Comparison of ~~Spray Freeze Dried Nanozirconia Granules Using Ultrasonication and Twin-Fluid Atomiz~~spray freeze dried nanozirconia granules using ultrasonication and twin-fluid atomisation

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Abstract

Granulation of nanostructured 3 mol% yttria stabilised zirconia using spray freeze drying was investigated to achieve flowable and crushable granules for subsequent die pressing. Commercial nanosuspension consisting of ~16 nm particles was concentrated to ~55 wt% solids content via a patented technique, followed by spraying into liquid nitrogen using either a vibrating ultrasonic probe or a twin-fluid atomizer and freeze dried to yield spherical granules. Control of the granule size fractions was investigated by changing the amplitude and the feeding rate of the nanosuspension during ultrasonication, whilst the flow rate of compressed air used for spraying was varied during twin-fluid atomi~~z~~sation. Granules retaining good crushability for pressing were in a size range of 125~~to~~–250 µm, which were achieved with ~60 wt% yields using the atomi~~z~~sation route, whilst a maximum of 35 wt% of granules in this size range were produced in previous research using ultrasonication.

Keywords: Nanostructure; Spray freeze drying; Atomi~~z~~sation; Ultrasonication; Dry pressing

1 Introduction

Nanocrystalline ceramics, i.e. those with mean grain sizes of less than 100 nm, have become of interest in recent years due to their novel mechanical, thermal and optical properties, which allow them to access a wide range of industrial applications~~[1].~~[1] The research presented here focuses on zirconia ceramics and, in particular, 3 mol% yttria stabilised zirconia (3YSZ). Conventional 3YSZ is a common material for engineering components, since it displays high strength and toughness. Furthermore, zirconia has the potential to be used in the bioceramics industries for bone replacement and dental applications due to its intrinsic bioinertness~~[2].~~[2] However, conventional 3YSZ suffers from hydrothermal ageing, which is a degradation process caused by a tetragonal to monoclinic phase transformation in the presence of water or water vapour, usually at elevated temperatures~~[3].~~[3] Recent results have suggested that the mechanical performance of nanostructured zirconia is at least as good as that of conventional submicron zirconia, whilst the nanostructured material is totally immune to hydrothermal ageing~~[4].~~[4]

The processing of nanoceramic components is difficult however, since ultrafine particles possess very high surface areas and hence have extremely high free energy; they stick together due to van der Waals forces~~[5].~~[5] This hinders the manufacture of high density green bodies and can lead to excessive grain growth after sintering~~[6].~~[6] Dry forming is the industrially preferred processing route for technical ceramics because of its high manufacturing efficiency and low cost. However, dry nanopowders are not free-flowing due to the random aggregation of nanosized primary particles~~[7].~~[7] Hence it is essential to granulate them into spheres to enhance their flowability before dry forming. Spray drying is a widely-used technique to produce ceramic powders with good flowability; however, spray dried nanogranulates retain very high strength and hence are difficult to crush completely at typical industrial pressing pressures of up to

200 MPa[8].[8] The residual uncrushed granules will affect the homogeneity of green bodies formed and in a sintered component, they act as flaw origins and thus reduce the strength of the component severely[9].[9]

At Loughborough University, nano3YSZ granules have been produced by using a spray freeze drying (SFD) technique; this process has also been used by many other researchers for producing soft ceramic granules consisting of submicron[10,11][10,11] and nanosized particles[7,12].[7,12] However, the granules produced were not always reported to be satisfactory for dry forming. Adolfsson and Shen[10][10] reported that some sintered components formed from SFD granules demonstrated low density and/or poor strength; the former was formed by granules with inhomogeneous structure and large internal defects, whilst the latter was due to the use of granules with high densities, which were difficult to crush completely during pressing. Vicent et al. [12]et al.[12] observed poor flowability from spray freeze granulated nanopowders; this was mainly due to the less spherical granules produced and their uncontrolled size distribution. The research presented here has solved these issues; the SFD granules within a size fraction of 125 to 250 μm have been used for dry forming and they display excellent flow and crush properties[1,8,9].[1,8,9] Homogeneous, flaw-free compacts with high green densities (~55% of theoretical) have been die pressed using these 125 to 250 μm granules[9]. 250 μm granules.[9] However, the ultrasonic spraying process that has been used to date only yields a maximum of 35 wt% granules in the desired size range[1].[1] mainly due to the lack of control over the spraying process.

A vibrating ultrasonic probe has been used to disperse the nanosuspensions into fine droplets, which are frozen in liquid nitrogen and subsequently freeze-dried to sublime off the ice[1].[1] Previously the nanosuspensions were supplied to the ultrasonic probe manually using a pipette; however, it was very difficult to control the feeding rate during the process. In this paper, a peristaltic pump and a pressure bottle have been used to feed the nanosuspension at controlled flow rates; nevertheless, it is difficult to use the ultrasonic spraying process for medium to large scale production of SFD granules. Stuer et al. [11]et al.[11] demonstrated the use of an ultrasonic spraying device that generated spherical, nearly monosized SFD granules of ~250 μm, yet this equipment can only process ~0.06 lL h^{-1} suspension. An alternative approach is introduced in this paper, a twin-fluid atomizer, which yields a significantly higher amount of suitably sized granules at controllable spraying rates.

