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Aqueous powder coating methods for preparation of grain boundary engineered ceramics

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Abstract

Coated powders provide a mechanism for uniform incorporation of inorganic dopants into ceramics, resulting in improved control of microstructures, grain boundary phases and properties. Incorporation of inorganic dopants into polymeric additive systems is a novel method of coating powders in aqueous suspension. Controlled adsorption of polymer–cation complexes can be used to coat powder surfaces in a suspension, which can be subsequently spray-dried without dopant segregation. This method streamlines the coating process, making it economical for large scale manufacturing. Two alumina formulations with controlled grain boundary chemistry were used as model systems to develop these methods. Alumina with 2.5% magnesium aluminosilicate glass grain boundary phase was prepared and sintered. The conventional mixed powder method was compared with sol–gel coated powder prepared in an alcohol–water solvent, and powder spray-dried from a suspension containing silicone emulsion with added magnesium stearate. The sol–gel coated powder densified at a temperature 100°C below that required for the conventional mixed oxide powder system. Poor mixedness from the emulsion method hindered microstructure development. High purity alumina with Mg-rich grain boundaries was prepared by coating particles with a Mg–polyacrylic acid chelate adsorbed from aqueous solution. Uniform distribution of magnesium at grain boundaries resulted in microstructure with uniform grain size for MgO additions as low as 100 ppm, while 400 ppm MgO was required to obtain similar microstructure using the mixed powder method. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Grain boundaries; Grain growth; Microstructure-final; Sol–gel process

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1. Introduction

Controlled microstructure and grain boundary chemistry are critical for reliable performance of many electronic ceramic components.[1] Important electronic and dielectric phenomena associated with semiconductors, dielectrics and ferroelectrics depend on small amounts of dopants and counterdopants that reside at grain boundaries in devices such as metal oxide varistors, PTCR thermistors and IBL capacitors. Microstructure development is also critically dependent on grain boundary chemistry. Sintering aids enhance diffusion at interfaces and grain growth inhibitors modify grain boundary movement. Uniformity of distribution of inorganic additives is critical for achieving uniform microstructure and reliable performance of grain boundary controlled devices.

A method that has been successfully utilized for processing a range of ceramics for electronic applications is the use of sol–gel coated powders.[2–5] Powders that have been coated with sintering aids and dopants have been repeatedly shown to sinter at lower temperatures and have more uniform microstructures than powders processed using the conventional method of mixing the additives in powder form. With coated powders, the additives are uniformly distributed over the surface of the powders in the green state, thus the diffusion distances and times are significantly reduced. In addition to improved properties resulting from more uniform microstructures and better dopant distribution, compositional changes that occur in some materials as a result of the loss of volatile components such as lead, tin and zinc, can be reduced by the lower sintering temperatures needed when coated powders are used. A disadvantage of sol–gel coated powders is that extra processing steps required to coat the powders can be difficult to incorporate into existing manufacturing systems.

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In this work, a new approach is proposed whereby the inorganic additives are incorporated into the polymeric additive systems that are required for green processing. The inorganic additives are uniformly distributed on the powder surfaces due to chemical and physical interactions between the polymers and the powder surface. This approach to coating powders eliminates the extra processing steps associated with conventional sol–gel methods, thus making coated powders a feasible method to introduce into an existing manufacturing system.

A number of novel processing routes have been identified to allow powder coating to be incorporated into conventional processing methods. These include in situ sol–gel coating where the gelation reaction occurs during normal mixing, emulsion methods, use of organometallic compounds, and formation of chelated complexes between adsorbed organic additives and inorganic ions. Silicone oil, in the form of an aqueous emulsion, was used as a sintering aid in alumina ceramics by Neergaard.[6] Polyacrylic acid (PAA) is a commonly used organic additive for ceramic powder processing, acting as either a deflocculant or a binder, depending on molecular weight. It is well known that PAA forms chelated complexes with multivalent cations. Thus, PAA was selected as a chelating agent for addition of inorganic cations in this work. A similar approach has been reported for nonaqueous systems by Caballero et al.,[7,8] who showed that adsorption of zinc stearate onto powder in isopropanol-based suspensions was an effective method of adding small amounts ($<1\%$) of zinc into barium titanate ceramics.

