JOURNAL OF MATERIALS SCIENCE 30 (1995) 2793–2798

Oxidation, densification and properties of extruded aluminium boehmite reaction-bonding mixtures

I.P. KILBRIDE*, A. J. BARKER
IRC in Materials for High Performance Application and School of Chemical Engineering, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

The feasibility of preparing a plastically formed reduced shrinkage alumina component was examined. Extrudable boehmite aluminium mixtures were prepared by mixing attrition milled aluminium powder with hydrothermally produced boehmite. Extruded rods were then heat treated up to 1700 °C in air. Oxidation and densification behaviour was studied. There was no microscopic evidence for the large-scale migration of molten aluminium into voids and at higher aluminium concentration the volume expansion due to oxidation resulted in expansion of the solid rather than filling of interstitial spaces. High concentrations of aluminium caused a vermicular grain structure to develop, typical of an unseeded boehmite. The development of this microstructure in the relatively coarse aluminium particles is significant for the application of this technology. Samples with an average flexural strength of 272 MPa were manufactured with reduced shrinkage over an equivalent seeded boehmite gel, although properties of the sintered solids in general reflected the low-density achieved relative to the theoretical maximum value.

1. Introduction

There is presently much interest in the reaction bonding and forming of oxide ceramics. The volume expansion of the reactive phase can reduce shrinkage during sintering, with the potential to give a near net shape without final machining of the ceramic. Low-shrinkage mullites [1] and alumina [2] have been formed in this way, typically by attrition milling followed by isopressing. It would be useful to combine this near-net-shape forming technique with other manufacturing methods, such as extrusion and injection moulding, in order to produce more complex shapes. These complex-shaped components should benefit particularly from the reduced shrinkage level.

It is still difficult to produce large ceramic components by the injection moulding or extrusion of organic polymer/powder mixtures. Problems often arise with distortion and bloating of components during the removal of these organic binders. Boehmite gels have been used as a binder [3] system for alumina. Boehmite has the advantage that it converts to alumina after firing. Several problems exist with this material. Firstly, pure boehmite gels suffer from a large shrinkage on sintering. Secondly, the phase transformations in the boehmite alumina system [4] often result in vermicular microstructures which resist densification. The oxidation of aluminium in air follows a similar route, that is, first transforming to the gamma phase. This may produce similar microstructures which also resist densification. Thus an understanding of oxidation and densification in boehmite aluminium mixtures may lead to enhanced microstructural control in a more typical aluminium reaction-bonding system. It may also be possible to form a variety of novel composite systems from these mixtures.

2. Experimental procedure

The boehmite was produced by hydrothermal decomposition of basic aluminum acetate in an autoclave at 200 °C, under saturated steam pressure for 2 h. The resulting slurry was dried at 110 °C. To the boehmite powder, 5 wt % fine alpha alumina (Baikowski Baikalox SM8) was added to promote the θ to α-alumina phase transformation [5]. This was achieved by redispersing the alpha alumina and boehmite in a ball mill in water for 30 min. The mean particle size of this seed powder was 0.18 μm.

Aluminium powder with a 5 wt % addition of the seed alumina was milled in a water-cooled attrition mill for 14 h with 1 kg of 6.3 mm carbon steel balls to 100 g powder in isopropanol. The formulations prepared are shown in Table I. Extrusion mixtures were made by mixing the appropriate quantity of boehmite and milled aluminium then adding 30 wt % water (40% to the gel samples without aluminium). The mixtures were ram extruded through a circular cross-sectional die of 3.04 mm diameter at 25 mm min^{-1},

---

*Present Address: Centre for Inorganic Chemistry and Materials Science, The University of Keele, Staffs ST5 5HP.