2 Experimental

Aqueous 3YSZ nanosuspensions with an initial solids content of ~24 wt% (5 vol%) and consisting of well dispersed nanoparticles of ~16 nm in size were used as the precursor. They were supplied by MEL Chemicals Ltd., Manchester, UK. The as-received suspensions were concentrated to ~55 wt% (~17 vol%) using a patented route described in detail elsewhere[13].[13] In brief, it involved changing the pH from ~3.5 to ~10.5 by adding tetra-methyl ammonium hydroxide (TMAH, Aldrich Chemicals Ltd., Dorset, UK), followed by adding an amount of the dispersant tri-ammonium citrate (TAC, Fisher Scientific UK Ltd., Loughborough, UK) equivalent to 3 wt% of the solids in the nanosuspension. The latter was then heated gently at 58 °C using a water bath, with continuous mechanical stirring to avoid agglomeration. The pH of the nanosuspension was regularly checked to ensure it remained above ~9.0, whilst multistage ultrasonic treatments were applied at regular intervals using a Soniprep 150-MSE ultrasonicator (MSE Scientific Instruments, Manchester, UK) to avoid agglomeration of the nanoparticles. The particle size distributions of the as-received, as well as the concentrated nanosuspensions were measured using a Mastersizer 2000 (Malvern Instruments Ltd., Malvern, UK); see Fig. 1. The particle size distribution is unchanged after concentration, indicating that the particles remain un-agglomerated. A volume fraction of 2% of Freon 11 (a solution of fluorotrichloromethane in methanol, Fisher Scientific UK Ltd., Loughborough, UK), used as an additive to weaken the resulting granules, was thoroughly mixed with the concentrated nanosuspensions in a sealed container for ~30 min utes before spraying[14]. before spraying.[14] The viscosities of the as-received and the concentrated nanosuspensions were determined using a Rheolab QC (Anton Paar GmbH, Graz, Austria) viscometer, as shown in Fig. 2. The viscosity for the latter remained less than ~20 mMPa s at shear rates in the range 200–800 s^{-1}, which was suitable to enable spraying<! –. The concentrated nanosuspension was stabilised at low viscosity because of the use of electrostatic dispersant TAC during concentration, accompanied by TMAH used as a pH modifier.

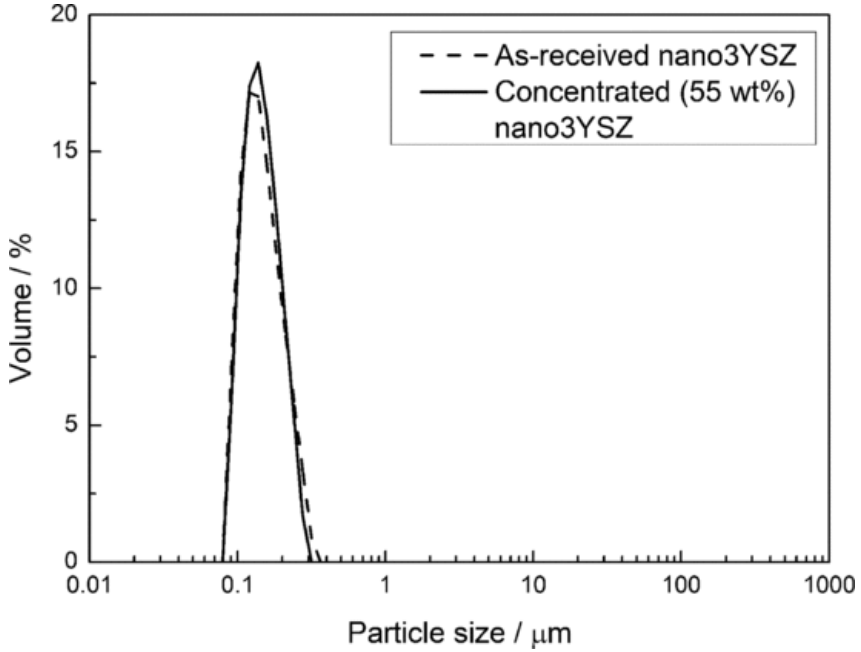

Fig. 1 Particle size distributions for as-received and concentrated nano3YSZ suspensions.

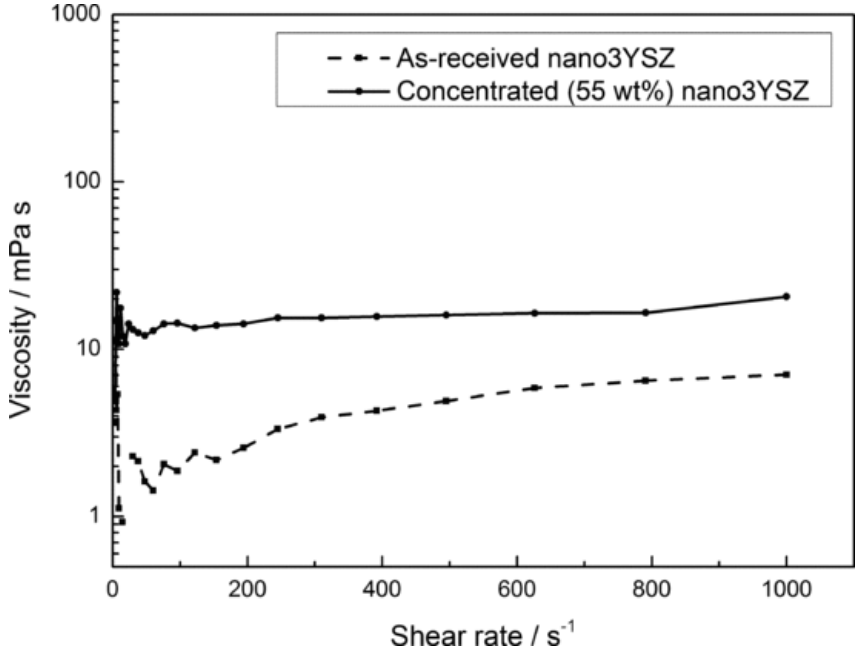

Fig. 2 Viscosity data for as-received and concentrated nano3YSZ suspensions.

