

Silicone-coated alumina powders by the emulsion technique

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Alumina powders were prepared using an emulsion technique to chemically bond silanol-terminated poly dimethylsiloxane (PDMS or silicone) to the surface of alumina powders. Stable aqueous emulsions of silicone were prepared using Tween-80 surfactant. Transmission optical microscopy was used to measure the oil-droplet and coated-particle sizes. Fourier transform-infrared spectroscopy was used to quantify bonding between the silicone and the Al_2O_3 . Coated powders were dry-pressed, and PDMS was compared to paraffin for dry-pressing behaviour and green strength. Densification studies were made on powders. X-ray diffraction and scanning electron microscopy were used to characterize the sintered ceramic.

1. Introduction

The increased interest in using ceramics in severe environments leads to greater emphasis on the production of reproducible, high-quality ceramics. Current research in ceramics emphasizes control of powder properties and development of robust economic processing techniques to achieve denser, more uniform microstructures. Composite particles, having a structure where a core particle is coated with a second phase, have attracted attention from various sources. Coatings are applied to improve chemical stability, disperse particles, control interfacial properties, and/or provide a well-dispersed minor phase.

A variety of coating techniques have been reported [1–5], but most of them are either expensive, slow, or specific to some materials system or process. Therefore, a generic coating technique was studied. This coating technique may be applied to a variety of systems, especially those with minor amounts of SiO_2 second phase. If other coatings are desired, the technique may be used provided an organic precursor can be emulsified. The coating technique described in this paper uses emulsions. The emulsions were prepared under acidic (pH = 2), basic (pH = 11) and neutral conditions. The most critical step in the preparation of the emulsions is the choice of the emulsifying agent or surfactant.

Surfactants may be characterized in several ways, including hydrophile-lipophile balance (HLB), critical micelle concentration (CMC), ionic versus non-ionic, and packing efficiency. All surfactants or emulsifying agents are amphiphilic, that is, they have a polar end, and a long non-polar chain. Emulsifying agents with an HLB value around 7 have a slightly polar end, and

favour a water in oil (W/O) type emulsion. Higher HLB values indicate highly polar, long-chain hydrocarbon surfactants which favour oil in water (O/W) type emulsions [6, 7]. The polarity of ionic surfactant ends changes with the environment, so it is not possible to report a single characteristic HLB value for the surfactant. The critical micelle concentration (CMC) describes the tendency of surfactants to form micelles as opposed to simply concentrating at existing interfaces. Ionic surfactants have an ion at the hydrophilic end. Because the goal is a generic coating technique, this is undesirable. These ions may decrease the resistivity of ceramic dielectrics processed using this technique. If the surfactant molecules pack efficiently at an interface, they will make a relatively strong film around the emulsion droplets.

Emulsions begin to break down when the droplets flocculate. The tendency of droplets in an emulsion to flocculate is controlled by engineering the attractive and repulsive forces acting between them. This is similar to the engineering of a stable particle suspension. The attractive forces are van der Waals, and for oppositely charged particles, electrostatic. Repulsive forces are steric and electrostatic. As surfactant-covered droplets approach each other, a local increase in polymer concentration causes an osmotic repulsion. A secondary steric repulsive force occurs because the chains have fewer available positions, raising the free energy of the system and repelling the particles. Electrostatic repulsion arises from the interaction of similarly charged particle surfaces. The use of ionic surfactants is one way to cause electrostatic repulsion. Even if the surfactant is not a charged molecule, the droplet surface may preferentially attract either H^+ or

OH^- ions. The electrostatic part of the attraction or repulsion will therefore change as a function of pH, and can be quantified by measuring the zeta potential [8].

Even after droplets flocculate, they do not necessarily coalesce. Once oil droplets flocculate, stability depends on the strength of the interfacial surfactant film. The strength of the film is a function of the molecular shape of the surfactant. Also, low surfactant concentration may prevent formation of a strong monolayer on the droplet surface [6]. The surface concentration will then increase by droplet coalescence and associated reduction of interfacial area until monolayer coverage is achieved. Thus, while initial droplet size is a function of the nature of the phases, the quantity and type of surfactant, and the processing methods, equilibrium droplet size is almost entirely a function of the concentration and nature of the surfactant.

