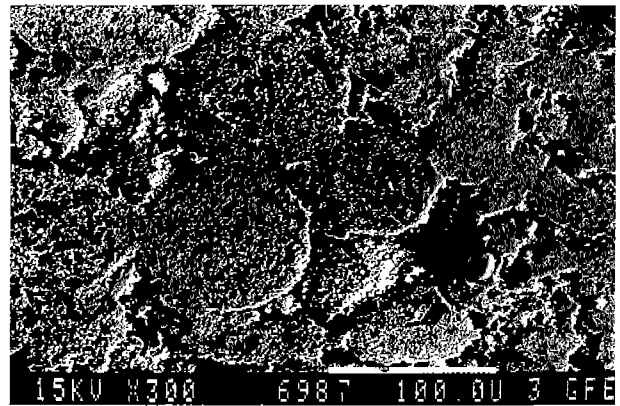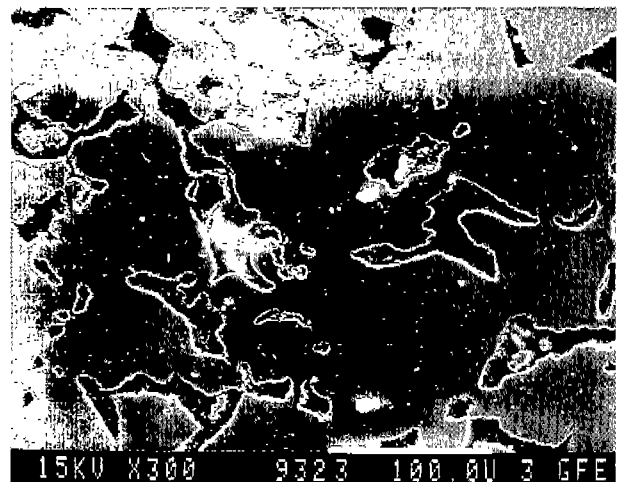
specimens show the similar morphology and the mullite phase along grain boundary is visible.

A flexural strength of pure alumina bar is 170 MPa. Pure alumina bars bonded with the paste, sintered for 1 h at 1500°C, shows a flexural strength of 78 MPa. This value is one half of that of pure alumina. However, a flexural strength of bars bonded with the paste having a composition of MgO-SiO$_2$ is not measurable due to the low strength.

IV. Conclusions

In the system Al$_2$O$_3$-MgO-SiO$_2$(+TiO$_2$), the liquid phase occurs in the temperature range of 1400 to 1450°C and the mullite phase starts to recrystallize from the liquid phase when the sintering time increases. The bulk density of alumina aggregates is influenced by the additive content. The highest density is observed for the specimens having 5 wt% of additives, but the specimens are degraded severely with increasing the additive content.

It is observed that complete wetting along grain boundary inside aggregate occurs for the A-16 alumina and the alumina prepared by sol-gel method, but the mullite phase is recrystallized along the grain boundary for the fused alumina aggregates. The flexural strength of the specimen, bonded by the paste having a composition of MgO-SiO$_2$-TiO$_2$, was about 78 MPa, which was one half value of that of pure alumina.

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