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Spray Freeze Granulation of Submicrometre α-Alumina Using Ultrasonication

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Abstract

Granulation is a key factor towards improvement of the flowability of fine ceramic powders to make them suitable for industrial dry pressing. Controlled granulation of fine alumina particles with a primary particle size of ~ 150 nm was carried out using spray-freeze drying, which led to the production of flowable granules with high crushability. The fracture surface of uniaxially die-pressed green bodies made from granules with density values of ≥ 50 % of theoretical showed a uniform microstructure. Sintering experiments were performed using conventional single- and two-stage radiant heating methods followed by density and grain size measurement and characterisation of the final dense compacts to study the efficiency of two-stage sintering in grain growth elimination. The results have been compared with those of alumina bodies prepared using similar suspension by the slip-casting route.

Keywords: Alumina, granulation, spray-freeze drying, two-stage sintering

I. Introduction

With its combination of high hardness, corrosion resistance, thermodynamic stability and relatively low cost compared to other advanced ceramics, alumina is a material that has gained wide acceptance by industry. It is used for applications ranging from hip implants to sliding and sealing elements, thread guides, cutting tools and grinding grits as well as many other applications [1, 2]. It is known that finer microstructures give rise to higher hardness, since decreasing the grain size limits the space for motion and multiplication of the lattice elements of microplasticity such as dislocations and twins [3]; thus sintered fine-grained alumina can possess a Vickers microhardness as high as 20 GPa [4].

As decades of study on conventional ceramic processing have revealed, the uniformity and homogeneity of particle packing in the green body has a great effect on the densification process and hence the final density of ceramics [5]. Whilst wet forming has been shown to yield homogeneous ceramics of high green density [6], the drying stage becomes increasingly slow as the particle size becomes finer and the component becomes larger, due to the fine nature of the porosity present. An alternative green forming approach is dry pressing, a well-established and fast method of manufacturing reasonably complex-shaped compacts with close tolerances using ceramic powders at low cost. However, the poor compaction behaviour of fine powders is related to both poor flowability and/or the high level of agglomeration present in the powder due to the van der Waals adhe-

sion between particles becoming significant as the particle size decreases [7].

Spray drying is generally used to improve the flowability of fine ceramic powders [8, 9]. It is essential that during the compaction stage, all the spray-dried granules break down into their primary particles, as any uncrushed granule will be of locally higher density and can sinter into very large grains, leading to loss of mechanical strength in the final compact [10]. Therefore, controlling the granule strength to achieve high crushability is as important as controlling their flowability. As the finer the powder particles, the stronger the agglomerates are, granules formed by spray drying nanozirconia powder produced in a previous study did not all crush even when pressed at 500 MPa, two and a half times the pressure often used in industry [9]. Spray-freeze drying, however is a technique that has been reported to yield soft granules by prohibiting the formation of a segregated binder layer, which can exist in spray-dried granules [11].

Spray-freeze drying has been used by Binner *et al.* [12, 13] to produce granulated nano zirconia powders, although the addition of 1 – 2 wt% of Freon 11 (a standard foaming agent) was required to achieve flowable and crushable SFD granules that could be compacted into 54 – 55 % dense green bodies showing no sign of any residual granules at pressures as low as 250 MPa. The granulated SFD powders containing Freon pressed quite satisfactorily using factory-floor pressing equipment without any sticking, delamination or capping problems [13].

Another challenge in developing fine-grained ceramics is the difficulty in retaining the fine structure during the

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sintering process. It is difficult to control the grain growth even when the green microstructure is homogeneous; hence the optimisation of sintering cycles for fine-sized compacts is essential. There are a number of approaches to controlling the grain growth during densification of fine powders including two-stage sintering [14 – 16] and various pressure-assisted techniques [6, 17, 18]. Chen *et al.* [15, 16] developed the sintering of nanostructured Y_2O_3 ceramics using a two-stage sintering route, where the green compacts were heated to a high temperature, known as T_1, for a very short time and then cooled down rapidly to a lower temperature, T_2, where they were held until becoming fully dense, typically about 20 hours. The key aspect of the process was that there was no grain growth reported during the second step. Bodisova *et al.* have reported successful elimination of grain growth in the final stage along with relative densities of up to 99.7 % for dry-pressed submicron alumina ceramics using a combination of the two-stage sintering and doping with metal oxides such as MgO, ZrO_2 or Y_2O_3 [19].