TABLE I List of formulations

Boehmite gel without α-alumina
Boehmite, 5 wt % α-alumina overall
33%, 66% and 87% additions of milled aluminium powder, 5 wt % α-alumina
0.2 and 0.4 wt % Na_2O to sample containing 33 wt % milled powder, 5 wt % α-alumina
0.2 Na_2O to sample containing 66 wt % milled powder, 5 wt % α-alumina

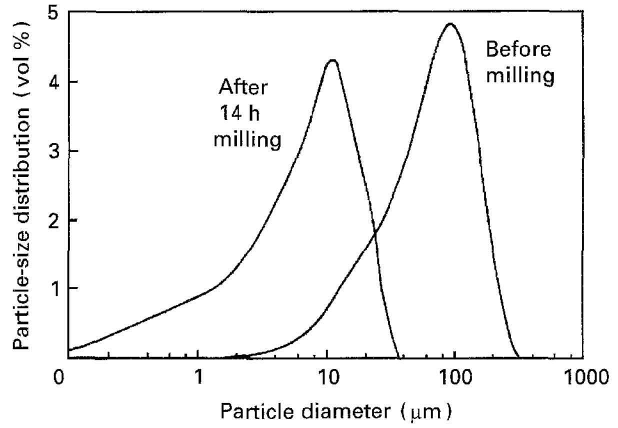

Figure 1 Particle-size distribution (vol %) of aluminium powder, 5 wt % α-alumina, before and after 14 h attrition milling.

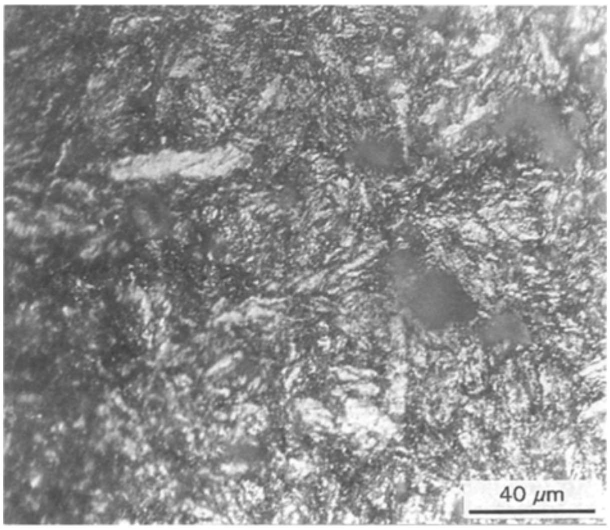

Figure 2 Optical micrograph of attrition-milled aluminium. Light areas are reflective aluminium particles.

the rods were then dried at 30 °C, under a constant 45% relative humidity. The additional mixes containing 0.2 and 0.4 wt % Na_2O were prepared by adding an equivalent quantity of NaOH.

Particle-size measurements were made using a laser diffraction particle-size analyser (Coulter LS130).

Dried rods were heated at 3 °C min^{-1} to 600, 800, 1000, 1500, 1600 and 1700 °C and were held for 2 h. They were subsequently measured for linear shrinkage, weight change and density. Optical micrographs were taken of polished surfaces; scanning electron micrographs (SEM) were made on green and fired fracture surfaces. Powder samples were dispersed in clear resin then polished. Flexural strengths were measured in three-point bending on rods with a loading rate of 0.5 mm min^{-1}. The span was ten times the diameter of the sintered rod and the rods were tested with an 'as-fired' surface finish.

