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Injection-Molded Alumina Prepared with Mg-Containing Binders

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It is generally accepted that MgO additions enhance the sintering of alumina. The distribution of the low concentration required is, however, difficult to attain and critical to the final properties and microstructures. To improve the MgO distributions in ceramic injection-molded (CIM) alumina, Mg-containing precursors, Mg-stearate and Mg-acetate, were added during the kneading step of the CIM process, and the results were compared with those from adding MgO particles. Of the three additives, the Mg-stearate showed the highest sintered density and bending strength. This was attributed to its high molecular weight and it being able to mix with other binder components homogeneously in the liquid state, which leads to a better distribution of the MgO. In contrast, the MgO powder was kneaded in the solid particle form, and its distribution was not uniform. The Mg-acetate also imparted poorer MgO distribution because the liquid Mg-acetate dehydrated in the early stage of the kneading and formed solid lumps before it was well mixed into the binder system. The resulting sintered densities and bending strength using these two additives were, therefore, inferior to those for specimens in which Mg-stearate was used.

I. Introduction

It is generally accepted that the addition of a small amount of MgO to alumina promotes densification and facilitates the preparation of alumina with near-theoretical density.[1,2] Because of the low concentrations needed, proper distribution of the MgO is difficult to attain and is critical to the properties of the resulting material. A number of methods have been used using Mg-containing chemicals, such as Mg-nitrates,[3–6] Mg-stearates,[6] Mg-acetates,[6–8] and Mg-carbonates.[9,10] In most studies, these chemicals were dissolved in a solvent or water prior to being mixed with alumina powders. The mixed powder slurries were milled and calcined to form the desired MgO particles. Most results showed that these Mg-containing chemicals allowed better-sintered properties than the straight MgO powders.

To make parts with complex shapes, ceramic injection molding (CIM) is frequently chosen as the preferred manufacturing process.[11] This process starts with the kneading of the ceramic powder and the binder. The kneaded feedstock is then molded, debound, and sintered. To attain high sintered density CIM alumina, MgO-doped alumina powders can be used. It is possible, however, that the MgO can be provided by adding Mg-containing precursors during kneading and then heating the powder mixture in air to form the needed MgO particles. In our preliminary study, Mg-containing chemicals, such as Mg-stearate, Mg-acetate, Mg-carbonate, and Mg-nitrate, which have been used for pressed-and-sintered parts in previous studies, were selected as candidates. Because the binder system used in this laboratory consists of polypropylene, paraffin wax, and stearic acid, the first selection criterion of these Mg-containing precursors was that they have a melting point below 169°C, which is the melting point of polypropylene. This eliminated Mg-carbonate and Mg-nitrate, the melting points of which were too high. Thus, Mg-acetate and Mg-stearate were selected for further studies. Because very little work has been reported on the effects of Mg-containing chemicals on the properties and processes of CIM alumina, an attempt was thus made in this study to examine whether the Mg-acetate and Mg-stearate are effective MgO dopants.

II. Experimental Procedure

Table I lists the characteristics of the alumina powder used in this study. It had an average particle size of 1.8 μm. To prepare the CIM specimens, alumina powders at 85 wt% or 56.8 vol% were kneaded with a multi-component binder, which consisted of 30 wt% polypropylene, 65 wt% paraffin wax, and 5 wt% stearic acid. To add the MgO, three methods were used. The first method was to add fine MgO powders that had a BET surface area of 18 m^2/g. The second method was to add Mg-stearate ($Mg(C_{18}H_{35}O_2)_2$), and the third, to add Mg-tetrahydrate acetate ($Mg(C_2H_3O_2)_2 \cdot 4H_2O$). The molecular weights of MgO, Mg-stearate, and Mg-acetate are 40.3, 590.7, and 214.3 g/mol, respectively. The amounts of these three additives were calculated so that the final MgO contents were 580, 1050, 1400, and 1760 ppm. The stearic acid and the polypropylene contents were kept constant in all specimens, while the amount of paraffin wax varied depending on the content of the MgO, Mg-stearate, and Mg-acetate.

To prepare the feedstock, the alumina powder was heated in a Σ-blade kneader to 190°C and held at that temperature for 1 h to dry out the absorbed moisture. After drying, polypropylene was mixed into alumina and kneaded for 15 min. The kneader was then cooled to 150°C and held there for 20 min to mix the paraffin wax. Stearic acid and Mg-containing precursors were then added into the mixture and kneaded for another 20 min.

