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Alumina ceramics based on seeded boehmite and electrophoretic deposition

A.R. Boccaccini[a,*], C. Kaya[b]

[a]*Department of Materials, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BP, UK*
[b]*Interdisciplinary Research Centre (IRC) and School of Metallurgy and Materials, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*

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Abstract

It is shown that seeding a commercial boehmite sol with crystallographically suitable seeds reduces both the crystallization temperature for the final α-$A1_2O_3$ phase and the sintering densification temperature. The seeding component was a tailored combination of δ- and α-alumina particles in nanometre and micrometer ranges, respectively, dispersed in water. Electrophoretic deposition (EPD) provided a quick, simple and cost-effective processing route to prepare dense monolithic alumina ceramics from the seeded boehmite suspensions. EPD-formed green bodies could be sintered and densified at temperatures as low as 1250 °C for 2 h.

Keywords: D. Alumina; Boehmite; Electrophoretic deposition; Seeding

1. Introduction

The use of sol–gel and colloidal routes in ceramic processing has many advantages, such as attainment of greater purity, higher homogeneity and ultrafine grain size distribution, in comparison to conventional powder-based processing techniques. Moreover, the high surface area to volume ratio of sol-derived precursors makes the material highly sinter-active, thus sintering temperatures can be lowered by several hundreds degrees [1].

Boehmite (γ-AlOOH) sol is one of the ideal candidate materials to manufacture high quality alumina ceramic components with controlled final sintered microstructure, as it contains very sinter-active ceramic particles on a nanometer scale [2]. It is now well-known that commercial boehmite sols can be seeded with isostructural crystals (seeds) in order to lower crystallisation temperature to form α-alumina and to enhance densification with refined microstructure through solid-state epitaxy [2,3]. The seeds can be also used to control final sintered microstructure in terms of grain size, pore size and pore size distribution. Without seeding, a commercial or hydrothermally produced boehmite sol requires very high sintering temperatures (>1600 °C) for complete densification. This is due to the extended pore network that develops during the reconstructive transformation to the final stable phase α-Al_20_3, according to the dehydration and high temperature phase transformation of boehmite [4]:

$$\gamma\text{-AlOOH} \rightarrow \gamma\text{-}Al_2O_3 \rightarrow \delta\text{-}Al_2O_3 \rightarrow \theta\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3 \quad (1)$$

Therefore, the final sintered microstructure of alumina derived from pure boehmite sol is very porous even after sintering for a long time (>6 h) at 1600 °C if the sol is not seeded [3]. On the contrary, when boehmite sol is seeded with crystallographically suitable modifiers, high-density alumina components with controlled microstructure are achievable at relatively low sintering temperatures (1100–1300 °C) [3]. Seeding with γ-Al_2O_3, α-Al_2O_3, and α-Fe_2O_3 particles has been tried [3, 5–9]. Because the addition of seeds to boehmite gels enhances the $\theta \rightarrow \alpha$ transformation, complete densification of α-Al_2O_3 may occur at temperatures as low as 1180 °C

* Corresponding author. Tel.: +44-20-7594-6731; fax: +44-20-7584-3194.
E-mail address: a.boccaccini@ic.ac.uk (A.R. Boccaccini).

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with a grain size of only 0.43 μm [3,5,6]. By also applying a sinter-forging technique, transparent alumina components can be obtained at temperatures as low as 1250 °C from γ-Al_2O_3 seeded boehmite [10].

In recent research, commercially available boehmite sols have been used to fabricate metal and carbon fibre-reinforced alumina matrix composites by using the electrophoretic deposition (EPD) technique [11,12]. In order to achieve the desired densification of the alumina matrix at relatively low temperatures seeding of the boemite sol was required.

In the present study the seeding process of the commercial boehmite sol is described in detail and the seeded sol is used to obtain α-alumina ceramics by EPD. Thus the seeding process was developed not only to lower the sintering temperature of the alumina matrix but also to produce a stable boehmite/seed suspension suitable for electrophoretic deposition. The main difference with previous studies on seeding of boehmite [3, 5–8] is the use in the present research of a novel, optimised aqueous "composite" solution composed of nanometric δ-alumina and micrometnc α-alumina particles as the seeding component. The reasons for using these "composite" seeds are given.