The question of how efficient two-stage sintering is in eliminating the grain growth during the final stage of sintering of polycrystalline alumina has been in existence for a long time. The main focus of the present work was to investigate the potential of producing fully dense alumina ceramics, whilst retaining the final-stage growth of grains using a two-stage radiant heating technique. The alumina green compacts were formed via wet forming (slip casting) and dry forming (granulation and die pressing) using an aqueous submicrometre alumina suspension of high solids content. The granules produced and both green and sintered compacts were thoroughly characterised in terms of density and microstructure including uniformity and mean grain size.

II. Materials and Methods

Fine α-alumina powder was obtained in the form of an aqueous suspension (BA15PS, Baikowski, France). Ultrasonic treatment was applied initially using a Soniprep 150-MSE ultrasonicator (MSE Scientific Instruments, Manchester, UK) for 3 minutes prior to rheological behaviour measurement of the suspension using an Anton Paar RheolabQC rotational rheometer (Anton Paar, Austria). The electrokinetic behaviour of the suspension was characterised using an AcoustoSizer II (Colloidal Dynamics Ltd., Sydney, Australia). Thermo Gravimetric Analysis (TGA) was carried out using SDT 2960 Simultaneous TGA/DSC (TA Instruments Ltd, UK) in argon.

Granulation of the alumina suspension was carried out using both the as-received and the Freon-added suspensions, where the former was mixed and stirred with 2 vol% Freon 11 (solution of trichlorofluoromethane in methanol, Scientific UK Ltd., Loughborough, UK). Spray drying of the alumina suspension was performed using a spray dryer (Production Minor, GEA Niro, Copenhagen, Denmark) with a rotary atomiser with the outlet and inlet stream temperatures maintained at 120 °C and 210 °C,

respectively. For spray-freeze drying, the suspension was sprayed using a probe operating at a fixed frequency of 23 kHz and amplitude of 12 μm, which is in the range of appropriate ultrasound amplitudes to form fine, fully-atomised droplets, as shown in a previous study [20]; the resulting fine droplets were converted into frozen granules instantly on contact with the liquid nitrogen. The frozen granules were then dried using a Benchtop Freeze Drier (Virtis® Benchtop SLC, New York, USA) of 7 Pa pressure and -60 °C temperature. The granulated powders were heat-treated at 70 °C/1 h to burn off the Freon and were then sieved to retain the fraction between 125 and 250 μm for subsequent pressing. Morphology of the spray-freeze-dried (SFD) granules was analysed using FEG-SEM. Flowability of the SFD powder was determined by measuring the flow rate using a Hall Flowmeter and conical flow funnels with orifices of 2.5 and 5 mm in diameter (British Standard BS EN ISO 4490:2008). Subsequently, both bulk and tap densities of the powders were calculated by measuring the volume of each powder sample after tapping 200 times. Green bodies were die-pressed using a Lloyds Mechanical Testing Machine (L10000 Tensometer, Lloyds Instruments, Fareham, UK) in a single-action, hardened steel die with a diameter of 10 mm and consolidated under a pressure range of 150 – 480 MPa for 1 minute. Slip casting was also used to prepare green bodies; the ultra-sonicated as-received suspension was cast directly into Plaster-of-Paris (PoP) (Prestia 23 casting plaster, Lafarge, Cambridgeshire, UK) mould. FEG-SEM was used to image the fracture surfaces of the green bodies to investigate the uniformity.

Densification was carried out using both single- and two-stage sintering methods in a conventional box furnace (Carbolite Ltd, Hope Valley, UK); the temperature being controlled by means of a Eurotherm 902 controller (Eurotherm UK Ltd., West Sussex, UK) connected to a thermocouple inside the furnace chamber. Both die-pressed (DP) and slip-cast (SC) samples were single-stage sintered at 1300 °C, 1350 °C and 1400 °C for 2 hours. For the two-stage sintering, both DP and SC green samples were initially sintered for 0.1 minute at T_1 values of 1300 °C, 1400 °C and 1450 °C in order to mimic the first stage of heating. Based on these results, the second step temperature, T_2, was chosen in a range of values of about 100 – 150 °C lower than T_1 for each experiment with a view to achieving optimal densification, Table 1. The relative density of the sintered bodies was measured using the Archimedes method and their microstructure was observed by FEG-SEM on polished surfaces, followed by thermal etching for 10 minutes. The grain size was calculated with the linear intercept method (ASTM E 112 – 96):

$$D = \frac{L \times A_1}{M \times N} \qquad (1)$$

where D is the equivalent average grain diameter, L is the length of the superimposed lines, A_1 is the shape correction factor (1.56) [21], M is the magnification and N is the quantity of intercepts.