The feedstock was molded into flat specimens, 4 mm × 12 mm × 100 mm, using the barrel, nozzle, and mold temperatures of 140°, 145°, and 40°C, respectively. To remove the binder in the molded specimen, specimens were immersed in heptane for 3 h at 60°C to remove about 90% of the soluble binder. The solvent-debound specimens were then heated at 2°C/min to 250°C, held there for 2 h, and then heated at the same rate to 450°C. After the removal of the remaining binder components, the specimens were heated again at a rate of 5°C/min to 1000°C and held there for 3 h so that the parts had reasonable strength to sustain the subsequent handling. The cycle time for thermal debinding was about 12 h.

The debound specimens were sintered in air at 1650°C for 3 h. After the sintering, the density was measured using the Archimedes method, and the bending strength was tested on surface-ground specimens using a four-point bend tester. To ensure that the binder had been successfully removed, the carbon content in the specimen was measured with a carbon analyzer (LECO CS-244, LECO Co., St. Joseph, MI). For microstructure examinations, specimens were polished and then thermally etched by heating at 5°C/min to 1500°C and being held there for 1 h. The microstructures were examined using a scanning elec-

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Table I. Characteristics of the Alumina Powder Used in this Study

Designation	A-43M
Average particle size (laser scattering)	1.8 μm
Surface area (BET) (m^2/g)	5.0
Carbon content (%)	0.0496
Loss on Ignition	0.35%
Pycnometer density (g/cm^3)	3.95
Supplier	SDK Co., Tokyo, Japan

tron microscope. The mean grain size was calculated using the equation: $D_m = 1.5\ L_i$, where L_i is the mean grain intercept of 10 random lines.[12] The standard deviations were also given to illustrate the uniformity of the grains. These specimens were also examined for the uniformity of MgO by an electron probe micro-analyzer (EPMA, JXA-8600SX, JEOL Co., Tokyo, Japan). Wavelength dispersive spectra were taken on 50 areas, all with the sizes of 0.25 mm × 0.25 mm. When a magnesium peak was detected, Mg mapping was then performed.

III. Results

(1) Thermal Analysis

Table II shows the melting points of the binder components measured by the differential scanning calorimeter. The melting points of the Mg-stearate and the Mg-acetate were 120° and 73°C, respectively. These were lower than the 169°C for polypropylene. Thus, both Mg-stearate and Mg-acetate can be kneaded with alumina powders and other binder components without any modification to the existing kneading process, in which the highest kneading temperature used was 190°C.

Figure 1 shows the TGA curves of the Mg-stearate, Mg-acetate, and MgO. It can be seen that the decomposition of Mg-stearate occurred between 200° and 480°C and about 7 wt% residue was left after it was heated to 700°C. This amount was close to the 6.8 wt% calculated from the chemical formula. The X-ray diffractometer analysis showed that this residue was MgO.

The Mg-tetrahydrate acetate, on the other hand, had two stages of decomposition. The first stage occurred between the melting point of 73° and 150°C. After being heated to 150°C, the weight loss was about 33.0%, which agreed with the water content of 33.6% calculated from the formula of Mg-tetrahydrate acetate. The second stage of the weight loss began at 340°C and ended at about 435°C. After the specimen was heated to 700°C, 18.0 wt% MgO residue was left, which was close to the calculated 18.7%.

To further understand the thermal behavior of Mg-tetrahydrate acetate, the powder was placed in a beaker and heated in an oven. It was observed that the Mg-acetate melted at 73°C and the water contained in the acetate started to evaporate. After being heated to 150°C, the dehydration was complete and pure Mg-acetate was left in the form of solid lumps. This suggests that the Mg-tetrahydrate acetate, although can be mixed in the liquid form during kneading at 150°C, it will transform into solid Mg-acetate as kneading proceeds. Therefore, its mixing behavior is in the solid state on a particle scale, similar to that of the MgO particle.