Alumina was selected as a model system for this study because its sintering behavior is well known. Two commonly used methods of processing alumina are (1) addition of talc and kaolin to form a glassy grain boundary phase which promotes densification via liquid phase sintering, and (2) addition of a small amount (~0.05%) of MgO to act as a grain growth inhibitor in reactive submicron alumina powder. In each case, the additives form grain boundary phases which control the development of the microstructure during sintering. Thus, these systems can be used to evaluate the effectiveness of different methods of distributing minor amounts of inorganic additives and dopants.

2. Experimental procedure

2.1. 97.5% Alumina

A set of three samples of 97.5% alumina composition were prepared in order to compare the conventional mixed powder method with a commonly used sol–gel method and an emulsion method. Alumina powder (A152SG, Alcoa Inc., Pittsburgh, PA) with mean particle size 1.3 μm and specific surface area of 5.9 m^2/g was used for these experiments. Magnesium and silicon ions were added to form a glassy grain boundary phase using the three methods. For the mixed powder method, 1.72% talc (Talcron MP40-27, Barretts Minerals Inc., Easton, PA) and 0.95% kaolin (Edgar Plastic Kaolin, Feldspar Corporation, Atlanta, GA) powders were added to the alumina and ball milled with water and 0.26% PAA deflocculant (Darvan 821A, R.T. Vanderbilt, Norwalk, CT) and 3.0% polyethylene glycol binder (Carbowax Compound 20M, Union Carbide Corporation, Danbury, CT). For the emulsion method, silicon was added in the form of 1.9% silicone oil (200 Fluid, Dow Corning Corporation, Midland, MI) and magnesium was added as 7.19% magnesium stearate (Witco Corporation, New York, NY). Slurry was formed by ball milling the powder and additives in water with 6% deflocculant and 5% surfactant (Tween 80, ICI Americas Inc., Bridgewater, NJ). These rather large amounts of deflocculant and surfactant were needed to stabilize the emulsion and disperse the magnesium stearate powder. These two slurries were spray-dried in a mixed flow spray-dryer with a pneumatic nozzle (Bowen No. 1, Niro Inc., Columbia, MD). Sol–gel coated powder was prepared by adding 41.1 g of alumina to a solution prepared by mixing 2.2 g of tetraethyl orthosilicate dissolved in 30 ml ethanol with 1.21 g of magnesium acetate tetrahydrate dissolved in 20 ml of water. The pH was adjusted to 3.33 by adding HCl, and the suspension was gelled by heating to 60°C for 2 days. No additional binder was added to the sol–gel coated powder. The powders were compacted in a steel die to about 90 MPa to obtain green density between 2.31 and 2.41 g/cm^3, and fired to 1500°C in a dilatometer (Innovative Thermal Systems, Almond, NY) to measure sintering behavior. Additional compacts were fired to 1600°C in a tube furnace.

2.2. 99.9% Alumina

A chelation approach was used to add magnesium to high purity alumina. In order to follow manufacturing methodology commonly used by industry, a set of 99.9% alumina samples was prepared by spray-drying slurries containing PAA deflocculant (Darvan 821A) and polyethylene binder (Carbowax Compound 20M). These samples were prepared from high purity alumina (A39SG, Alcoa Inc., Pittsburgh, PA) with mean particle size 0.5 μm and specific surface area of 10.0 m^2/g and from a similar alumina (A16SG, Alcoa Inc., Pittsburgh, PA) with particle size 0.5 μm and specific surface area 10.1 m^2/g, and containing 0.04% high purity MgO powder (added by the vendor). The two grades of alumina are prepared from the same Bayer process feed stock by the vendor. The A39SG undergoes an additional washing step to reduce the sodium content and does not contain the added MgO.[9] The two alumina powders were blended to give a final MgO contents of 0, 50, 100, 200 and 400 ppm by the mixed powder method. These powders were compared with powders prepared using the chelation method, using PAA and magnesium acetate. Slurries with solids content of 40 vol.% were prepared by ball milling the alumina in deionized water for 8 h, with the PAA deflocculant. The deflocculant consists of a PAA solution that is neutralized with NH_4OH and contains 40% solids. Viscosity was measured using a rotating cylinder viscometer (Model LVDT, Brookfield Engineering Laboratories, Stoughton, MA) at a shear rate of 12.7 s^{-1}. For the chelation method, additional PAA was required to obtain low viscosity. After ball milling, the binder was added in the form of an aqueous solution at a level of 3.0% polymer based on the dry weight of the alumina powder, and the slurries were spray-dried. The resulting granulated material was compacted to 70 MPa and sintered in air, heating at 5°C/min with a 30-min soak at 1650°C. Sintered density was measured using mass and geometry. Microstructure was analyzed using a scanning electron microscope on fracture surfaces.