Table 1: Summary of the two-stage sintering experiments for (a) die-pressed and (b) slip-cast samples.

(a) Sample	T_1 /°C	t/min	T_2/°C	t/h
DP-1300 – 1250 – 5	1300	0.1	1250	5
DP-1400 – 1250 – 5	1400	0.1	1250	5
DP-1450 – 1250 – 2	1450		1250	2
DP-1450 – 1250 – 5		0.1		5
DP-1450 – 1300 – 5			1300	5
(b) Sample	T_1 /°C	t/min	T_2/°C	t/h
SC-1300 – 1250 – 5	1300	0.1	1250	5
SC-1400 – 1250 – 2	1400	0.1	1250	2
SC-1400 – 1250 – 5				5
SC-1400 – 1300 – 2		0.1	1300	2
SC-1400 – 1300 – 5				5
SC-1400 – 1300 – 10				10

III. Results and Discussion

The solids loading of the as-received alumina suspension was measured to be ~ 59 wt% with a mean particle size of 150 nm and a specific surface area of 15 m^2g^{-1}. The flow curve of the as-received suspension, Fig. 1(a), after 3 minutes of ultrasonic exposure to break up any existing agglomerates that can be produced during previous drying or calcination stages [22], displayed shear-thinning behaviour with a low viscosity of ~10 mPas at a shear rate of 100 s^{-1}. The obtained low viscosity values demonstrated that the as-received suspension with high solids content was suitable for further processing into green bodies. The zeta potential measurements using diluted suspensions with solids content of ~ 5 wt%, Fig. 1(b), showed that the isoelectric point (IEP) of the suspension was 9.6; since the inherent pH of the as-received suspension was 3.6 with a zeta potential value of ~ 60 mV (which is indicative of stable dispersions [23]), no agent had be added in order to improve the dispersion.

The Thermogravimetric Analysis (TGA) of the as-received alumina suspension, Fig. 1(c), demonstrated that ~ 0.4 % of the weight loss for the suspension occurred below 100 °C, which was due to the evaporation of water. The weight loss between 100 °C and 250 °C, ~ 0.5 %, was presumably due to dehydration of more strongly chemisorbed water present in the sample. Finally, the loss in the range of 250 °C and 475 °C could be caused by the evaporation of the other additives used in preparing the suspension, such as polymer dispersants. Therefore, prior to the sintering process, a slow heating cycle up to 700 °C for 2 hours was applied to both die-pressed and slip-cast green bodies in order to remove any residual organics.

Fig. 2 shows the granules produced by spray drying the as-received alumina suspension and spray-freeze drying the alumina suspension without and with 2 vol% of Freon. As expected, both spray drying and spray-freeze drying techniques yielded spherical granules. It can be observed that the alumina particles were packed closer in the spray-dried powder compared to the spray-freeze-dried ones. This is due to the water being removed from the droplets by a stream of hot air during the spray drying process, which results in the presence of more water in the central core of the droplet and leads to shrinkage and denser packing of the particles within the granules. On the other hand, the addition of Freon, as described elsewhere [12,13], was expected to reduce the strength of the granules by introducing Griffith flaws after subsequent burn-off. The retrained fraction of 125 – 250 μm of the spray-freeze- dried powders, which had been shown to maximise the flowability in the previous work [12] was studied further. The consequences of adding Freon on the flowability, fill and tap density are summarised in Table 2. It can be seen that the size and shape of the granules, and hence their flowability, were not significantly affected by the addition of Freon. Fig. 2, however, reveals that the granule surfaces contain more defects when the Freon was used; this weakened the granules and enabled them to crush more easily at lower pressures. The spray-dried powder showed considerably low flow rate values due to the morphology and rough surface of its granules compared to spray-freeze-dried powders.