Table II. Melting Points of the Binder Components Measured by the Differential Scanning Calorimeter

Type	Melting point (°C)
Mg-stearate	120
Mg-tetrahydrate acetate	73
Stearic acid	72
Paraffin wax	70
Polypropylene	169

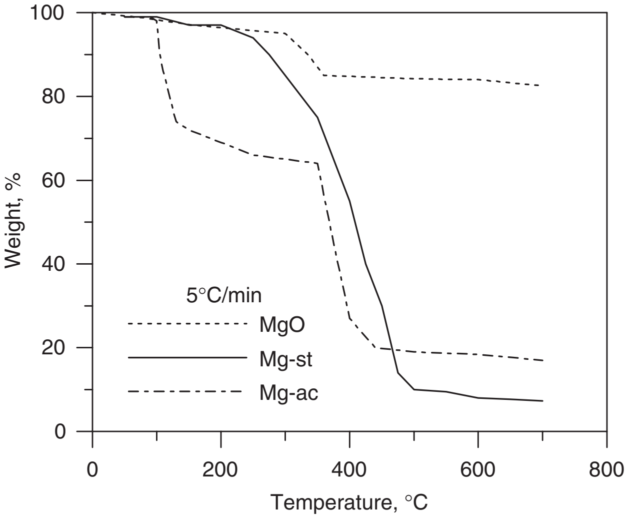

Fig. 1. Thermogravimetric curves of Mg-stearate, Mg-acetate, and MgO.

The MgO powder also showed weight loss of about 16 wt% after being heated to 700°C. An X-ray diffractometer was thus used to examine the compositions in the as-received MgO powder and the powder that had been heated to 700°C. The diffraction patterns shown in Fig. 2 confirmed that the $MgO \cdot xH_2O$ was present in the as-received powder.

(2) Debinding

To examine the solvent debinding behavior of each binder component, a solvent dissolution test was performed. The results showed that paraffin wax and stearic acid could be dissolved in heptane, while Mg-stearate and Mg-acetate were insoluble. The weight loss data of the molded specimens suggest that 95% of the soluble binders, i.e., paraffin wax and stearic acid, were extracted after solvent debinding. The solvent-debound specimens were subsequently thermally debound in air. Previous literature has indicated that the carbon left behind by the binder will impede the sintering of alumina.[13,14] Thus, the carbon content was monitored to ensure that it did not impair sintering. The results show that the carbon contents in all the specimens were similar

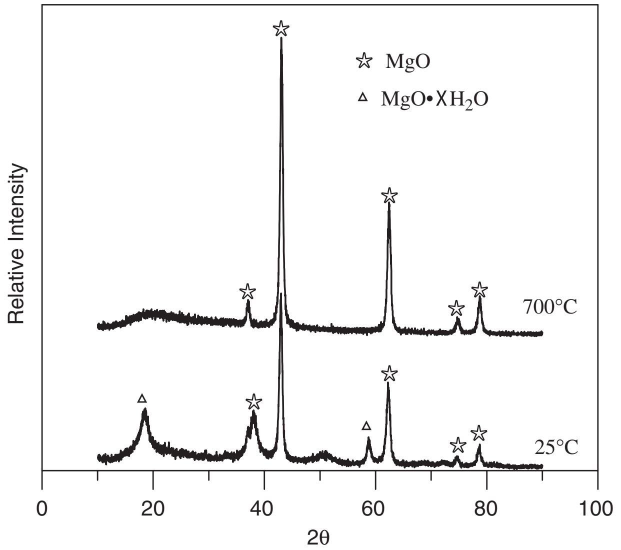

Fig. 2. X-ray diffraction patterns of the MgO before and after being heated to 700°C in air.

to that of the as-received alumina. This confirmed that the organic materials did not leave residues and thus impede the subsequent sintering.

(3) Sintered Density

Figure 3 shows the densities of the sintered specimens. When the amount of Mg-stearate increased, the density increased, reaching a maximum of 96.0%, and then decreased slightly. The parts with the addition of MgO particles exhibited a similar trend. However, the maximum density was only 95.4%, which was obtained with 1400 ppm MgO additions. When Mg-acetate was used, the densities were slightly lower than those attained using MgO particles. In all specimens that were prepared with MgO or Mg-containing precursors, the density passed through a maximum and then decreased slightly as the MgO content further increased. The same trend was also reported by Peelen[15] and was believed to be caused by the presence of the second phase.