Spray freeze drying was performed by spraying the concentrated nanosuspensions into liquid nitrogen using either an ultrasonication or an atomi~~z~~sation process. Figs. 3 and 4 show the setup of the equipment for both of these routes. A vibrating ultrasonic probe (MSE Scientific Instruments, Manchester, UK) with a flat tip surface of 9.5 mm diameter operating at a fixed frequency of 23 kHz was used in the former method. The size distributions of the resulting granules were varied by changing the amplitudes applied, as well as the feed rate of the nanosuspensions; the latter was controlled by using either a Masterflex C/L peristaltic pump (Cole-Parmer, London, UK) or a pressure bottle, as shown in Fig. 3~~-~~(a) and (b), respectively. For the atomi~~z~~sation route, a twin-fluid atomizer (BUCHI Labortechnik AG, Flawil, Switzerland) was employed to spray the nanosuspension at various flow rates by varying the flow rates of the compressed air used for spraying; this was measured using a flow met~~e~~re. Frozen granules were collected from the liquid nitrogen and subsequently underwent freeze drying using a VirTis Benchtop BTK-2 K Freeze Drier (SP Scientific, Stone Ridge, NY, USA) for ~48 h~~ours~~. The condenser temperature was set at ~~–~~62 °C and the vacuum was maintained at ~7 Pa (50 m~~t~~Torr). After freeze-drying, the granules were sieved to yield granules within the targeted size range of 125~~ to –~~250 μm for die pressing. No binder or plasticiser was used in the granulation process described here.

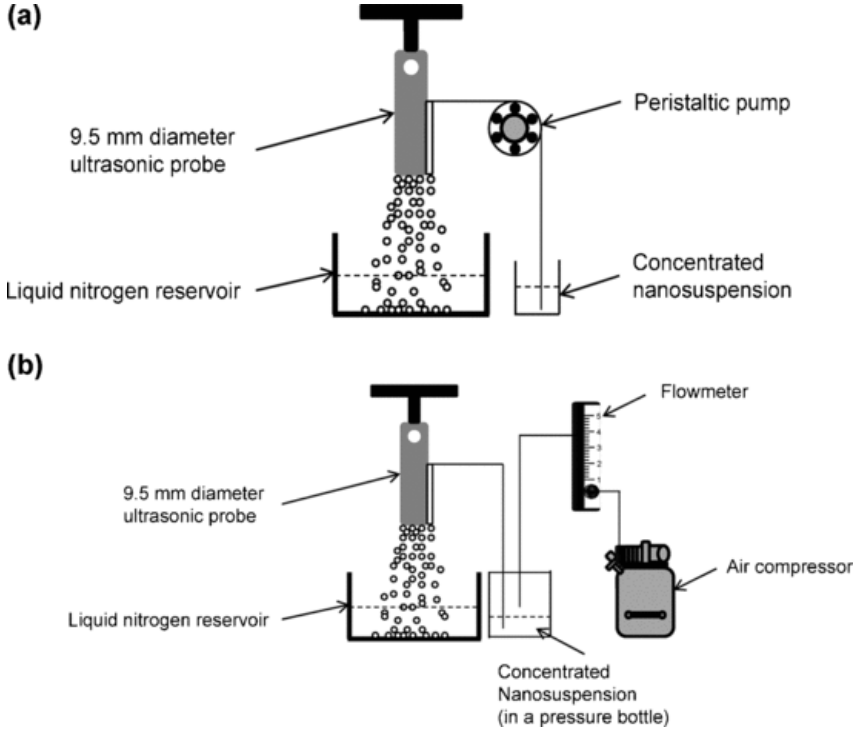

Fig. 3 ~~a~~(a) Ultrasonication spray freeze granulation using a peristaltic pump. ~~b~~(b) Ultrasonication spray freeze granulation using a pressure bottle.

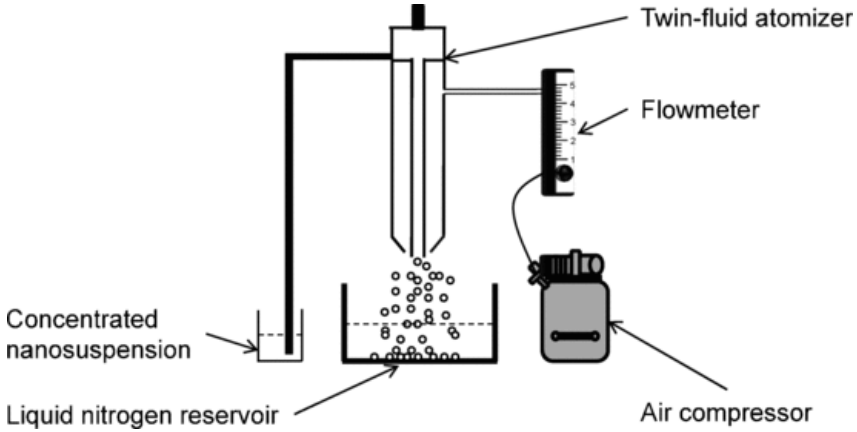

Fig. 4 Spray freeze granulation using a twin-fluid atomizer.