In this work, emulsion coating is used to prepare powders with an alumina-rich core and a silica-rich surface. This morphology is desirable for several reasons. First, the polymeric precursor causes dispersion of the particles in the slurry by steric stabilization. Second, it acts as a lubricant for dry processing. Third, it polymerizes in the green body to lend strength. Fourth, it acts as a sintering aid; during firing, the SiO_2 coating flows, allowing lower temperature processing. This will be especially effective if the SiO_2 coating is uniform. Fifth, the sintered ceramic can be annealed to allow interdiffusion of the silica coating and alumina core to form an alumina/mullite composite.

2. Experimental procedure

The processing technique studied involves the introduction of alumina powders into aqueous silicone emulsions. The target morphology is an alumina core, with a silicone coating.

Alcoa A16-SG α -alumina powder was treated with silanol-terminated PDMS from Hüls America. Three molecular weights were used in the initial screening experiments: 550, 1750, and 58 000. A series of surfactants were tried as emulsifying agents. The most successful was Tween 80, a polyoxyethylene sorbitan trioleate non-ionic surfactant. Detailed processing of molecular-weight 1750 silicone emulsions was investigated.

2.1. Emulsion preparation

Emulsions were prepared by ultrasonating a mixture of 40 g (41 cm^3) silicone with 60 g (60 cm^3) water and surfactant with 90 W power for 1 min. The amount of surfactant used was based on manufacturer's recommendations. During sonication, the sample changed from two transparent layers to a uniformly turbid emulsion. These emulsions were stored at room temperature for several days and were observed for their stability.

Stable emulsions were characterized by measuring the zeta potential of the PDMS droplets at a series of

pH values. Zeta potential was measured with an electrokinetic sonic amplitude (ESA) measurement apparatus. For these measurements, the emulsions were diluted with de-ionized water to 3 vol% PDMS droplets.

2.2. Powder preparation

Stabilized emulsions were adjusted to pH = 2 and pH = 11 using HCl and NH_4OH , respectively. About 73.4 g (734 m^2) Al_2O_3 powder were slowly added to the emulsions (0.73 mol PDMS/litre emulsion) with constant mechanical stirring. After 9 h, the powders were separated by centrifuging.

Powders were prepared at neutral pH to form a bilayer of surfactant on the surface of alumina. 73.4 g alumina powder (734 m^2) was dispersed in 60 g de-ionized water. Surfactant was added drop by drop. After 2 g Tween-80 was added, the powders flocculated. At this concentration, there was a single layer of surfactant on the alumina surface. The hydrophobic end of the surfactant was oriented toward the water, and the powders agglomerated to exclude water from their surfaces. After the addition of a further 5 g, the powders spontaneously redispersed. At this concentration, there was a second layer of surfactant on the alumina surface. The hydrophobic ends were protected from the water, and the powders dispersed because they no longer needed to exclude water from their surfaces. Once the double layer was formed, 40 g PDMS were added and the solution ultrasonicated with 90 W power for 1 min to introduce the PDMS between the surfactant layers. The mixture was aged 9 h then centrifuged. The properties of powders prepared in all three ways were nearly identical. Emulsions of molecular-weight 1750 silicone in water at pH 11 using Tween 80 are arbitrarily chosen to represent all preparation methods. All dry-pressing, sintering, and microstructural data are for this method.

2.3. Emulsion morphology

The PDMS droplet size in the stable emulsions was measured by optical transmittance microscopy. Samples were prepared by placing a small amount of dilute stable emulsion with or without alumina, on a glass plate and removing the moisture in a drying oven (for about 2 h at 100°C). The samples were observed at $\times 400$ and $\times 1000$ magnification.

2.4. Surface composition

Chemical characterization of the surface of pure alumina powders and PDMS solutions was done by Fourier transform-infrared spectroscopy (FT-IR). Powder samples were prepared by mixing 300 mg KBr with 300 mg as-received or coated powder and pressing into an infrared-transparent disc.

Chemical environment affects the frequency of the hydroxyl stretch. Hydrogen-bonded hydroxyls generate a sharp peak between 3600 and 3500 cm^{-1} [9].