Green densities of the granules with and without Freon after die pressing are plotted in Fig. 3; it can be seen that at every pressure the granules containing Freon displayed a higher density, as expected. Whilst relative green densities of up to 53 % could be obtained, this required pressures as high as 480 MPa, which is outside of the range of most ceramic manufacturers. However, as it is possible to achieve relative densities of over 98 % with retained fine microstructure using dry-pressed green bodies with densities of ~ 51 %, lower pressures of ~ 250 MPa can be used for the Freon-based granulated powders.
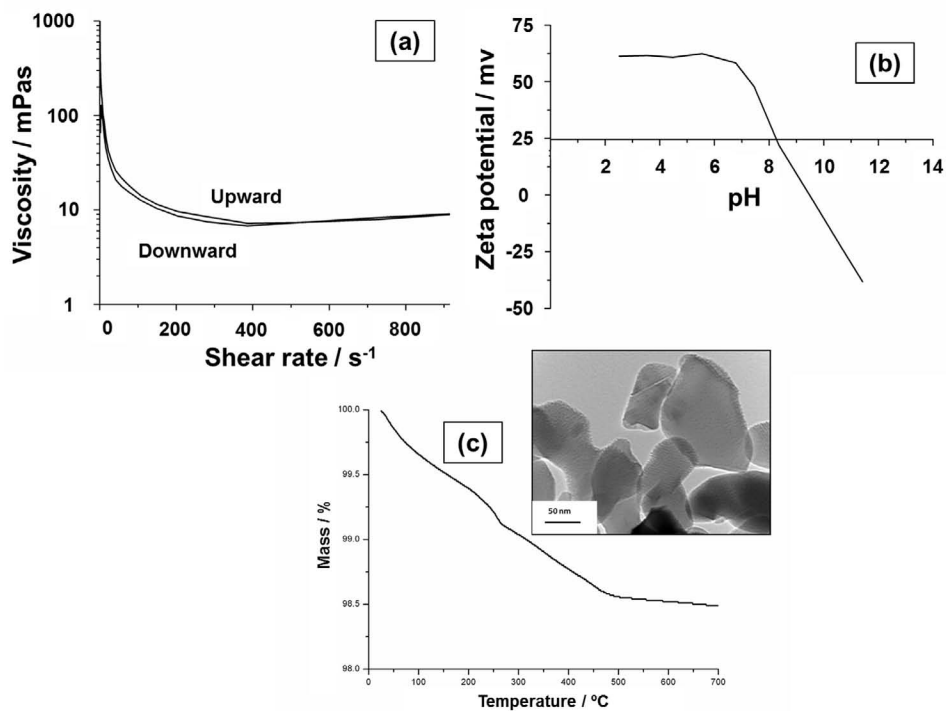
Fig. 1: (a) Viscosity values as a function of the shear rate, (b) zeta potential vs pH and (c) TGA of the as-received suspension; inset shows a TEM micrograph of the alumina particles.
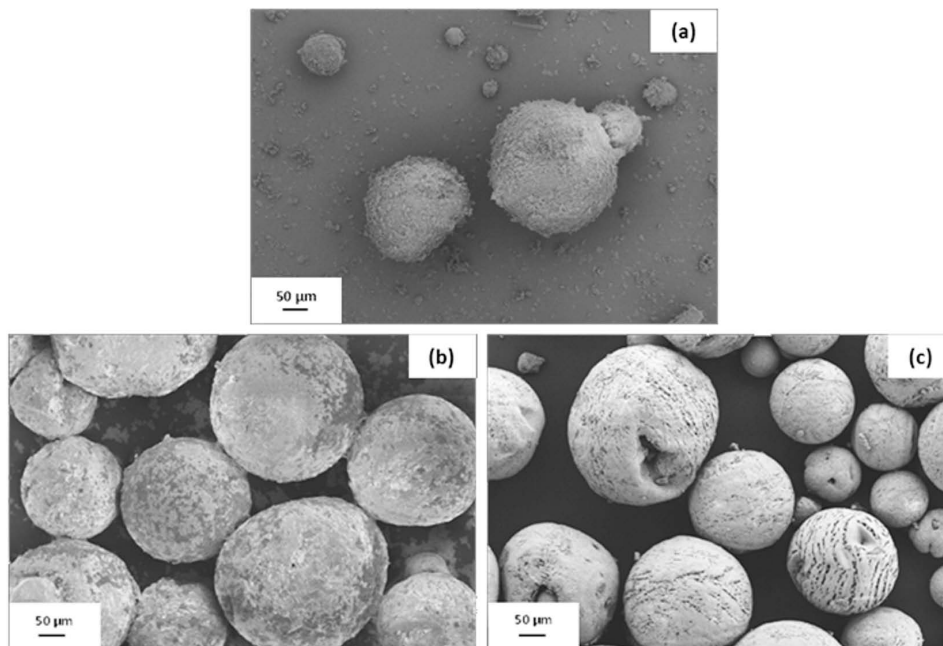