To characterise the flowability of the as-produced SFD granules using the two different methods, calibrated conical flow funnels with standard dimensions and discharge orifices of 2.5 mm, 5.0 mm and 7.5 mm were used to measure the mass and volume flow rates (see British Standard BS EN ISO 4490:2008). An industry standard spray-dried submicron 3YSZ powder, TZ-3YSB (Tosoh Corporation, Yamaguchi, Japan) was used as benchmark and its flowability data was also measured for comparison. The compaction performance was studied by pressing the SFD granules into cylindrical pellets of ~10 mm in diameter and ~2.4 mm thick using a hardened steel die at 200 MPa; the densities of the pressed materials were measured geometrically by taking the mass and dimensions of each pellet.

The strengths of individual granules were tested using a manual granulate strength testing system (etewe GmbH, Karlsruhe, Germany) located at the Fraunhofer Institut fuer Keramische Technologien und Systeme (IKTS) in Dresden, Germany. This involved the crushing of single granules, which were placed on a platform. During the test, the platform moved towards the tip surface of a micromet~~e~~re at a controlled speed of 10 μm s^{-1}. The fracture was recorded by video and the granule size was measured. A total of 200 granules with sizes between 50 μm ~~to~~and 250 μm were measured individually in each batch of powder. The force used to crush the granule and the displacements of the platform were used to calculate the granule fracture strength.

The surface and internal structure of the granules, as well as the fracture surfaces of the pressed green pellets, were characterised using a Leo 1530VP high resolution field emission gun scanning electron microscope (FEGSEM, Leo Elektronenskopie GmbH, Oberkochen, Germany).

3 Results and ~~D~~discussion

3.1 Granule size distributions

Fig. 5 shows the effect of the feeding rate on the resultant granule size distributions for the ultrasonic spraying process; the amplitude applied was 12 μm. At a very low feeding rate of 0.14 ~~l~~L h^{-1}, ~60 wt% of the granules were produced with sizes of less than 125 μm, whilst the yield of the granules in the same size range was only ~26 wt% when the nanosuspension was supplied at a much higher flow rate of 0.85 ~~l~~L h^{-1}. During the spraying process, many small sized cavities were created within the exposed nanosuspension through the vibration of the ultrasonic probe, which then collapsed and the local shockwave generated provided a strong hydrodynamic shear force to tear the nanosuspension into fine droplets~~[15].~~[15] It is worth noting that the ultrasonic waves were generated locally only at the tip of the probe, where the actual spraying process took place. When the feeding rate was low, there was a longer duration for the nanosuspension to stay at the probe tip; this could generate more cavities and hence more small-sized granules. However, when the feeding rate was high, there was insufficient residence time at the probe tip, resulting in the generation of fewer cavities within the supplied nanosuspension before it fell from the probe tip; hence the granules generated were larger. In addition to the cavitation theory, fine droplets could also be formed from the breakage of the crests of liquid capillary waves generated via the implosion of cavities; the size of the droplets produced is proportional to the wavelength of ultrasound applied~~[16].~~[16] In this paper, the ultrasound used for spraying had a fixed frequency of 23 kHz; hence the wavelength remained the same among different experiments and did not affect the size of the resultant granules.

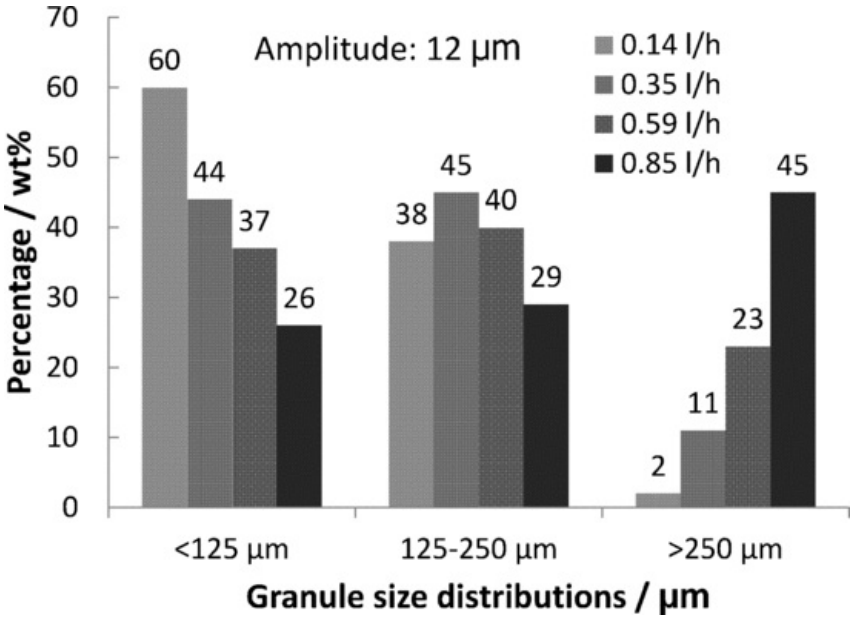

Fig. 5 Size distributions of the SFD granules produced at different feeding rates using the ultrasonication method with peristaltic pump.