Free hydroxyls generate a broader peak between 3500 and 3250 cm^{-1} .

2.5. Powder compaction

After the slurries were dried, the dry-pressing properties of the resulting powders were compared to those of paraffin-coated alumina. Paraffin is a standard dry-pressing lubricant. All powders were dry-pressed using an hydraulic press with pressures up to 130 MPa. Densities of both types of pellet were recorded at a series of pressures. Densities increased with pressure, then stopped increasing above some threshold pressure. The dry-pressing measurement technique and calculation of per cent inorganics are described in detail elsewhere [10]. The pellets were 12.75 mm in diameter, and 2–3 mm high.

2.6. Flexure testing of green strength

Powders were also dry pressed into rectangular bars of 4.5 mm \times 6 mm \times 62 mm at threshold pressures found in the preceding experiment. Green strength, σ_g , was measured at a loading rate of 0.12 mm min^{-1} in a four-point bend self-aligning fixture. From the green strengths of the bars, the Weibull parameters, m and σ_0 , were calculated by the method of maximum likelihood [11].

2.7. Sintering and characterization of compacts

Dry-pressed pellets were sintered in argon. They were held for 1 h at various temperatures from

1000–1600°C in 100°C increments. Microstructures and elemental distributions were examined using scanning electron microscopy (SEM). The crystalline phases present were identified using X-ray diffraction (XRD).

3. Results and discussion

3.1. Surfactant selection

The experimental results which led to the selection of a suitable surfactant for silicone/water system are given in Table I. Several conclusions were based on these initial results. First, higher concentrations of surfactant make more stable emulsions. Second, only Tween 80, Supralate FAS and Airvol HV 540 emulsions are stable for a week. Tween-80 is a polyoxyethylene sorbitan trioleode non-ionic surfactant. Airvol HV 540 was eliminated because of the large amounts required, and its need to be mixed hot. Supralate FAS was dropped from consideration because it is an ionic surfactant, and is likely to increase the conductivity of electronic ceramics. Third, lower molecular weight PDMS is easier to emulsify. This is a result of the polar nature of the silanol end-group. The PDMS itself, because of its amphiphilic nature, can be considered a weak surfactant. If the PDMS is self-emulsifying, we would expect the OH groups to be primarily at the droplet surface. An attempt was made to verify this using FT-IR, but the surfactant OH peak occluded the silanol peak. The experiment was not definitive.

Only 0.2 g Tween-80 is required to emulsify 40 g silicone in 60 g water. At these concentrations, the oil-droplet size in the Tween-80 emulsion is between 1 and 6 μm , with the mean at 2.5 μm .

TABLE I Results of the initial surfactant screening experiment. Except where indicated, 40 g PDMS was dispersed in 60 g water/surfactant solution. Surfactant concentration was chosen to give an initially stable emulsion

Surfactant	HLB	CMC (by weight (%))	Mass of surfactant (g)	PDMS molecular weight	Fraction Emulsified after one week	Notes
Airvol HV 540			3	1750	All	a
			3	550	Partial	
Airvol MV 523			3.1	1750	Partial	a
Airvol WS42			3	550	None	
Supralate EP	≈ 20	0.06	0.06	58000	None	b
			0.06	1750	Partial	
			0.06	550	Partial	
			0.12	550	Partial	c
Supralate FAS	≈ 20	0.02	0.02	1750	Partial	b
			0.02	550	Partial	
			0.46	550	All	c
Supralate XL	≈ 20	0.06	0.6	1750	Partial	b
			0.4	550	Partial	b
Tween 85	11		1.1	1750	Partial	
			1	550	Partial	d
Tween 80	15	0.0045	1	1750	All	
			1	550	All	

^a Flocculated droplets of emulsion observed.

^b Surfactant mass based on previous experiment.

^c HLB is a function of the chemical environment for anionic surfactants.

^d 45 g PDMS emulsified in 61 g water/surfactant solution.