2. Experimental

A commercially available boehmite (γ-AIOOH) sol (Remal A20, Remet Corp. USA) having 40 nm average particle size and particle sizes varying in the range of 20–60 nm was used. The sol contains 20 wt.% solids-loading and the boehmite particles have a rod-like shape. This commercial boehmite sol has been already used in previous research as precursor for the fabrication of alumina matrix composites by EPD [11,13]. The as-received boehmite sol was seeded by adding 0.5 wt.% of a seeding aqueous suspension. This was composed of 99.5 wt.% nanosize (13 nm) δ-alumina particles (Aluminium Oxide C, Degussa AG, Germany) and 0.5 wt.% α-alumina particles (BDH Chemicals, UK) of mean particle size 0.3 μm. The nanosize particles contain some impurities (Fe, Si, Ti) in ppm concentration as reported by the supplier. A bright-field TEM micrograph showing the spatial arrangement of the nanosize δ-alumina particles used as seeds is shown in Fig. 1. It was found that after adding 0.5 wt.% α-alumina particles the seeding suspension was kinetically stable and well dispersed, as there were no large heteroflocculated agglomerates. The seeding particles were first dispersed in distilled water, then the dispersion was added to the boehmite sol whilst this was stirred magnetically. Finally, the seeded boehmite sol was ball-mixed for 12 h using high-purity TZP balls in a plastic container. The resulting sol contained 17.5 wt.% solids-loading.

Details of the EPD technique applied in ceramics processing have been given by Sarkar and Nicholson in a complete review article [14]. In the present work, a simple EPD cell containing two stainless steel electrodes connected to a power supply was used to obtain alumina deposits (green bodies). The schematic of the EPD cell is shown in Fig. 2. The pH of the stable boehmite

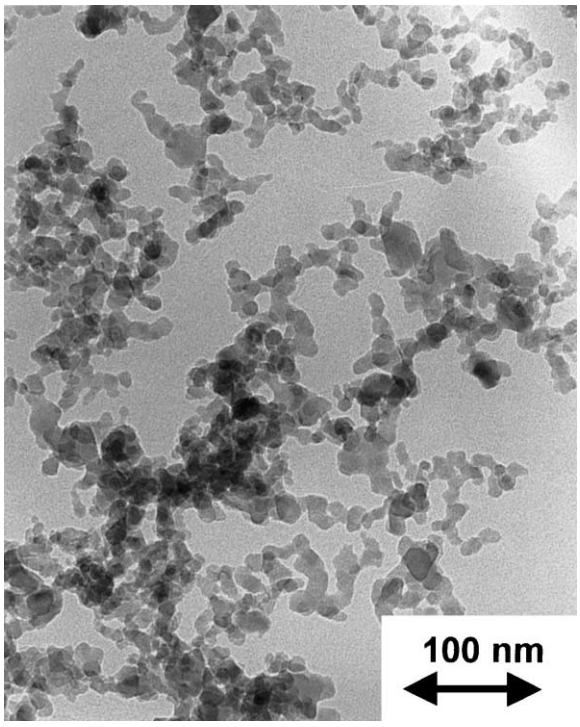

Fig. 1. Bright-field TEM micrograph showing the δ-$A1_2O_3$ nanosize particles used as seeds.

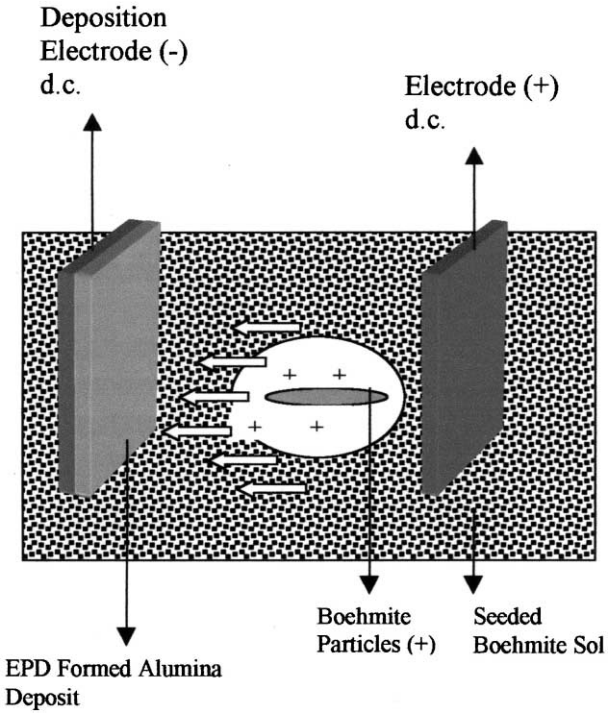

Fig. 2. Schema of the EPD cell used to obtain alumina deposits from boehmite suspensions at pH = 4.1.