(4) Microstructure

The microstructure examination supports the previous density results. Figure 4(a) shows the microstructure of sintered alumina without any Mg-containing additives. The grain sizes were not uniform. Typical large grains with tabular shapes were present, indicating grain boundary energy anisotropy. The pores were quite irregular in shape. The fracture surfaces shown in Fig. 4(b) indicate that most of the fractures are of the transgranular type. Poorly sintered areas are clearly shown and are indicated by the arrows. Figures 5–7 show the microstructures of the specimens that contain 1050 ppm MgO and were prepared using MgO particles, Mg-acetate, and Mg-stearate, respectively. With MgO powders or Mg-acetate, the density was improved, tabular grains disappeared, and the grain size was much more uniform than that of the pure alumina. However, the pore shapes were still quite irregular. The localized low-density areas, as shown in Fig. 5(b) and Fig. 6(b), while less than that in the pure alumina, were still present, indicating a poor MgO distribution. When the Mg-stearate was used, the uniformity of the grain size and the density were both improved. The pores were also more rounded. These microstructure results are in agreement with those reported for pressed-and-sintered alumina.[6]

Table III shows the average size of the grains shown in Figs. 4–7. The grains in pure alumina are the smallest among the four specimens. However, its standard deviation is the highest, at 3.7 μm, or 71% of the mean value, because of the presence of tabular grains. When MgO was added, the grain size increased slightly, as in previous findings.[1,15] The grain size uniformity also improved. Mg-acetate and Mg-stearate also show grain sizes similar to those of the MgO-added alumina. It is noted that

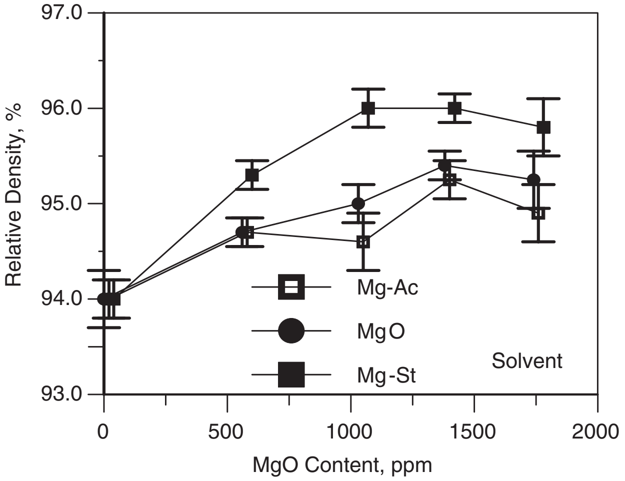

Fig. 3. Sintered densities of the specimens increases as the amount of MgO increases.

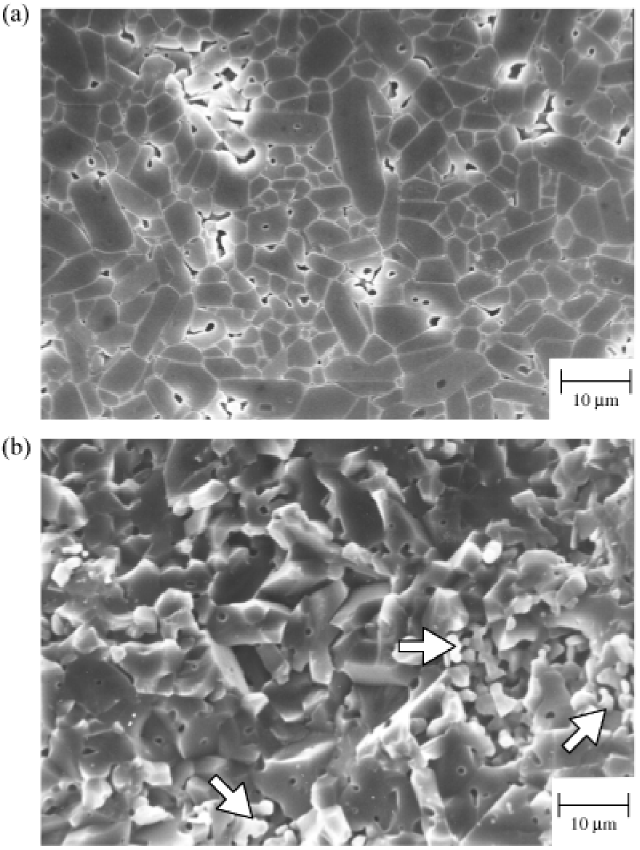

Fig. 4. (a) Microstructure and (b) fracture surface of alumina without MgO additions showing tabular grains and some poorly sintered areas, as indicated by the arrows.