3. Results

3.1. 97.5% Alumina

Fig. 1 shows the sintering behavior of the three samples prepared from 97.5% alumina. The shrinkage curve of the specimen prepared from the sol–gel coated powder was shifted to a lower temperature by about 100°C, compared to the specimen prepared using the mixed powder method. Because of the uniform distribution of Mg and Si ions over the powder surface, and mixing of the additive ions on a atomic scale, sintering behavior occurred at a lower temperature for the sol–gel coated powder. In contrast, reaction of talc and kaolin powders involves diffusion distanced on the order of the particle size before the liquid grain boundary phase can form. The powder prepared using the emulsion method did not sinter to high density. The onset of densification was at a temperature between that of the other two specimens, but densification stopped after a small amount of shrinkage. The density of this material (see Table 1) was only 82.8% after firing to 1600°C, compared to 93.8% for the material prepared with powder additives. The emulsified silicone droplets provided a method to distribute Si uniformly at the powder surfaces, but the magnesium stearate is insoluble in both silicone oil and water, and was not distributed on a molecular level, thus hindering the formation of the glassy liquid phase. Consequently, the specimen was unable to sinter to high density. The shift in the cooling curve at 450°C for this specimen is from a displacive phase transformation of tridymite[10] indicating the presence of crystalline silica and confirming the incomplete incorporation of the Si into a liquid phase.

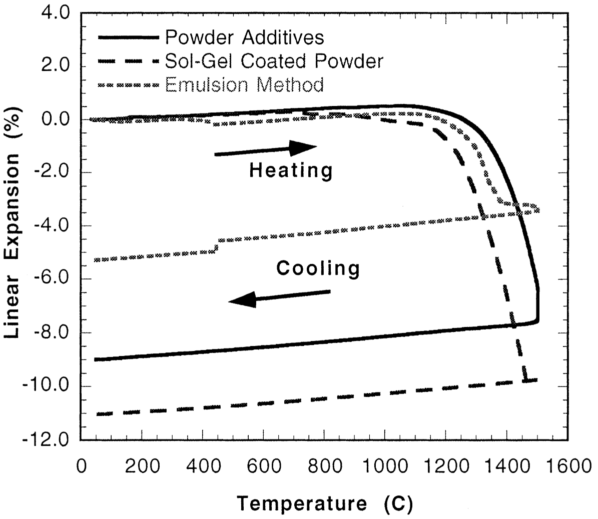


Fig. 1. Shrinkage behavior of 97.5% alumina compositions.

3.2. 99.9% Alumina

When the slurries were prepared for the 99.9% alumina specimens, addition of magnesium acetate at the levels required for the final compositions to contain 100, 200 and 400 ppm MgO caused the slurries to coagulate into viscous pastes. Additional deflocculant (see Table 2) was required to obtain viscosity in the desired range of 80–100 mPa s (measured at a shear rate of 12.7 s^{-1}).

Table 1
Sintered density of 97.5% alumina specimens[a]

Method	Density at 1500°C (%)	Density at 1600°C (%)
Powder additives	74.4	95.2
Sol–gel coated	76.7	–
Emulsion method	61.0	84.1

[a] Theoretical density = 3.90 g/cm^3.