Results showed that the use of a feeding rate of 0.35 ~~l~~L h^{-1} yielded the most granules, ~45 wt%, within the desired size range, however, spraying at this feeding rate but using different amplitudes did not affect the yields significantly, as shown in Fig. 6. The yield of the granules within the 125–250 µm range was increased by ~2 wt% to ~~–~~47 wt% when the maximum amplitude of 16 µm was applied, whilst reducing it to 7 µm resulted in ~1% loss by weight. Since the resultant granules were separated into each size fraction by sieving, considering the resolution of the experiments, it can be concluded that there was no significant effect within the 125–250 µm size range by using different amplitudes. However, a clear trend showed that more granules with sizes above 125 µm, especially those above 250 µm, were produced by increasing the amplitude from 7 to 16 µm. Whilst it is expected that higher amplitudes, hence greater ultrasound intensities, should yield smaller droplet sizes, it was observed that when a high amplitude, e.g. 16 µm, was used for spraying, the nanosuspension supplied was shaken off from one side of the probe tip without being atomized fully to form fine droplets; the granules produced were hence coarser compared to those obtained using a lower amplitude, e.g. 12 µm. This can be explained as ~~their~~ there being insufficient interface energy between the nanosuspension and the ultrasonic probe; if the momentum was too high the suspension was shaken off from the probe without being atomized. The same effect was observed by Rajan and Pandit[~~16~~16] and they proposed that there is a range of ultrasound amplitudes that can be used to generate fine droplets with smaller sizes; below or above this range coarse droplets are formed without being atomized fully. In this paper, the lowest amplitude applied was 7 µm; below this the ultrasound intensity was insufficient to atomize the nanosuspension into fine droplets; yet at this amplitude the granules produced had ~44 wt% within the desired size range, whilst much smaller granules with their sizes less than 125 µm were produced, indicating a good spray was obtained.

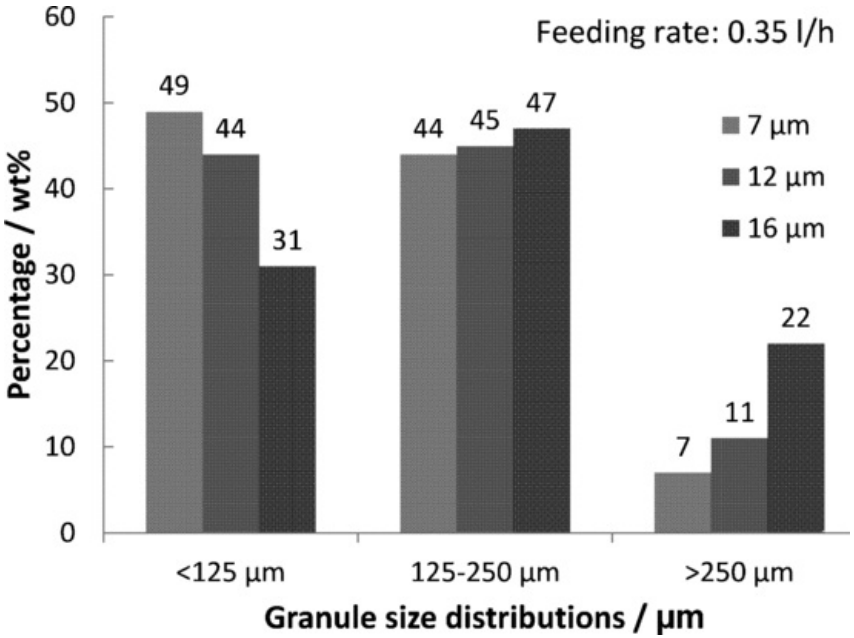

Fig. 6 Size distributions of the SFD granules produced at different amplitudes using the ultrasonication method with peristaltic pump.

Since it was difficult to achieve a stable flow of nanosuspension using a peristaltic pump, a pressure bottle was employed to deliver constant flow rate and the amplitude used for spraying was kept at 12 µm. However, this did not improve the yields of granules within the desired size range further (see Fig. 7) even when the nanosuspension was supplied at similar flow rates to those delivered by the peristaltic pump. This indicates that the size of granules was affected by the configuration of the ultrasonic probe, rather than the method for dispensing the nanosuspension during ultrasonication. It should be noted that surface tension of the nanosuspension plays an important role in droplet formation during spraying. This was not studied in the current research, since to change the surface tension would have required the use of additives and these were not desired in the final granules. Any excess organics would be retained in the granules, producing gas bubbles during debinding and yielding undesired porosity in the die-pressed components. Granules with excessive organics also retained high strength and hence were difficult to crush completely during die pressing.

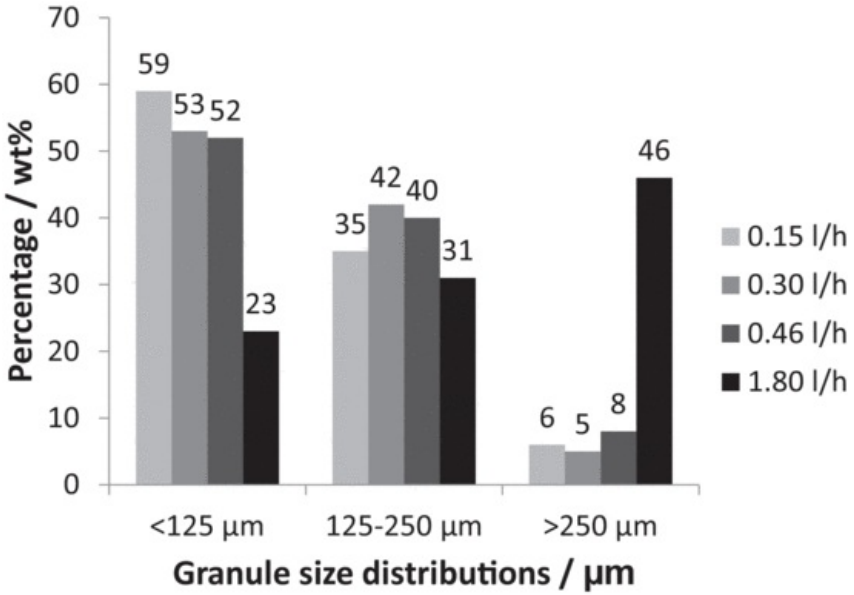

Fig. 7 Size distributions of the SFD granules produced at different feeding rates using the ultrasonication method with pressure bottle.