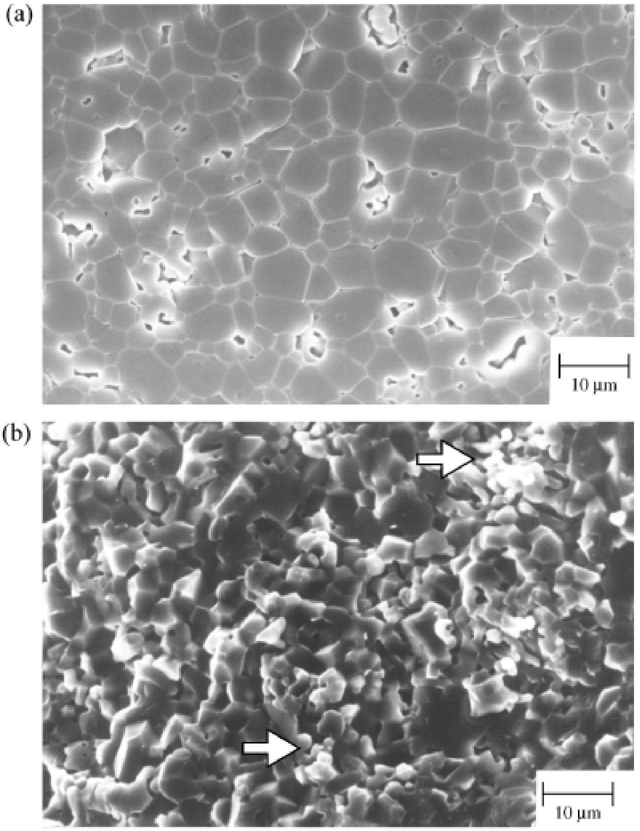

Fig. 5. (a) Microstructure and (b) fracture surface of alumina with 1050 ppm MgO powder additions showing some poorly sintered areas, as indicated by the arrows.

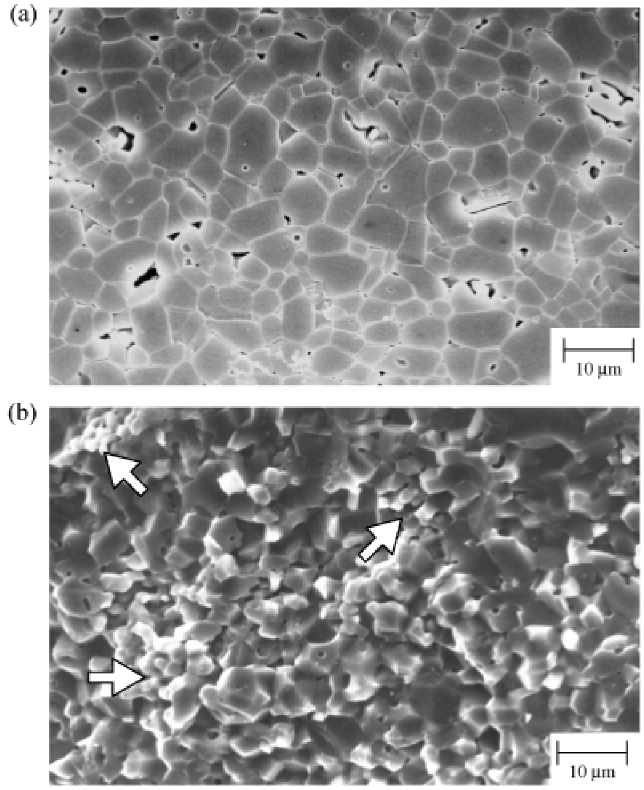

Fig. 6. (a) Microstructure and (b) fracture surface of alumina with 1050 ppm MgO formed from the Mg-acetate showing some poorly sintered areas, as indicated by the arrows.