3.2. Degree of coating

The infrared trace for pure alumina is shown in Fig. 1. The OH stretch occurs in the region of 3000–3300 cm^{-1} . The OH band position shows the presence of hydrogen-bonded hydroxyls. Fig. 1 also contains the infrared spectrum of commercially pure silanol-terminated PDMS with MW 550, and coated alumina powders. Characteristic peaks of both alumina and PDMS appear in the coated alumina spectrum, except the OH stretch. In the process of coating, the concentration of OH is reduced below the sensitivity of infrared spectroscopy, as seen in Fig. 2. To see this, the water must be removed from the emulsion because water also has an OH stretch. The lack of an OH peak in dried emulsions show that the Al–OH surface sites are completely occupied by silicone, resulting in covalent Al–O–Si bonds. Al–O–Si bonds have a characteristic FT–IR peak, but it would be hidden beneath the Al–O–Al peak.

It is interesting to speculate on the fate of the OH groups from the surfactant. Because they do not appear in the FT–IR, they must have either evaporated, or chemically reacted. Evaporation is unlikely, so the surfactant is either competing with the PDMS for surface sites on the alumina, or reacting with PDMS end-groups.

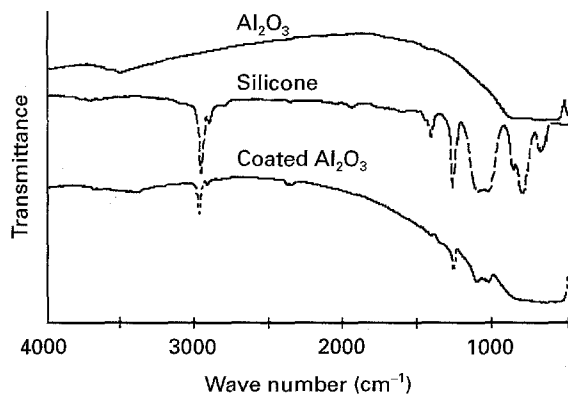


Figure 1 Infrared spectra for as-received alumina, as-received silicone, and emulsion-treated alumina. Note that the characteristic peaks of silicone and alumina appear in the treated alumina, except OH. See also Fig. 2.

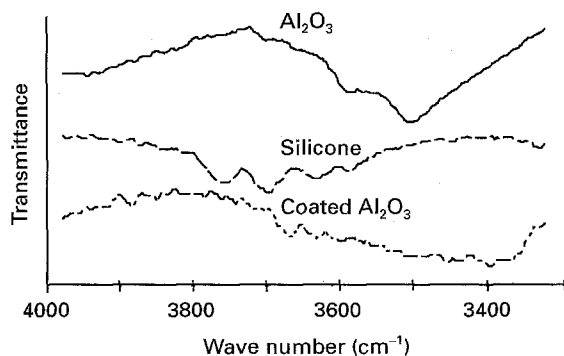


Figure 2 Detail of Fig. 1 showing the OH peak region.

3.3. Dry-pressing behaviour

PDMS-treated powders are compared with paraffin-coated powders, which showed lower or similar densities at each pressure (Fig. 3). This shows that PDMS can act as a lubricant. The dry-pressing behaviour of the emulsion-prepared PDMS/alumina system compares well with the properties of solution-prepared PDMS/alumina.

Silicone–Al₂O₃ modulus of rupture bars also have greater green strength than paraffin–Al₂O₃ bars (see Table II). We attribute this, in part, to easier deformation of the organic phase. This leads to two effects: first, better organic–solid contact, and second, smaller critical flaws. The greater density of parts pressed from PDMS-coated powders also contributes to higher strengths.

3.4. Sintering

Sintering studies of dry-pressed pellets prepared by this technique show that densification begins at 1200 °C (Fig. 4). Maximum densities of around 93% theoretical for alumina are reached at 1500 °C. Fig. 5 shows a scanning electron micrograph of a sample sintered at 1500 °C. Image analysis on scanning electron micrographs shows that the samples had 2% pore volume. As expected, the presence of silica lowers the sample density. The 1%–2% drop in density from 1500 °C to 1600 °C is evidence of the transformation of silica and alumina to mullite. XRD patterns were taken at 1500 °C for each preparation method, and do not differ significantly. XRD patterns at 1500 °C show alumina, with traces of sillimanite, mullite and cristobalite. Patterns at 1600 °C show significantly more mullite.