Fig. 2: FEG-SEM micrographs of (a) spray-dried alumina granules using the as-received suspension and spray-freeze-dried alumina granules (b) without and (c) with 2 vol% added Freon.

Table 2: Volumetric flow rate and density values for different spray-freeze-dried powders.

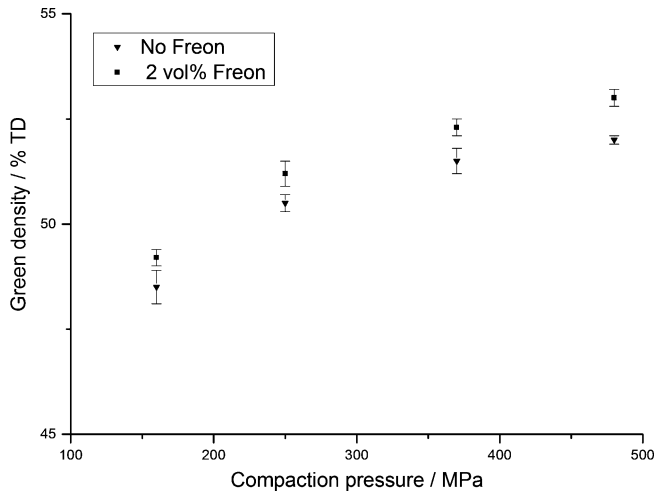| Orifice size/mm	2.5		5	
SFD powder	No Freon	2 vol% Freon	No Freon	2 vol% Freon
Flow rate/gs^{-1}	0.25	0.27	1.80	1.79
Fill density/gcm^{-3}	0.59	0.58	0.59	0.59
Tapped density/gcm^{-3}	0.67	0.68	0.66	0.67

Fig. 3: Compaction characteristics of the spray-freeze-dried granules.

Fig. 4 shows the FEG-SEM micrographs of die-pressed green bodies without and with 2 vol% of Freon at 250 MPa. These micrographs demonstrated that a very uniform and homogeneous green body of relatively high density could be achieved, with no visible residual granule relics after the addition of Freon due to the increase in the crushability of the granules. During the pressing process, the granulated powders prepared using Freon did not display any tendency to stick to the dies and there was no evidence of any delamination issue observed in the yielded compacts. When the as-received suspension was slip-cast into green bodies, it also resulted in homogeneous compacts, Fig. 4(c), with their relative density found to be 53.5 ± 0.5 % of the theoretical. Whilst a high level of

humidity resulted in longer drying times (up to 5 days) to achieve fully dried bodies, lower humidity led to an elevated risk of cracking. Therefore, initial drying of the slip-cast bodies was carried out under ambient conditions of about 20 °C and 50 % humidity for 3 days before removal of the samples from the moulds. The compacts were then placed on a Teflon sheet for further drying in an oven at 60 °C for 12 h; the Teflon sheet assisted with sample shrinkage by providing minimal resistance to shrinkage.

Density and mean grain size values of the samples after single-stage sintering at different temperatures for 2 h are plotted in Fig. 6, where it is immediately observable that achieving > 99 % relative density led to exaggerated growth of the alumina grains. Although a density up to ~ 99.43 % could be achieved after sintering at 1400 °C for the slip-cast samples, densification was accompanied by exaggerated grain growth, yielding a mean grain size of ~ 1.18 μm. It is necessary to mention that in order to avoid the effect of heating rate on density and grain growth, the conventional heating trials were conducted using a constant heating rate of 10 K/min.