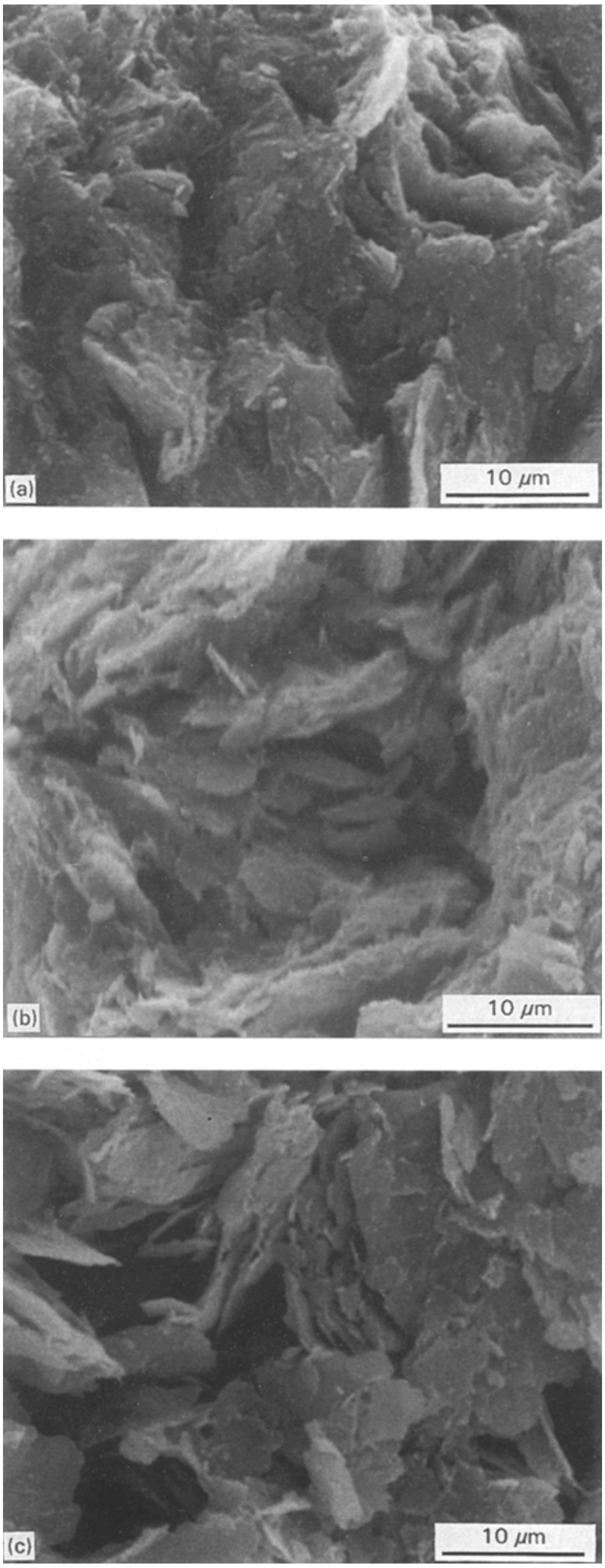

Figure 3 Scanning electron micrographs showing fracture surfaces of unfired rods: (a) 33 wt % Al, (b) 66 wt % Al, (c) 87 wt % Al.

3. Results and discussion

Fig. 1 shows the effect of attrition milling on the aluminium powder. After 14 h the mean particle size has

TABLE II Effect of oxidation at 600, 800 and 1000 °C on the properties of aluminium boehmite mixtures: weight change, Δ (wt %); ρ, density (g cm^{-3}); linear dimensional change, ΔL(%).

Temp. (°C)	33 % Al			66% Al			87% Al		
	Δ(wt %)	ρ (g cm^{-3})	ΔL(%)	Δ(wt %)	ρ (g cm^{-3})	ΔL(%)	Δ(wt %)	ρ (g cm^{-3})	ΔL(%)
600	− 12.6	1.33	− 0.7	0.0	1.27	0.65	1.4	1.27	− 1.1
800	− 4.6	1.53	− 0.67	21.5	1.62	0.30	15.8	1.59	0.0
1000	− 4.0	1.90	− 2.68	24.7	1.69	0.0	35.2	1.60	4.2

been reduced from 80 μm to about 8 μm. This final particle size is higher than has been used in previous studies [2] (by an order of magnitude, typically micrometre or submicrometre after attrition milling). Fig. 2 is an optical micrograph of the milled powder, the light areas being the reflective polished surface of the aluminium particles. The milled powder contains plate-shaped particles and appears to confirm the laser size analysis. These smaller plates may be produced by the work-hardening and subsequent break-up of the original flake aluminium by the milling action. The 8 μm mean particle size corresponds to a fine commercially available aluminium powder. The plate-like morphology of the milled aluminium will allow shorter diffusion distances through the plane of the plate compared to a typically spherical powder.

Fig. 3 shows scanning electron micrographs of unfired samples. The sample containing 33 wt % aluminium, Fig. 3a, appears microscopically similar to a pure boehmite rod of a similar density. The nanometre-sized boehmite particles are not individually visible at this magnification. In this picture, the aluminium particles appear to be coated by the much finer boehmite particles. In samples containing more aluminium, Fig. 3b and c, the platelets become much more obvious. Relatively large voids can be seen in the sample containing the 87 wt % aluminium. There may also be some evidence of alignment of the plates by the extrusion process given that the fracture surface seen in Fig. 3c was at right angles to the extrusion direction.