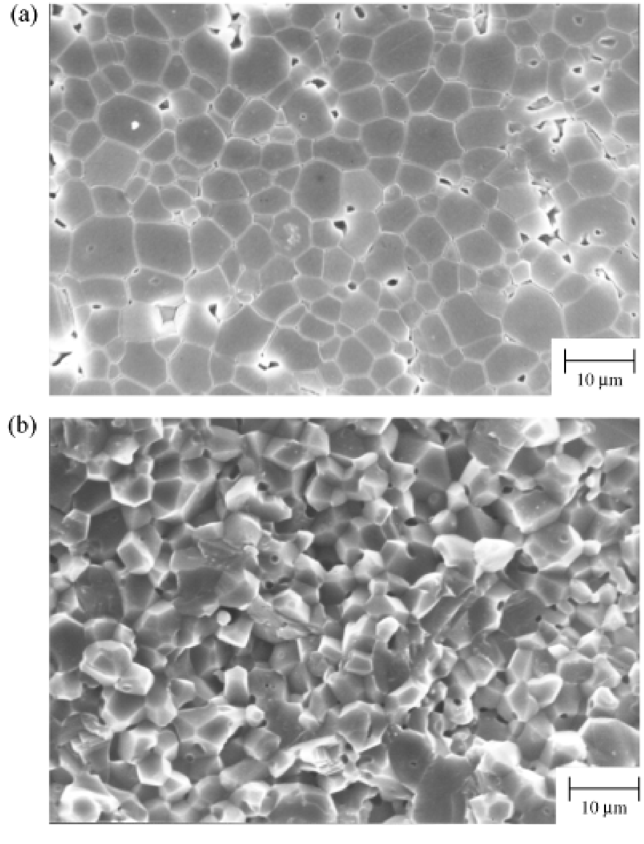

Fig. 7. (a) Microstructure and (b) fracture surface of alumina with 1050 ppm MgO formed from the Mg-stearate showing evenly sintered microstructures.

Table III. The Average, Maximum, Minimum, and Standard Deviation of the Grain Size of the Sintered Alumina Shown in Figs. 4–7 Measured Using the Line-Intercept Method

	Pure alumina	MgO	Mg-acetate	Mg-stearate
Average grain size (μm)	5.2	6.0	5.7	6.8
Standard deviation (μm)	3.7	2.9	2.9	2.9
Maximum grain size (μm)	21.7	12.9	10.8	13.4
Minimum grain size (μm)	0.8	1.6	1.2	1.2

the MgO addition promotes grain growth and the density. The smaller grains in the less dense pure alumina are mainly attributed to the presence of the larger amount of pores, which act as grain growth inhibitors.

The uniformity of the MgO distribution was examined by EPMA. Fifty areas, all 0.25 mm × 0.25 mm, were scanned for each specimen. Figure 8 demonstrates one area of the specimen that was prepared using the Mg-acetate. It shows the presence of MgO-rich areas. No such areas were found in specimens with Mg-stearate additives or MgO.

(5) Mechanical Properties

The bending strength results shown in Fig. 9 illustrate that the pure alumina had a low strength of 195 MPa. When Mg-stearate was used, the strength increased as the amount of MgO increased, reaching 302 MPa at 1400 ppm MgO. As the MgO further increased, the strength decreased. This is very possibly caused by the formation of the second phase, which also has a similar effect on the density.[15] In comparison, the maximum strengths of the alumina with the addition of MgO powders and with the Mg-acetate were lower, at 255 and 238 MPa, respectively.

IV. Discussion

The present work shows that the MgO powders are less effective sintering aids than the Mg-stearate. One of the reasons is that it has a high density or low specific volume, and a low molecular weight of 40.3 g. Thus, to add the same amount of MgO, such as 1050 ppm, only 0.065 vol% of MgO powders is present in the feedstock. In contrast, the molecular weights of Mg-acetate and Mg-stearate are 214.3 and 590.7 g, respectively. To attain 1050 ppm MgO, 0.893 vol% of Mg-acetate and 3.40 vol% of Mg-stearate are required. Thus, the 52 times greater volume of the Mg-stearate provides more uniform MgO distribution and requires shorter homogenization time.