Table 2
Magnesium acetate and PAA deflocculant amounts used to prepare 99.9% alumina slurries with viscosity of 80–100 mPa s by the chelation method

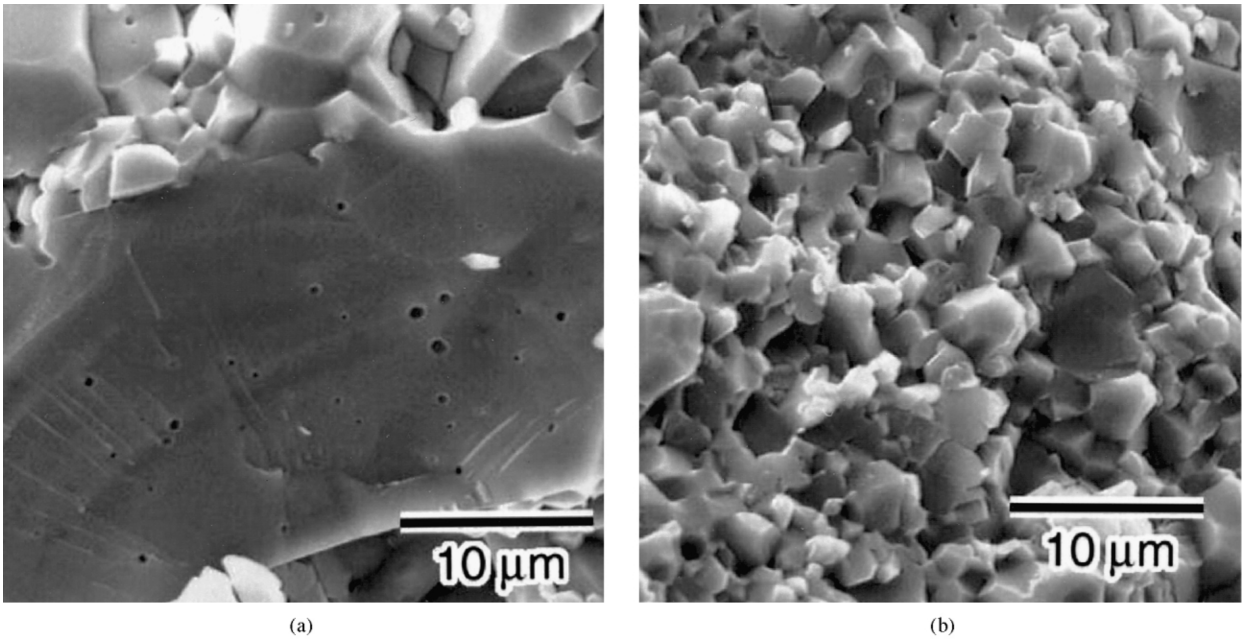
MgO level (ppm)	$Mg(C_2H_3O_2)_2 \cdot 4H_2O$ (wt.% of dry powder)	Darvan (wt.% of dry powder)	$Mg^{2+}:COO^-$
0	0	0.75	0.000
50	0.027	0.75	0.037
100	0.053	0.95	0.057
200	0.106	1.15	0.095
400	0.213	1.35	0.157

Coagulation occurred as a result of chelation of Mg^{2+} ions by the PAA, reducing the effectiveness of the PAA as a deflocculant. While the alumina powder can normally be dispersed with 0.75 wt.% of the deflocculant, up to 1.35% was required in the presence of Mg^{2+} ion at the levels added in this study. There are two possible explanations for this behavior. Chelation occurs by the formation of ionic bonds between negatively charged carboxyl side groups of the polymer and the positively charged magnesium cations. Dispersion of alumina by PAA is by an electrosteric mechanism combining both a steric component due to adsorbed molecules and an electrostatic component due to the charged polymer sidegroups. Formation of the chelate reduces the number of negatively charged groups that contribute to the electrostatic component of dispersion. Additionally, presence of any non-chelated Mg^{2+} in the suspending liquid compresses the electrical double layer at the powder surface. Both of these effects reduce the repulsive potential between alumina particles, resulting in destabilization of the suspension and in an increase in viscosity. Addition of excess PAA was found to reduce the suspension viscosity to an acceptable level. Excess PAA was not required in the case of the slurries prepared using the mixed powder method.

MgO has been known to act as a grain growth inhibitor in alumina for almost 40 years, since the pioneering work by Coble.[11] The exaggerated grain growth that occurs in the absence of MgO is illustrated in Fig. 2, which shows typical microstructures that resulted from sintering compacts prepared without MgO [Fig. 2(a)] and with 400 ppm MgO [Fig. 2(b)] using the mixed powder method. In Fig. 2(b), grains are of fairly uniform size of less than 5 μm while, in Fig. 2(a), a single grain has dimensions exceeding the 30 μm dimension of the photomicrograph, while other grains have sizes less than 5 μm.