In the previous research mentioned above[1], the maximum yield of granules within the desired size range, 125–250 µm, was up to 35 wt%. For the current research presented here, whilst using the peristaltic pump to control the feeding rate of the nanosuspension improved the yield of the granules produced within the desired size fraction by more than 10 wt% to a ~~wt% to a~~ 47 wt% maximum, another issue was the difficulty of scaling up the laboratory scale ultrasonic spraying process. The major limitation of this method was the low volume handling capacity, due to the small area of the vibrating surface. The best conditions achieved to date involved spraying the nanosuspension at the fairly low flow rate of 0.35 µL h^{-1}; this may not be acceptable for industry scale processing of some ceramic powders. Whilst larger probe or the use of multiple transducers could be envisaged, in this work, a twin-fluid atomizer was investigated. The principal was to use high velocity compressed air to tear the supplied nanosuspensions into fine droplets. The distance between the nozzle tip and liquid nitrogen surface was kept at ~15 cm, which was the same for the ultrasonication method to minimise the difference between two approaches. Whilst the 'time of flight' for the droplets formed before they were frozen in liquid nitrogen can affect the shape of the granules produced, it has been proved that the granules obtained using the current condition were mostly spherical and displayed good flowability. Increasing the distance between the nozzle tip and the liquid nitrogen surface did not improve the shape or the flowability of the granules obtained further; instead, a liquid nitrogen bath with a much bigger surface area, and hence more liquid nitrogen was needed to capture all droplets formed. The depth of liquid nitrogen was maintained at ~15 cm throughout the experiment to keep all the droplets frozen and to ensure no further agglomeration can occur.

The resultant granule size distributions were controlled by using different amounts of air for spraying, as shown in Fig. 8. It can be seen that the use of a higher air flow rate, i.e. 4.1 µL min^{-1} enabled higher flow rates of suspensions to be sprayed; see Table 1. However, spraying under these conditions resulted in more than 90 wt% of the granules produced having sizes below 125 µm. Reducing the air flow rate to 3.8 µL min^{-1} achieved a maximum yield of 60 wt% granules within the desired 125–250 µm size range; the corresponding feed rate of the nanosuspension was measured at ~1.2 µL h^{-1}, which was much higher than could be achieved using the ultrasonic spraying method. When the supply of the compressed air was reduced further to 3.2 µL min^{-1}, ~53 wt% of the granules were produced with their sizes above 250 µm due to insufficient formation of fine droplets. It is also noted that the resultant granules from the twin-fluid atomi~~z~~sation route demonstrated overall narrower size distributions compared to the granules produced via the ultrasonication method; this enabled higher yields of the granules produced within the desired size range using the twin-fluid atomi~~z~~sation route.

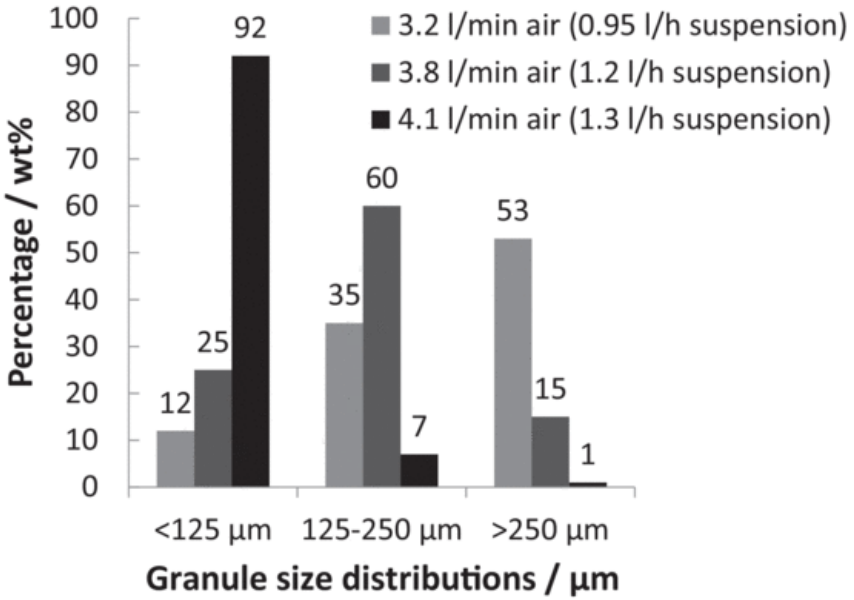

Fig. 8 Size distributions of the SFD granules produced at different air flow rates using the twin-fluid atomi~~z~~sation process.

Table 1 Volume flow rate of the feeding material during twin-fluid atomi~~z~~sation.