Moreover, the Mg-stearate has a low melting point of 120°C and thus can be mixed with other binder components homoge-

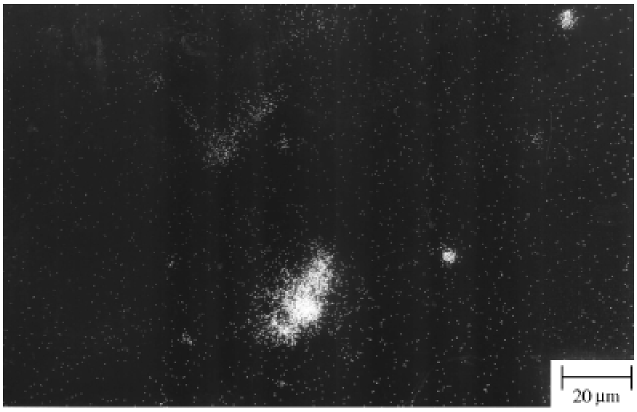

Fig. 8. Mapping of the Mg element in a specimen that was processed with the Mg-acetate.

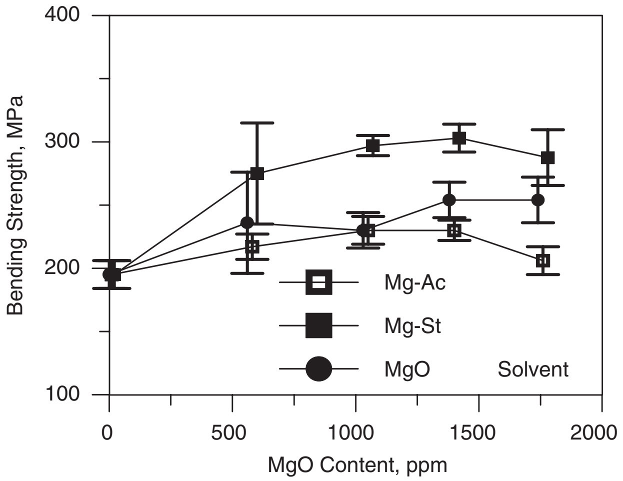

Fig. 9. Bending strength increases as the amount of MgO increases.

neously in the liquid form during kneading at 150°C. In contrast, when fine MgO powders are used, they have to be mixed in the solid particle form. On the other hand, Mg-acetate, despite also being in the liquid form at the kneading temperature of 150°C, did not provide better results than the Mg-stearate or even the MgO powder. The most likely reason is that, as it is heated, it melts at 70°C and begins to dehydrate between 70° and 150°C, as indicated by the TGA curve shown in Fig. 2 and the vapor observed during kneading. Once it dehydrates, it forms solid lumps. This means that if the dehydration occurs slowly, the Mg-acetate can still be mixed well into the feedstock while it remains a liquid. However, if Mg-acetate dehydrates before it is well distributed in the mixing material, the Mg-acetate loses its liquid form and thus its advantage of being mixed uniformly. When such a case happens, the MgO distribution of the Mg-acetate could even be worse than that of the straight MgO particles, as the MgO lump needs to be further pulverized. As indicated by the presence of the MgO-rich area in Fig. 8, early dehydration was very likely the case that occurred in this study. Therefore, the Mg-acetate and MgO had similar sintered densities, as shown in Fig. 3, while the use of high molecular weight Mg-stearate allows better MgO distribution, and thus a higher sintered density is obtained.

In addition to the effect of MgO distribution on the sintered densities, the microstructures and fracture surfaces shown in Figs. 4–7 also indicate that the pore shape was affected. When Mg-stearate was used, the pore size was smaller and the shape was more rounded than in specimens using MgO powder and Mg-acetate. Because pores with irregular shapes act as flaws and stress concentration regions, the bending strengths of Mg-stearate-containing specimens were thus higher than those of others.

V. Conclusions

The density and microstructure of injection-molded alumina are significantly influenced by the MgO doping method. The addition of MgO particles does not provide homogeneous distribution and, thus, lower sintered densities and bending strengths were obtained. The use of magnesium acetate, a MgO precursor, did not improve the dispersion either, as Mg-acetate dehydrated and became solid in the early stage of kneading before it was well mixed with the other components and alumina powders. Thus, it provided no advantage over the method of adding straight MgO particles. When high molecular weight magnesium stearate was used, the MgO precursor was intimately mixed into the binder system in the liquid state. The uniform distribution of the MgO, which formed during debinding, led to better-sintered properties than possible when using the straight MgO particles and Mg-acetate.

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