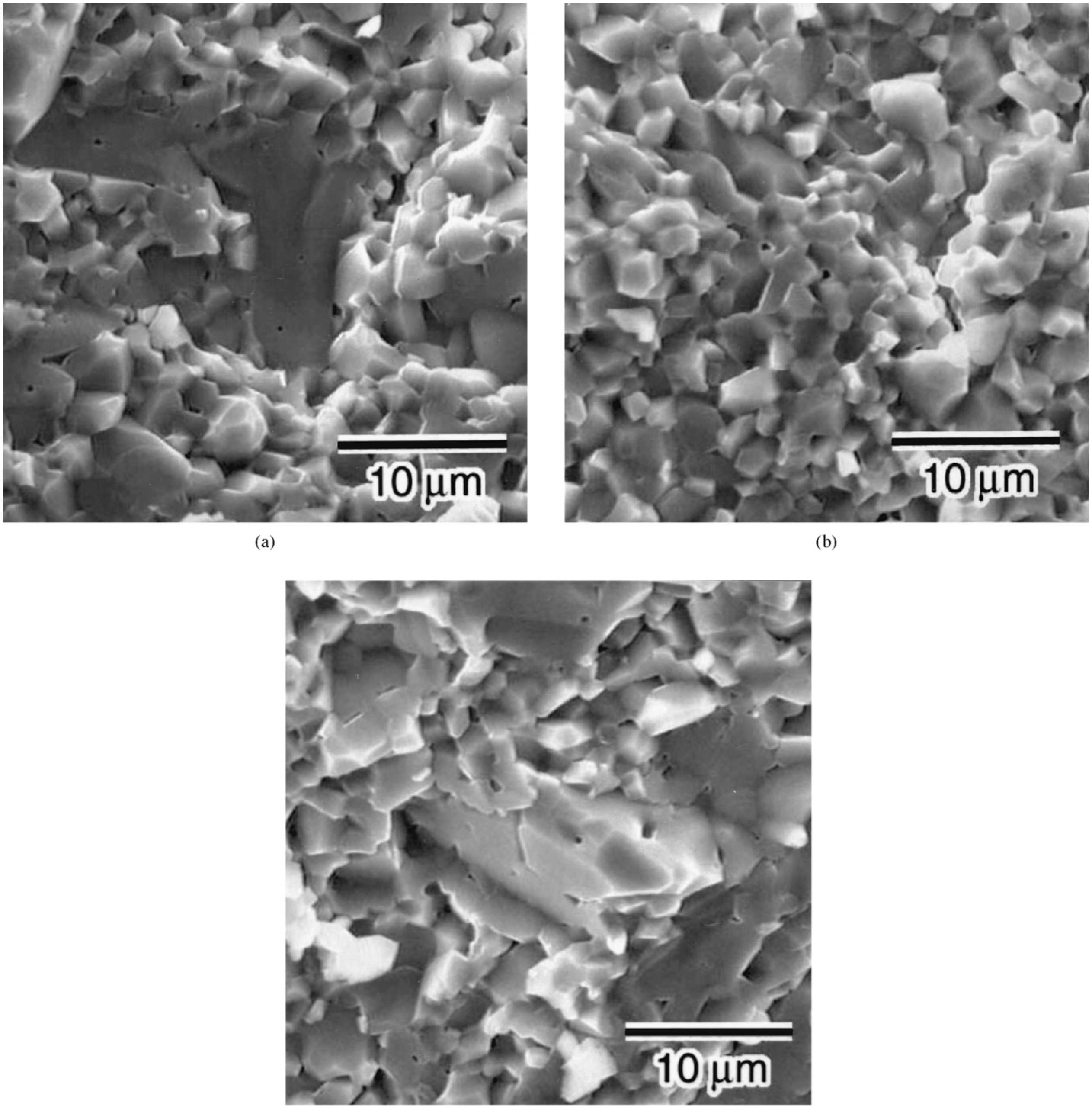
Fig. 3 shows the influence of MgO addition on microstructure for both the mixed powder and the chelation methods. When sintered to 1650°C the density of all specimens was about 95% of theoretical regardless of MgO content or the method by which MgO was added. When the MgO addition using the mixed powder method was reduced from 400 ppm [Fig. 2(b)] to 200 ppm [Fig. 3(a)], grains exceeding 15 μm were observed. However, when the chelation method was used, uniform grain size of about 5 μm or less was observed for MgO addition as low as 100 ppm [Fig. 3(b)], and oversized grains (~20 μm) were only observed at 50 ppm MgO [Fig. 3(c)]. In this work, the chelation method resulted in more uniform distribution of Mg ions than the mixed powder method, as evidenced by the resulting improved uniformity of the sintered microstructure. This result is similar to that obtained previously for Zn-doped barium titanate by Cabellero et al.[8] They demonstrated that while 0.5% ZnO was required to achieve a uniform fine-grained microstructure using a mixed powder processing route, the same effect could be achieved using only 0.1 wt.% zinc stearate, which had been adsorbed onto the powder in an isopropanol dispersion.