Table II gives the weight change, shrinkage and density of rods heated to 600, 800 and 1000 °C for 2 h in air. Firstly there is an initial loss of weight below 600 °C in the 33 wt % aluminium sample. This is accounted for by the decomposition of the boehmite binder to gamma alumina at 500 °C (pure boehmite would lose approximately 15% of its original mass). A significant proportion of the aluminium is oxidized below 600 °C. The density of the sample appears to increase with the increase in mass due to oxidation. Contraction occurs on the decomposition of boehmite, but the sample expands slightly with the oxidation of the aluminium at higher temperatures. There was significant densification at 1000 °C when sintering was initiated.

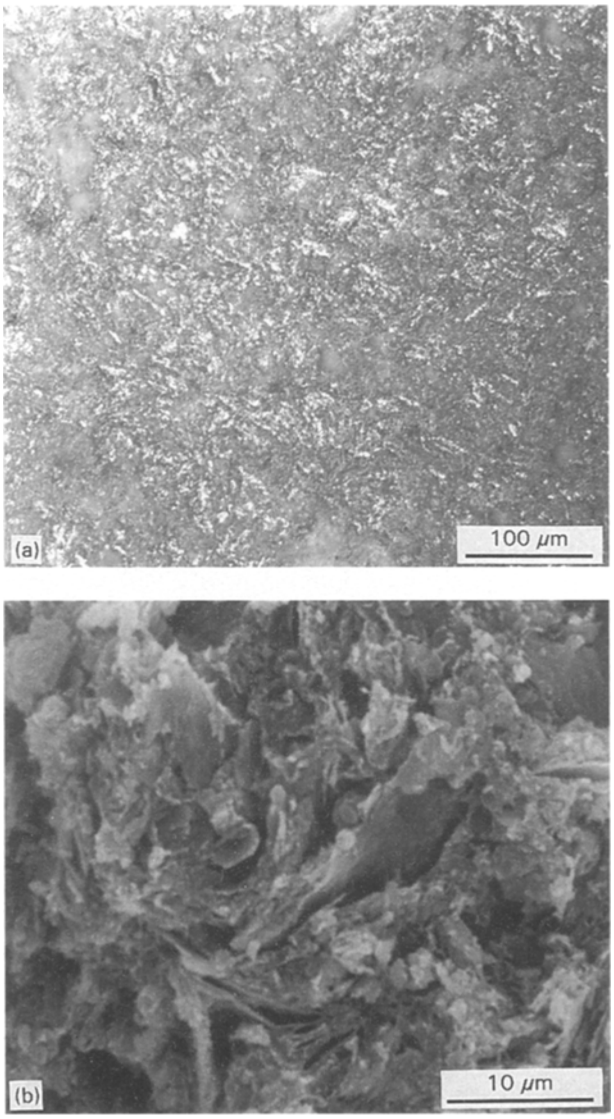

Figure 4 Micrographs showing the effect of heat treatment at 800 and 1000 °C. (a) Optical micrograph of polished surface of sample containing 87 wt % Al after heating to 800 °C for 2 h. Light areas show unoxidized aluminium. (b) Scanning electron micrograph 66 wt % Al sample after treatment at 1000 °C.

For samples containing 66 wt % aluminium, there is a large positive weight change followed by some expansion below 600 °C, the samples then appear to densify above 600 °C. This would be consistent with a volume expansion (of about 23%) following oxidation of a solid phase, causing the sample to expand below 600°C, while the metal was still in the solid phase. However, the 87 wt % aluminium samples first contracted (due to sintering of the metallic component at this high concentration) below 600 °C. The sample then expands above the melting point of the aluminium. The implication is that although there is liquid aluminium present, the liquid does not flow into void spaces within the ceramic and the expansion accompanying oxidation simply goes into expansion of the solid component rather than increasing density. Fig. 4

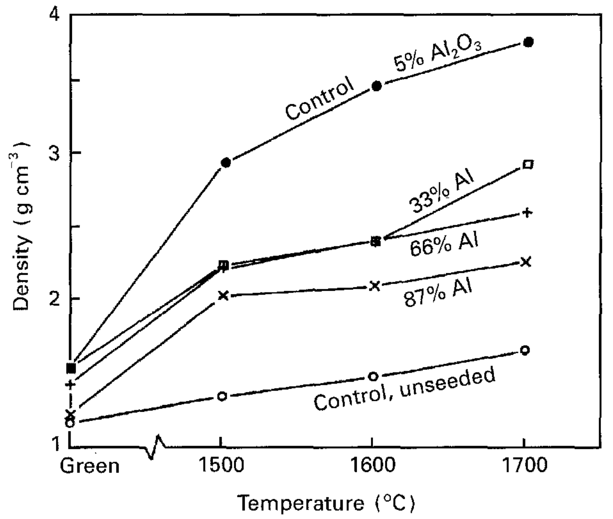

Figure 5 Green and fired densities (1500–1700 °C) of extruded specimens.