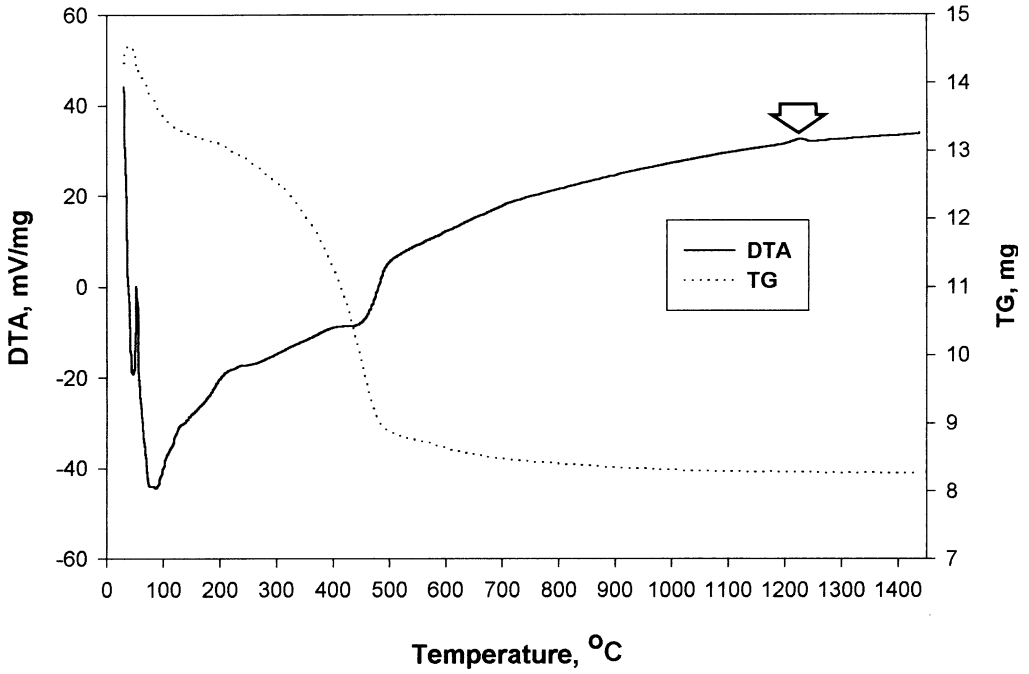

Fig. 3. DTA and TGA traces (heating rate 10 °C/min) for the seeded boehmite sol, showing the decomposition and phase transformation temperatures and also the weight loss as a function of temperature.

suspension was 4.1 At this pH values boehmite and alumina particles in suspension (including δ- and α-$A1_2O_3$ seeding particles) are positively charged, as shown elsewhere [11–13]. On application of an external voltage, the particles migrate and deposit on the cathode. The EPD experiments were conducted under constant voltage conditions using an applied voltage of 8 V d.c. for 3.5 min, resulting in the formation of a deposit thickness of about 1 mm. The distance between the two electrodes was adjusted to be 15 mm. The EPD-formed green deposits were placed in humidity-controlled chambers (75 and 50% relative humidity) for 1 day in each chamber. After drying, the deposits were easily removed from the electrodes and left in normal air for one more day before being pressureless sintered at different temperatures for 2 h.

Dried samples were subjected to differential thermal analysis (DTA) and thermogravimetric analysis (TGA) in order to determine the phase transformation temperatures of the transitional aluminas and the corresponding weight loss, respectively.

Samples sintered at different temperatures for 2 h were analysed using XRD (CuK_α radiation). Sintered samples were prepared for scanning electron microscopy (SEM) by polishing using 3, 1 and 0.25 μm diamond pastes and subsequent thermal etching at 1100 °C for 20 min. A high-resolution scanning electron microscope (Field Emission Gun, FEG SEM, Hitachi S-4000, Japan) was employed to observe the microstructure of sintered samples. An image analyser was used to measure the mean grain size on SEM micrographs. At least 200 grains were counted.