Fig. 5 shows the density values obtained after heating the samples for 0.1 minute at different temperatures, with the aim of planning the two-stage sintering process. As expected, the slip-cast samples were always denser. The results of all the subsequent two-stage sintering experiments for both the slip-cast and die-pressed bodies are plotted in Fig. 6. It is quite evident that the use of the two-stage sintering method resulted in a slightly finer mean grain size for a given density. However, complete suppression of the final-stage growth that has been previously reported by Chen and Wang[15] has not occurred here[24].
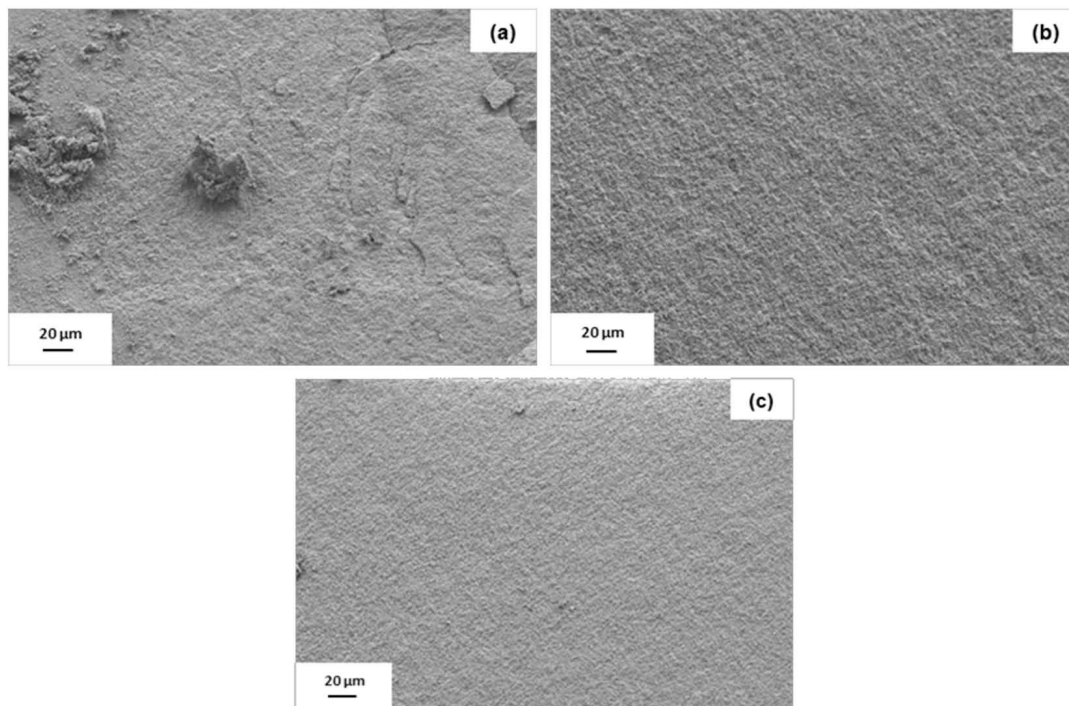

Fig. 4: FEG-SEM micrographs of the fracture surfaces of die-pressed (DP) green bodies (a) with no and (b) 2 vol% added Freon; both pressed at 250 MPa and (c) slip-cast (SC) green compact.
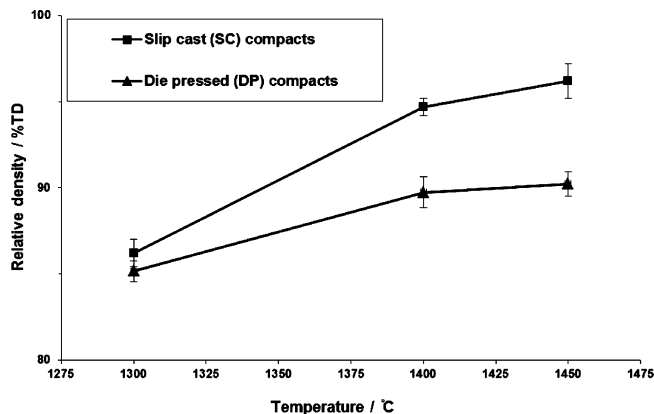
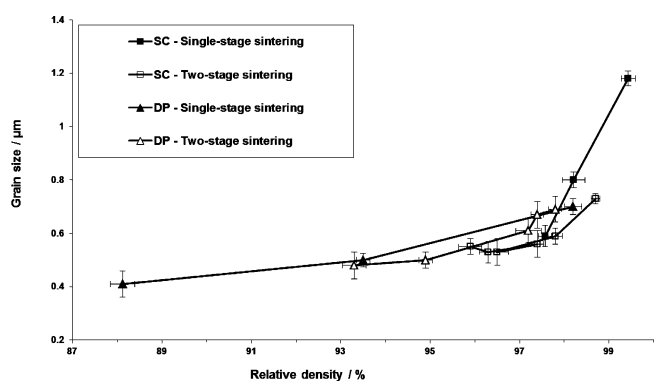**Fig. 5:** Densities achieved after T_1 sintering stage for DP and SC samples.