would tend to confirm this with the optical micrographs showing unoxidized aluminium at 800 °C. The particles appear to have retained the plate-like morphology, although they appear slowly to reduce in area as they oxidize from their surface. The scanning electron micrograph of the 66 wt % sample after treatment at 1000 °C also shows this, with no evidence of spheroidization of the liquid aluminium or of liquid migration. This is not unreasonable, as it is known that aluminium wets alumina poorly without some fluxing agent [6]. Microstructurally, it appears not dissimilar to the green state, although there is possibly some fine gamma alumina in evidence.

The density of samples after sintering at 1500, 1600 and 1700 °C is shown in Fig. 5. The samples containing 87 wt % aluminium in the green state only achieve an average density of 2.3 g cm^{-3} as opposed to 3.82 g cm^{-3} for the seed boehmite samples after sintering at 1700 °C. The densification is significantly retarded over control samples by any aluminium addition. With sodium additions, shown in Table III, improved density was achieved up to a maximum of 3.45 g cm^{-3}. Fig. 6 shows the microstructures of the samples fired at 1700 °C. All of the samples with aluminium added show vermicular grain structures similar to the microstructure found in sintered unseeded boehmite [5]. Obviously the α-alumina seed particles can be better distributed in samples containing only boehmite due to its fine particle size, whereas no seeding can occur within a relatively large aluminium plate. Because the effective distance between seeds is higher in samples with aluminium, they cannot so

