

Dense nanostructured zirconia by two stage conventional/hybrid microwave sintering

Jon Binner*, Ketharam Annapoorani, Anish Paul,
Isabel Santacruz¹, Bala Vaidhyanathan

IPTME, Loughborough University, UK

Available online 17 October 2007

Abstract

The processing of 3 mol% yttria partially stabilised zirconia nanopowder into components has been investigated via slip casting low viscosity but high solids content nanosuspensions and subsequent pressureless sintering via one and two stage sintering involving both pure conventional heating and hybrid conventional-microwave heating. Very homogeneous and uniform green bodies with densities up to ~54% of theoretical could be produced, the major limitation being cracking on drying when the highest solid content suspensions were used. This could be partially overcome via the use of humidity drying. The pressureless sintering of the bodies revealed that the two stage sintering process allows a much finer average grain size to be retained than conventional single stage firing, whilst the use of hybrid heating gave further improvements. Greater than 99% dense ceramics with average grain sizes of ~65 nm could be produced from a powder with an average particle size of ~16 nm.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Slip casting; Pressureless sintering; Nanostructured zirconia

1. Introduction

Nanostructured materials have received much attention in recent years; their appeal is their potential to display unusual physical and mechanical properties such as superplasticity in ceramics at elevated temperatures, transparency for usually opaque materials, controlled band gaps in electronic materials, very high magnetoresistance and superparamagnetic properties, and higher hardness and strength in both metals and ceramics.¹ Other benefits include a reduction in the sintering temperatures required, allowing metals and ceramics to be co-fired to a greater extent as well as saving energy, whilst the use of nano-sized components will allow devices to be shrunk significantly in size whilst simultaneously increasing their functionality. However, whilst commercial nanopowders offering these properties have now been produced successfully, sometimes in relatively large quantities, a number of challenges still need to be surmounted if engineering parts are to be manufactured. Whilst ‘bottom up’ approaches may be the long-term solution, these

will not be commercially available for several years—and will require industry to completely retool. Therefore there is considerable mileage to be gained by examining what can be achieved practically now using a ‘top down’ approach based on existing manufacturing facilities. If components can be produced without losing the nanostructure, there is the potential to use the materials for mechanical, thermal, magnetic, electric or electronic applications such as tools, wear and structural parts, magnets, capacitors, varistors and electronic substrates.²

2. Experimental

The work presented is based on the processing of 3 mol% yttria partially stabilised zirconia (3YSZ) nanopowder with an average particle size of ~16 nm (Fig. 1). It is produced by MEL Chemicals in the UK as aqueous suspensions of ~5 vol% solids content.

The as-received suspension was concentrated to yield nanosuspensions with solids contents up to ~34 vol% but with viscosities as low as ~0.2 Pa s; details of the process are being published elsewhere and a patent application has been submitted and published.^{3,4} In brief, the process relies on modification of the precursor suspension pH using solid tetramethylammonium hydroxide, TMAH (Aldrich Chemicals Ltd., Dorset, UK),

* Corresponding author. Tel.: +44 1509 223330; fax: +44 1509 223949.

E-mail address: j.binner@lboro.ac.uk (J. Binner).

¹ Present address: CSIC, Madrid, Spain.

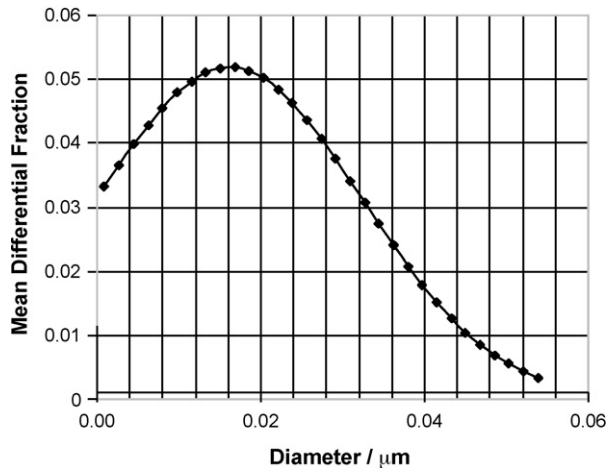


Fig. 1. Average particle size distribution for the precursor 3YSZ powder suspension.

the latter having the advantage over ammonia solution of not involving the initial further dilution of the precursor nanosuspension, followed by the use as dispersant of either Dispex A40, an ammonium polyacrylate-based dispersant (Allied Colloids, Bradford, UK) or, for better results, a low molecular weight electrostatic surfactant, triammonium citrate, TAC (FSA Laboratory, Loughborough, UK), in both cases combined with the use of multistage ultrasonics to break up any agglomerates present. Of the two concentration methods investigated, evaporation was faster and hence was adopted. These suspensions were subsequently slip cast using standard plaster of Paris moulds into either cup (10ϕ mm \times 10 mm \times \sim 1 mm wall thickness) or rectangular (40 mm \times 10 mm \times 3 mm) green bodies which were subsequently dried at room temperature either with or without control of the humidity during the process.