3. Results and discussion

Typical DTA traces of dried seeded boehmite samples (heating rate: 10 °C/mm), as shown in Fig. 3, exhibit endothermic peaks at about 100 and 250 °C, which may be ascribed to the removal of water from the boehmite. The TG curve, also shown in Fig. 3, shows a total weight lost of about 40.2%. Fig. 3 demonstrates also that weight loss and endothermic reactions are terminated at about 450 °C. This should be an indication of the boehmite transformation (from γ-A1OOH to γ-$A1_2O_3$) being completed at this temperature. The other phase transformations of transitional aluminas (γ-, δ-, θ-) to α-alumina, as shown in Eq. (1), which should take place at 800, 1000 and in the range 1100–1200 °C, respectively, were not detected by the DTA technique. Only a peak at 1230 °C is, however, clearly visible for the DTA conditions investigated, which should correspond to the final α-alumina formation. The presence of α-alumina was confirmed by X-ray diffraction (XRD) analysis, as shown in Fig. 4. The XRD pattern corresponds to a sample sintered at 1250 °C for 2 h. The only detectable phase within the sintered matrix is α-alumina with no additional peaks corresponding to non-transformed transitional aluminas.

A SEM image of a sample sintered at 1250 °C for 2 h is shown in Fig. 5. The α-alumina microstructure exhibits a relative narrow grain size distribution, with equiaxed grains smaller than −2 μm and some larger elongated grains. There is no intra-granular pore formation which indicates that the densification rate may

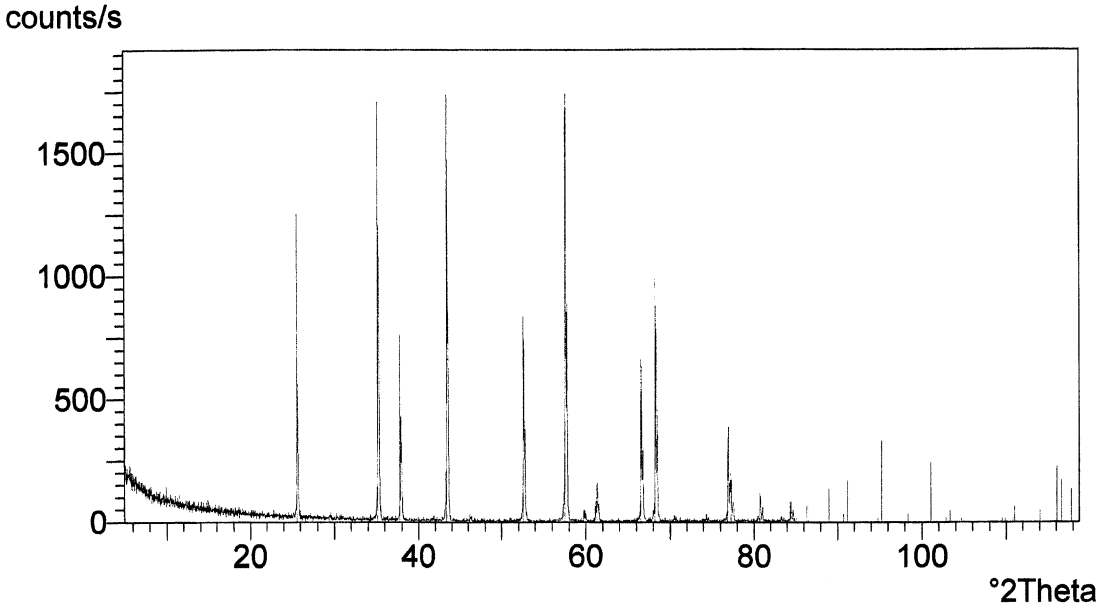

Fig. 4. X-ray (CuK_α) diffraction pattern of sintered alumina ceramic, showing the final α-alumina matrix structure after sintering at 1250 °C for 2 h. All peaks correspond to α-alumina (JCPDS-ICDD Card No: 43-1484).

have been faster than the grain growth rate [15] at the processing temperature (1250 °C). There are however some inter-granular pores adjacent to elongated grains, indicating that these pores are probably formed during α-Al_2O_3 discontinuous grain growth. The presence of impurities in the nanosize δ-$A1_2O_3$ particles used as seeds may have some influence on the limited preferential grain growth of the alumina matrix. This is at this stage an speculation, however recent work using the same material [16], has confirmed discontinuous grain growth due to SiO_2 and TiO_2 impurities.