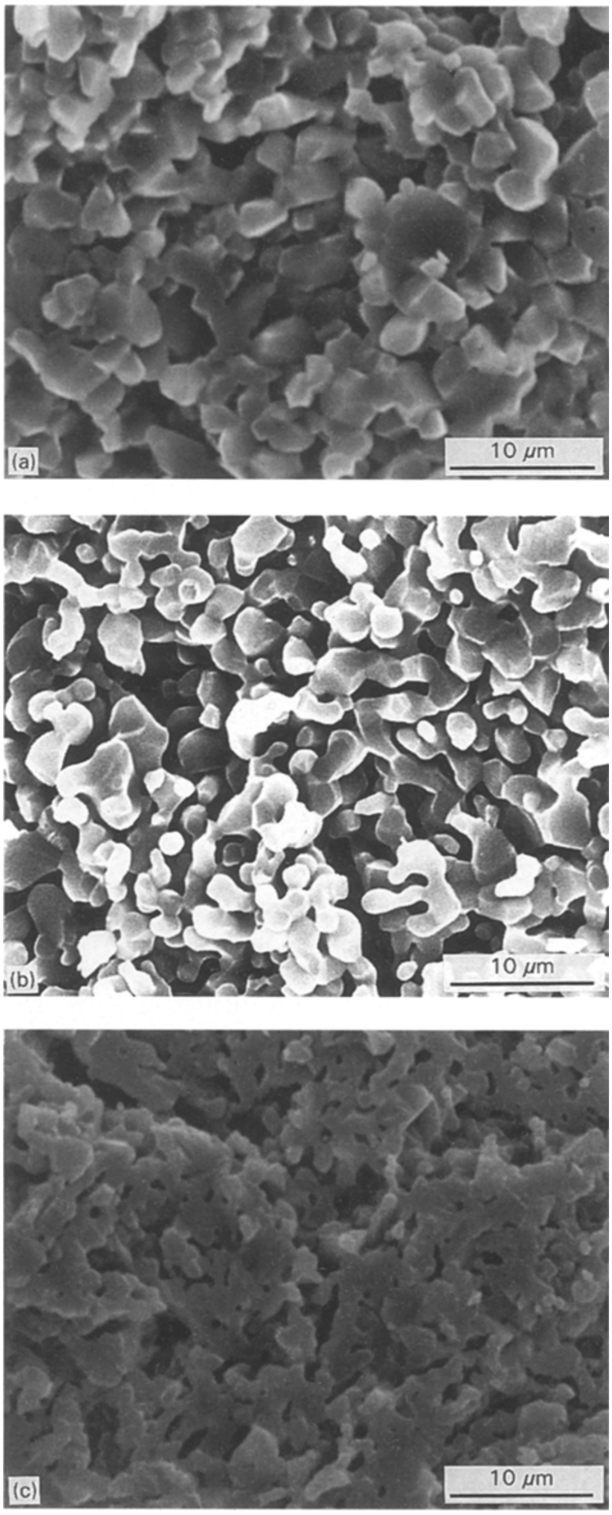

Figure 6 Scanning electron micrographs of (a) boehmite gel with 5 wt % α-alumina, (b) unseeded boehmite, (c) 33 wt % Al, (d) 66 wt % Al and (e) 87 wt % Al.

TABLE III Effect of sodium additions to densification of sample at 1700 °C

	33 % Al	33 % Al 0.2 % Na_2O	33 % Al 0.4% Na_2O	66% Al	66% Al 0.2% Na_2O
Density (g cm^{-3})	2.97	3.26	3.45	2.65	2.87
Strength (MPa)	213	251	272	130	154

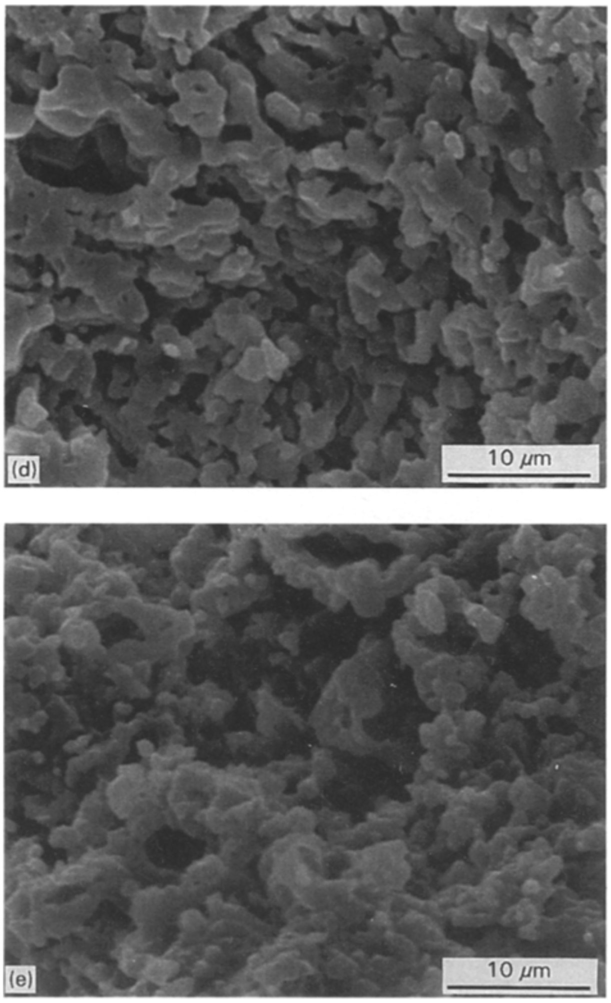

Figure 6 (continued)

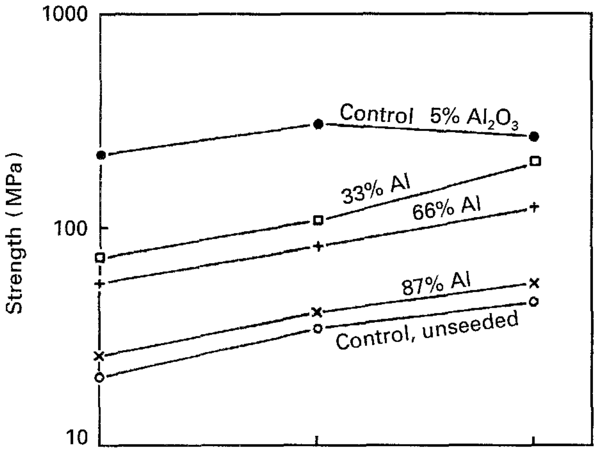

Figure 7 Flexural strength of extruded samples after sintering at 1500–1700 °C.