The green bodies were sintered using both a conventional, single stage and a new two stage sintering approach, originally developed by Chen and Wang⁵; these are illustrated schematically in Fig. 2. The conventionally sintered samples were heated at 7°C min^{-1} to a sintering temperature T_1 and held for up to 8 h and then furnace cooled back to room temperature. The two stage sintered samples were heated at the same 7°C min^{-1} to an initial temperature, T_1 , but after only 0.1 min immediately cooled back down to temperature T_2 as rapidly as possible before holding for periods of up to 30 h. For the single stage

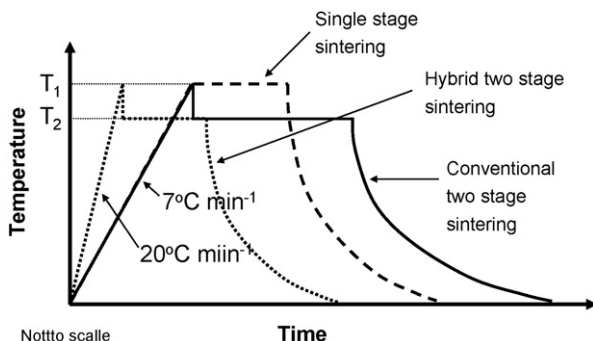


Fig. 2. Schematic of sintering schedules used.

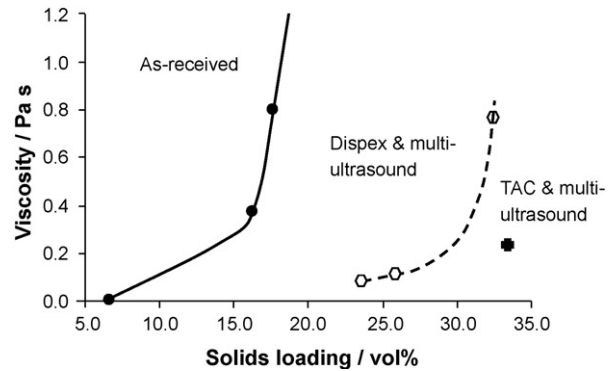


Fig. 3. Nanosuspension viscosities as a function of solids content.

sintered samples, T_1 was varied from 900 to 1150 $^\circ\text{C}$ whilst for the two stage sintered samples T_1 was always 1150 $^\circ\text{C}$ and T_2 was varied between 1000 and 1050 $^\circ\text{C}$. Sintering was performed using a hybrid microwave/radiant sintering furnace that could be operated in either pure radiant or hybrid microwave/radiant mode. The microwave frequency was 2.45 GHz; up to 2 kW of microwave power was available. In the present work, a fixed level of 600 W of microwaves was used throughout the sintering cycle for the hybrid heated samples, with the amount of radiant power being varied to yield the desired temperature–time profile. The temperature was measured and controlled using optical thermometry (Orbis Technologies, USA), which previous work has shown is the most accurate method.⁶ Corroborative temperature distribution measurements were performed using a thermal imaging camera (FLIR Systems Thermovision[®] A40, USA).

After sintering, the samples were characterized in terms of their densities, using the Archimedes technique in deionised water, and their grain size, after gold coating, using a field emission gun scanning electron microscope (FEG-SEM). For the latter, the procedure followed that laid out in British Standards.⁷

3. Results and discussions

The rheology of the optimised precursor nanosuspension is shown in Fig. 3. It can be seen how the viscosity of the as-