The sample shown in Fig. 5 had a high sintered density of 98.3% TD, confirming the suitability of the processing technique developed here, based on a novel seeding material for commercial boehmite sols and electrophoretic deposition, to achieve fairly dense α-alumina ceramics at relatively low temperatures. The main difference with previous studies on seeding of boehmite sols [3, 5–8] is not only the use in the present research of a novel seeding "composite" suspension, but also the use of electrophoretic deposition to obtain the green bodies. Previous studies have used uniaxial and isostatic cold-pressing (die compaction) [3, 9, 16], extrusion of gels [2] and hot-forging [10] to prepare alumina compacts from seeded boehmite precursors. The formation of alumina ceramics by EPD of a seeded boehmite sol is reported here for the first time. Moreover the suitability of the seeded boehmite sol to be used for the fabrication of fibre-reinforced alumina matrix composites by using EPD and pressureless sintering has been demonstrated recently [11].

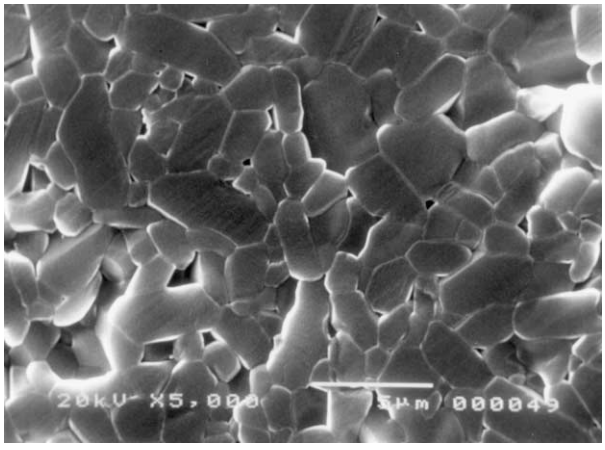

Fig. 5. High-resolution SEM micrograph showing the fine and dense α-alumina microstructure of an EPD-formed sample after sintering at 1250 °C for 2 h. Note the absence of intra-granu!ar porosity.

There are several reasons that led us to develop composite seeds for the boehmite suspension, as presented in this study, which are related to the use of EPD for forming green bodies. On the one hand there is the requirement of producing a stable suspension suitable for the EPD technique containing particles that travel with the same speed to the deposition electrode. This is more difficult to achieve if all the seed particles are "large" micrometer-size α-alumina, since they will move in suspension with a different velocity to that of the nanosize boehmite particles. Moreover, during the suspension preparation steps, micrometer size α-alumina particles will tend to segregate, thus impairing the

attainment of a stable suspension for EPD. If a homogeneous distribution of the seeds is not achieved in the EPD-formed green body, the final good quality of the alumina ceramics produced, in terms of low porosity and homogeneous fine-grained microstructure, will not be obtained. The homogeneous dispersion of the micrometric α-alumina particles in the nanosized δ-alumina suspension has eliminated these problems, as presented here.

It is not clear at this stage how the combination of α- and δ-alumina seed particles affects the process of densification and crystallisation of the α-alumina microstructure. It can be speculated however that using nanosize δ-alumina seeds may have the advantage of lowering the sintering temperature since they are more sinter-active than crystalline α-alumina micrometric particles. However a certain concentration of α-alumina particles within the seeding mixture is required as they should provide the sites for the onset of the crystal growing process during sintering. Our results show that using nanosize δ-alumina particles combined with a small amount of micrometric α-alumina particles is effective to accelerate the densification rate and the reaction kinetics during sintering. It must be pointed out however that the results in terms of final density and grain size distribution of the final alumina microstructure are similar to those obtained by the standard method of α-alumina seeding, as reported in the literature [3,5,8,16]. Whether or not a seeding suspension composed solely of nanosize δ-alumina particles can lead to similar results in EPD-formed bodies is the focus of on-going research.

4. Conclusions

The results confirm that dense α-alumina ceramics with very fine grain size and no intra-granular porosity can be produced from the seeded boehmite sol developed here, which was obtained by seeding with a tailored combination of δ- and α-alumina particles in nanometre and micrometer ranges, respectively, followed by EPD and pressureless sintering. Sintering temperatures as low as 1250 °C are sufficient to obtain satisfactory results in terms of development of a pure α-alumina matrix and attainment of high densification. The present results are in broad agreement with literature reports, where other seeds, including γ-$A1_2O_3$, α-$A1_2O_3$, MgO and α-Fe_2O_3 have been used [3, 5–9]. The α-alumina material developed here is a candidate to be used as a matrix in fibre reinforced ceramic composites fabricated by EPD.

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