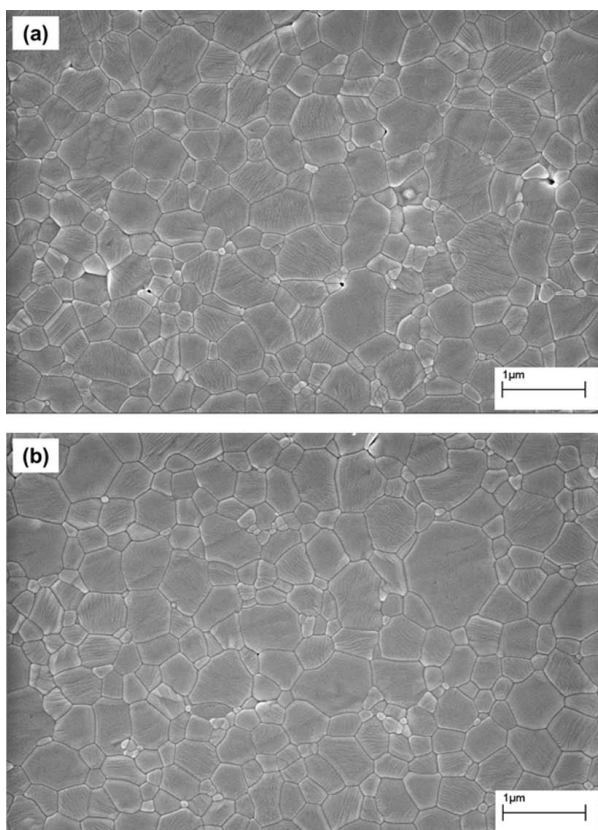**Fig. 6:** Variation in grain size with density for both DP and SC samples.

Fig. 7: FEG-SEM micrographs of sintered bodies using T_1 = 1400 °C and T_2 = 1250 °C/5 h: (a) die-pressed at 250 MPa and (b) slip-cast.

The difference between sintered slip-cast and die-pressed bodies (representative micrographs of the microstructure of DP and SC bodies after two-stage sintering at T_1 of 1400 °C and T_2 of 1200 °C/5 h is displayed in Fig. 7 and is associated with the fact that the latter had lower green densities and coarser microstructures compared to the former. The plot also illustrates that, unlike the work of Chen and Wang [15, 16], the microstructure of the submicron alumina bodies did not remain frozen during sintering at T_2; rather a relatively small amount of grain coarsening was observed. Bodisova *et al.* [25] have reported similar results for the sintering of nano zinc oxide and submicron alumina, respectively; the data was also comparable with the results reported for the two-stage sintering of ZrO_2 [6,24]. As has been reported previously [6], it is believed that the sintering mechanism is not changed by the two-stage process, but rather the effect of the first stage is to increase the effective "green" density prior to completing densification during the second stage.

IV. Conclusions

It has been possible to spray-freeze dry an as-received sub-micrometer alumina suspension of ~ 59 wt% solids content to obtain a powder suitable for dry pressing. Use of a foaming agent led to weaker granules, whilst maintaining the high flowability of the spray-freeze-dried powders. The analysis of the spray-dried granulated powder showed that it did not flow well owing to the roughness observed on the surface of the granules. Using both wet and dry pressing methods, green bodies with relative densities of ~ 50 % and over were prepared. Although the two-stage sintering method did not eliminate grain growth during the second stage, as reported by Chen and Wang in Y_2O_3 ceramics [15], here it still resulted in much smaller average grain sizes for slip-cast samples than in conventional single-stage sintering route. It can be concluded that the sintering mechanism occurring during the second stage is not dissimilar to a single-stage process but slightly shifted towards higher density values. Further work is underway at Loughborough University to investigate this.

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