The adsorption of chelated complexes provides a mechanism by which small amounts of additives can be distributed at powder surfaces on a molecular scale. In



(a) (b)

Fig. 2. Fracture surfaces of 99.9% alumina specimens sintered to 1650°C. (a) High purity alumina without MgO addition shows exaggerated grain growth while (b) alumina containing 400 ppm addition of MgO shows uniform grain size of less that 5 μm.



(a) (b)

(c)

Fig. 3. Fracture surfaces of 99.9% alumina specimens fired to 1650°C. (a) Specimen containing 200 ppm addition of MgO using the mixed powder method shows oversized grains. When the chelation method was used, oversized grains (b) were not observed at 100 ppm MgO, but (c) were present at 50 ppm MgO.

the case of the chelation method used in this work, a Mg^{2+} level of 6 $\mu g/m^2$ of powder surface area (which corresponds to a MgO level of 10 $\mu g/m^2$) was required to prevent irregular grain growth, while four times that amount of Mg was required when added in the form of an oxide powder. In order to prevent exaggerated grain growth, MgO must be distributed at the grain boundaries. When specimens are prepared by the mixed oxide method, additive ions must diffuse along the grain boundaries before grain growth begins in order to be effective. Diffusion distances can be on the order of several particle diameters. In contrast, when coated powders are used, the additives are distributed at the grain boundaries from the earliest stages of microstructure development. The chelation method used in this work provides a mechanism by which coated powders can be prepared in aqueous systems without significantly altering existing manufacturing process flow.

4. Summary and conclusions

Two alumina systems were used as model systems for developing aqueous methods of introducing inorganic additives. An emulsion method using silicone oil and magnesium stearate was compared with an alcohol-based sol–gel coating method and a conventional mixed powder method to prepare 97.5% alumina with a glassy grain boundary phase. Poor mixedness of the emulsified silicone and the magnesium stearate resulted in poor densification relative to the other methods, while the sol–gel coated powder densified at a temperature of about 100°C below the mixed powder method.

High purity alumina containing between 0 and 400 ppm MgO grain growth inhibitor was prepared by spray-drying and compacting powders containing PAA deflocculant and polyethylene glycol binder. Sintered microstructures were compared for specimens prepared by the mixed powder method and by a chelation method. For the mixed powder method, MgO level was varied by blending a powder that contained MgO powder with a second alumina without MgO. The chelation method samples were prepared by forming a complex between magnesium ions (from magnesium acetate) and the polyacrylic acid used as a deflocculant. Formation of the complex reduced the effectiveness of the polyacrylic acid as a deflocculant so extra deflocculant was required to obtain low viscosity suspensions. Oversized grains were observed after sintering for specimens prepared using the mixed oxide method for MgO level of 200 ppm. In contrast, uniform grain size was observed in specimens prepared using the chelation method for MgO addition of 100 ppm, while oversized grains were only observed when MgO level was reduced to 50 ppm. These results demonstrate the effectiveness of the formation of chelated complexes of polyacrylic acid as a means of uniform incorporation of small amounts of metal cations.

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