Air flow rate~~/ l min−1~~3.23.84.1 (L min^{-1})	3.2	3.8	4.1
Volume flow rate of the concentrated nanosuspension~~/ l h−1~~ (L h^{-1})	0.95	1.2	1.3

3.2 Flowability

Fig. 9 shows the mass and volume flow rates, through the conical flow funnels, of the benchmark powder and the SFD granules produced within the size range of 125~~ to ~~250 µm using both the atomi~~z~~sation methods. The benchmark Tosoh powder demonstrated significantly higher mass flow rates, but similar volumetric flow rates, compared to the SFD granules; the Tosoh powders are spray dried and are much denser than the granules produced via spray freeze drying. For the SFD process, most of the granules yielded by the twin-fluid atomi~~z~~sation route were spherical, and hence these flowing powders had higher mass flow rates compared to the granules prepared using the ultrasonication method; see Fig. 10. The irregularly~~-~~shaped clusters produced by the latter method, were formed as agglomerates of two or more smaller granules. This indicates collision and coalescence of the fine droplets during freezing, since the cone angle of the spray produced by the ultrasonic probe was not as large as that for the twin-fluid atomizer. In terms of the volume flow rates, the SFD granules produced via the twin-fluid atomi~~z~~sation process offered the best flowability compared to the others investigated, although the differences were not very large. Whilst the spherical shape of the resulting granules ensured their good flowability, it is worth noting that the SFD granules were sieved into a specific size fraction, which also contributed towards improving their flowability.

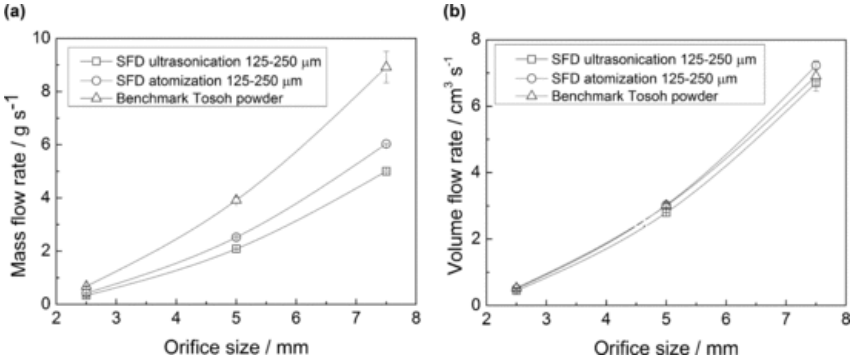

Fig. 9 Mass (left) and volume (right) flow rates of the SFD granules (125–250 μm) and the benchmark powder.

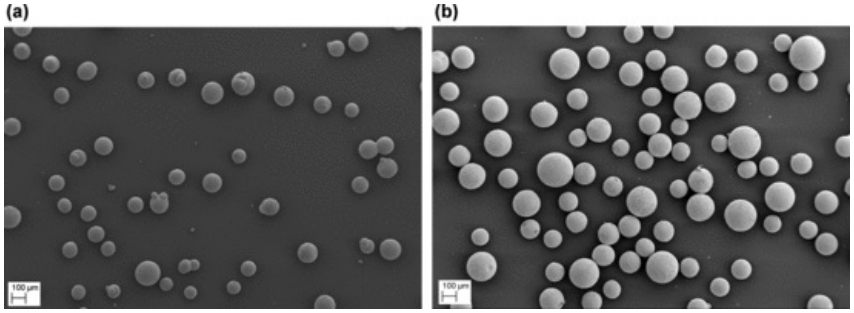

Fig. 10 SFD granules obtained via the ultrasonic spraying (left) and the twin-fluid atomisation (right) process.

3.3 Crushability

Homogeneous, flaw-free fracture surfaces were obtained from the green compacts die pressed at 200 MPa using the 125–250 μm SFD granules produced by both methods; see Fig. 11. High green densities up to 55% of theoretical were obtained after removing all the residual organics at 700 °C. This suggests that the granules produced using either the ultrasonic spraying, or the twin-fluid atomisation route, exhibited very good crushability for die pressing.

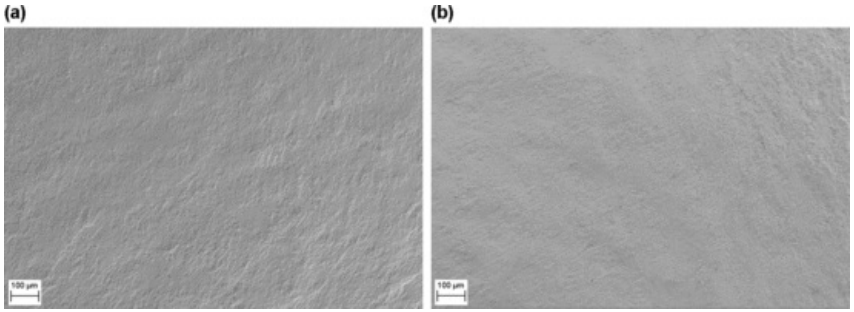

Fig. 11 Fracture surfaces of green compacts pressed at 200 MPa using SFD granules produced using ultrasonic spraying (left) and twin-fluid atomisation (right) methods.

Fig. 12 shows an example of an SFD granule produced using the twin-fluid atomisation process; granules obtained via ultrasonication showed similar surface morphology and microstructure. Whilst the atomisation method determined the size distribution of the granules, their internal structure was determined by the water content and the rate at which freezing took place; this was broadly similar in both cases. By analysing the internal microstructure of the granules, it was found that their good crushability originated from the ice crystal structure retained within the granules; this was formed by the sublimation of the ice dendrites during the freeze-drying process. The speed of the freezing process resulted in a high nucleation rate of ice crystals, giving

the fine microstructure that can be seen in Fig. 12. The Freon addition was immiscible with the aqueous nanosuspension and the drops provided an increased density of nucleation sites during freezing, which resulted in the formation of a large number of ice dendrites. Hence, the resultant SFD granules retained a porous structure with micron-sized holes distributed uniformly; this improved their crushability significantly.