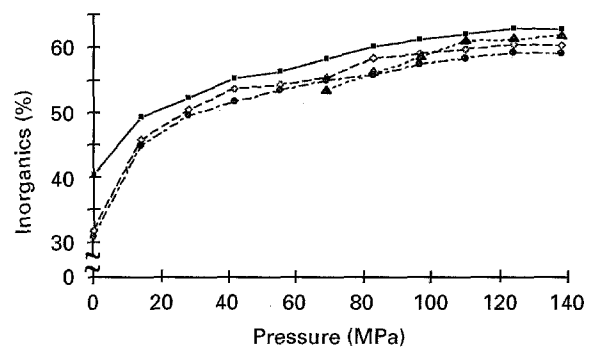


Figure 3 Density of inorganics for (—◇—) bare alumina powders, and alumina powders coated with silicone using (—■—) an adsorption technique, (—▲—) silicone emulsion-treated powders, and (—●—) paraffin-coated powders.

TABLE II Green strength and Weibull modulus of PDMS and paraffin-coated alumina

	Green strength, σ_0 (MPa)	Weibull modulus
Paraffin-coated Al ₂ O ₃	1.7 ± 0.1	2.3 ± 0.1
PDMS-coated Al ₂ O ₃	4.0 ± 0.04	5.8 ± 0.6

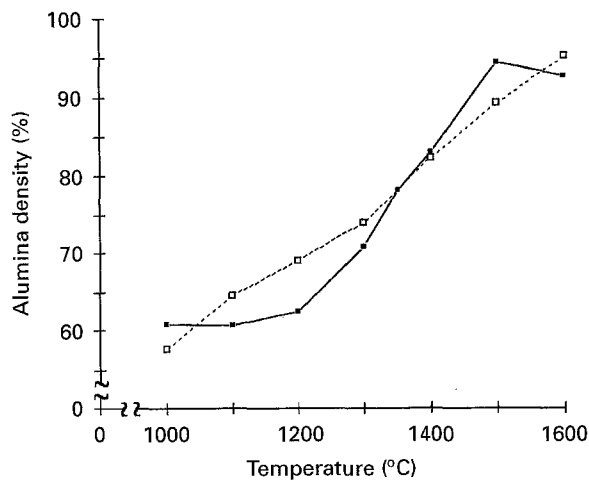


Figure 4 Comparison of sintering of (—■—) silicone-treated alumina powders with (---□---) bare alumina powders.

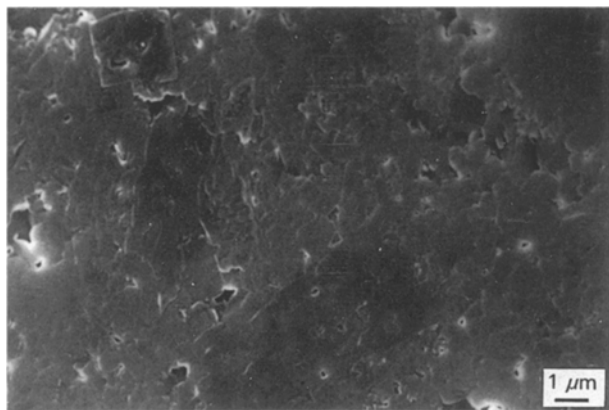


Figure 5 Scanning electron micrograph of a pellet sintered at 1500°C.

4. Conclusion

Tween-80 is an effective surfactant for preparing PDMS/water emulsions. $\text{Al}_2\text{O}_3\text{-SiO}_2$ composite powders were made by emulsifying PDMS in water using Tween-80 surfactant. Coated powders were suc-

cessfully prepared under acidic, basic and bi-layer conditions. Powders prepared by these three techniques are similar. FT-IR shows the alumina is coated by silicone. The silicone-coated powders prepared by this technique can be dry-pressed without additional binders or lubricants. The dry-pressing behaviour of PDMS-coated alumina is comparable to paraffin-coated alumina powders. Green strength is superior to paraffin/alumina. The sintered pellets have ~93% theoretical density of alumina at 1500°C. Image analysis shows 2% porosity. We attribute the discrepancy to the presence of small amounts of lower density silica and mullite.

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