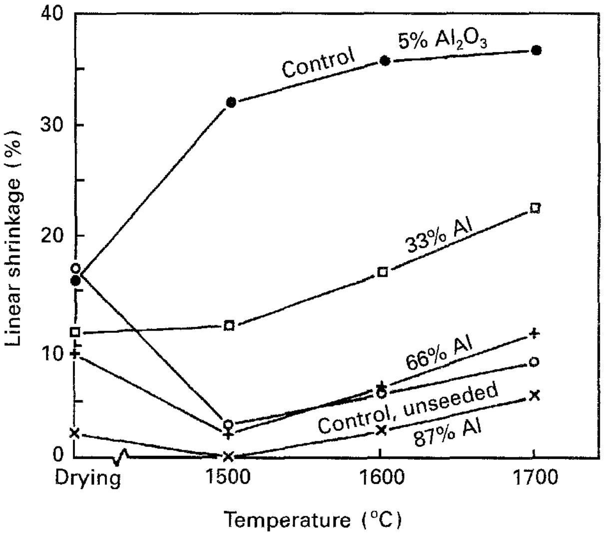

Figure 8 Linear shrinkages (%) after drying and sintering 1500–1700 °C.

effectively seed the transformation of the aluminium oxidation products, that is, the θ to α-alumina transition at about 1200 °C. The typical vermicular structure (equivalent to that found in unseeded boehmite) then develops, which inhibits further densification. This appears not to have occurred in other studies because of the fine particle size of the aluminium used therein and the proximity of a high proportion of α-alumina. However, this problem should be relatively easy to overcome, as it has been for pure boehmite. Nucleation within large aluminium grains could be achieved using α-alumina dispersion-strengthened aluminium, or with alloying elements such as iron which transform to a crystallographically suitable oxide to promote the transition [7]. Alternatively, additives which flux the aluminium (possibly copper in copper-aluminium alloys) and allow flow over the boehmite surface, should also encourage transition.

Fig. 7 shows the three-point bend strengths of the fired samples. These are related to the density of the sample, i.e. for a similar density, samples with aluminium additions to the green state have equivalent strengths to the seeded boehmite. Should the density be increased to above 95% theoretical density, strengths of about 350 MPa might be expected. This would be acceptable for an extruded alumina rod or component.

Fig. 8 shows the shrinkages associated with the various samples after drying and sintering. Comparing the 33 wt % aluminium addition sample with the 5 wt % seeded boehmite for an equivalent fired density, the sample with aluminium shrank significantly less than the standard gel. For sintered samples at a density of 3.0 $\mathrm{g\,cm^{-3}}$ shrinkage was reduced from 33 % to 23% approximately. Addition of the aluminium also reduced the shrinkage during drying of the gel.

4. Conclusion

Boehmite gel was a successful binding agent for aluminium powder. At higher aluminium concentrations, the volume expansion occurring during the oxidation of the metal tended to expand the solid, and not to improve the density. Aluminium particles retained their morphology up to 1000 °C and there was no evidence of gross liquid-aluminium migration. A vermicular grain structure was found to have developed after high-temperature treatment in samples with aluminium. It is this structure which is most likely to be inhibiting densification in these mixtures. The mechanism causing the development of the vermicular structure is probably analogous to that found in unseeded boehmite; fine gamma alumina formed by oxidation of aluminium does not easily transform to alpha alumina. Control of the transition should be relatively easy to achieve by adapting methods already available for boehmite itself. This may lead to the use of coarse aluminium in the reaction-bonding process. Ultimately, this would be desirable because it would remove the need to attrition mill or to use very fine metal powder. This should allow reaction bonding of alumina to become a relatively simple and inexpensive process.

References

1. SUXING WU and N. CLAUSEN *J. Am. Ceram. Soc.* **74** (1991) 2460.
2. SUXING WU, D. HOLZ and N. CLAUSEN, *ibid.* **76** (1993) 970.
3. A. Y. CHEN and J. D. CAWLEY *ibid.* **75** (1992) 575.
4. K. OTHMER, "Encyclopedia of chemical technology", Vol. 2 (Wiley, New York, 1978) pp. 218–44.
5. M. KUMAGAI and G. L. MESSING, *J. Am. Ceram. Soc* **67** (1984) C230.
6. O. M. AKSELSEN, *J. Mater. Sci.* **27** (1992) 1989.
7. J. L. MCARDLE and G. L. MESSING, *Adv. Ceram. Mater.* **3** (1988) 387.

Received 15 June
and accepted 14 November 1994