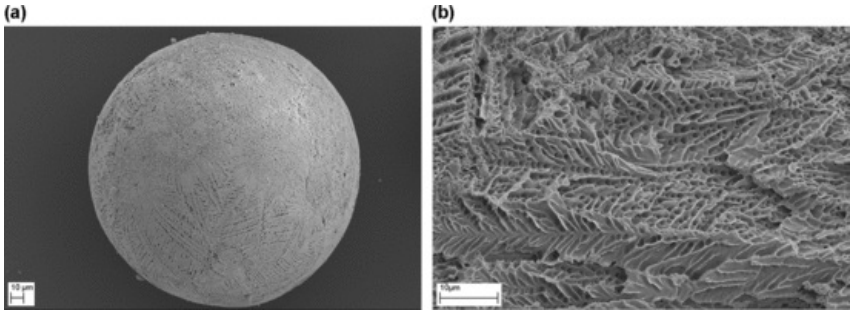

Fig. 12 SFD granule (left) and its internal microstructure (right).

To investigate the crushability of the SFD granules further, the strength of the individual granules in different size fractions produced via the twin-fluid atomi~~z~~sation process was measured using the manual granulate strength testing system. Fig. 13 shows that the first fracture points for all the SFD granules appeared at stresses less than 2 MPa; this suggests that individual granules crush at pressures far below the pressure used for die pressing of 200 MPa. The latter is needed to overcome the friction stresses at the die walls and between and within the granules. It is also worth noting that the stresses required to crush individual granules decreased with increasing granule size; the large granules crushed more easily than the smaller granules. Within the size fraction of 125~~ to ~~250 μm the granules showed similar strengths, whilst those smaller than 125 μm were significantly stronger. Similar observation was made in the previous research with the SFD granules produced using the ultrasonication method~~[9].~~[9]

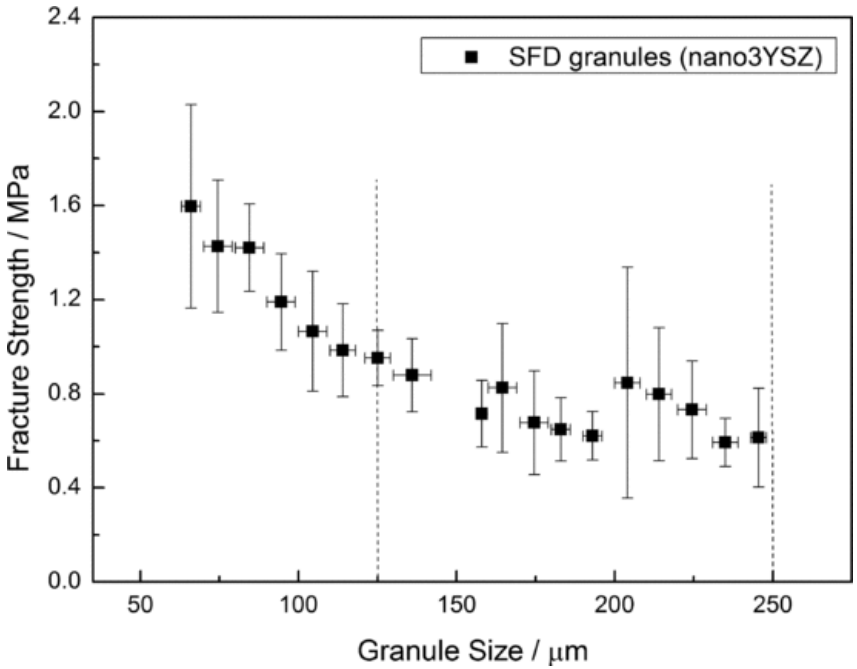

Fig. 13 Granule strength profile of the SFD granules.

4 Conclusions

In this research, a peristaltic pump has been used to control the feeding rate of nanosuspensions during an ultrasonic spray freezing process; this has improved the yields of the granules produced within the desired size fraction, viz.

125–250 μm, from 35 wt% to ~47 wt% comparing to the previous research on spray freeze drying conducted at Loughborough University. A twin-fluid atomizer has also been used for spray formation and has allowed further increases in the yields to ~60 wt% particles in the size 125–250 μm, without compromising the good flowability and crushing properties of the resulting granules. The use of this twin-fluid atomization process also allowed a much higher feed rate of the nanosuspensions and it is believed that it can be scaled up more easily for industrial-scale processing of the SFD granules. The granules obtained from the twin-fluid atomization process displayed the best flowability in terms of their volume flow rates due to the formation of individual spherical granules. In terms of crushability, the individual granules produced via the atomization process retained low strength and as were as good as those produced via the ultrasonication method, resulting in flaw-free green bodies with densities up to 55% of theoretical when die pressed at 200 MPa.

Uncited reference

[17]Ref. 17.

Acknowledgements

The authors would like to acknowledge MEL Chemicals for providing the precursor nano3YSZ suspensions and Prof. Manfred Fries and Ms. Susanna Eckhard from the Fraunhofer Institut fuer Keramische Technologien und Systeme (IKTS) in Dresden, Germany for providing access to the manual granulate strength testing equipment and assistance in using it.

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