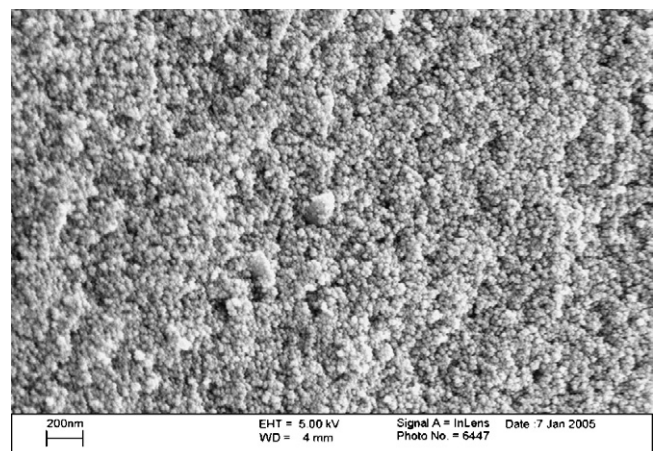


Fig. 4. Green nanostructure of slip cast nanosuspension.

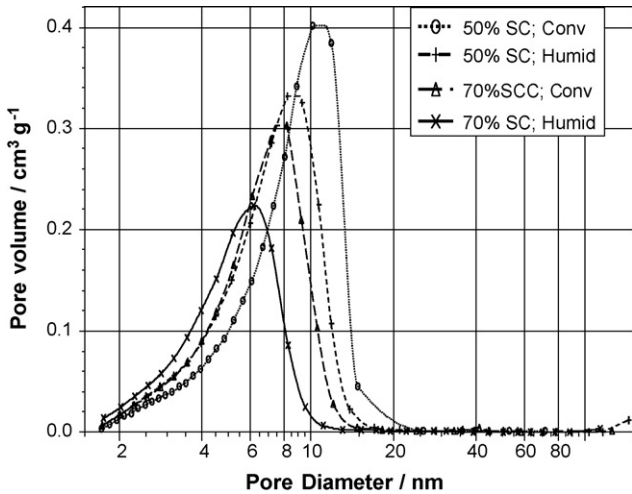


Fig. 5. BET pore volume measurements as a function of nanosuspension solid content (SC) used for slip casting and the room temperature drying technique, conventional (conv) or humidity (humid) drying.

received suspension increased very rapidly with concentration, exceeding 1 Pa s by ~15 vol%. Whilst the use of Dispex A40, together with appropriate exposure to ultrasound to destroy any agglomerates present, allowed much higher solids contents to be achieved whilst retaining a low viscosity, it may be seen the short molecule TAC was even more successful. Up to ~34 vol% suspensions could be produced whilst retaining the viscosity below ~0.3 Pa s.

When these nanosuspensions were slip cast, very homogeneous green bodies were formed, Fig. 4, however cracking was found to be a major problem for the higher solid content suspensions. For conventional drying, the maximum solids content that could be cast without cracking was ~12 vol%, however

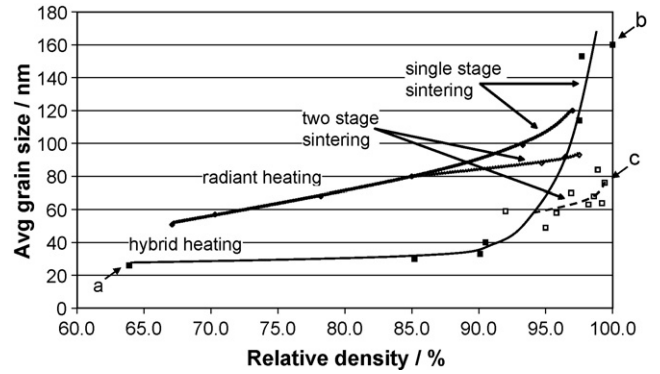


Fig. 6. The effect of single- and two-stage sintering of nanostructured 3YSZ ceramics using radiant and hybrid heating.

when humidity drying was used, and optimized, suspensions with solids contents of up to ~20 vol% could be slip cast without cracks being observed in the dried bodies. These higher solids contents not only allowed higher green density bodies to be achieved, up to ~54% of theoretical, but also resulted in a finer pore structure, Fig. 5, that, in turn, resulted in higher sintered densities for the same sintering conditions.

The average grain size of the sintered nanostructured samples is plotted as a function of sample density in Fig. 6, whilst representative micrographs of the structures at three different points on the sintering curves, labelled a, b and c, are shown in Fig. 7. Two results are immediately observable from Fig. 6. The first is that the use of hybrid heating has consistently resulted in a finer average grain size for a given final density and the second is that the use of two stage sintering does indeed seem to result in the ability to retain a very fine grain size, whilst achieving effectively full densification.

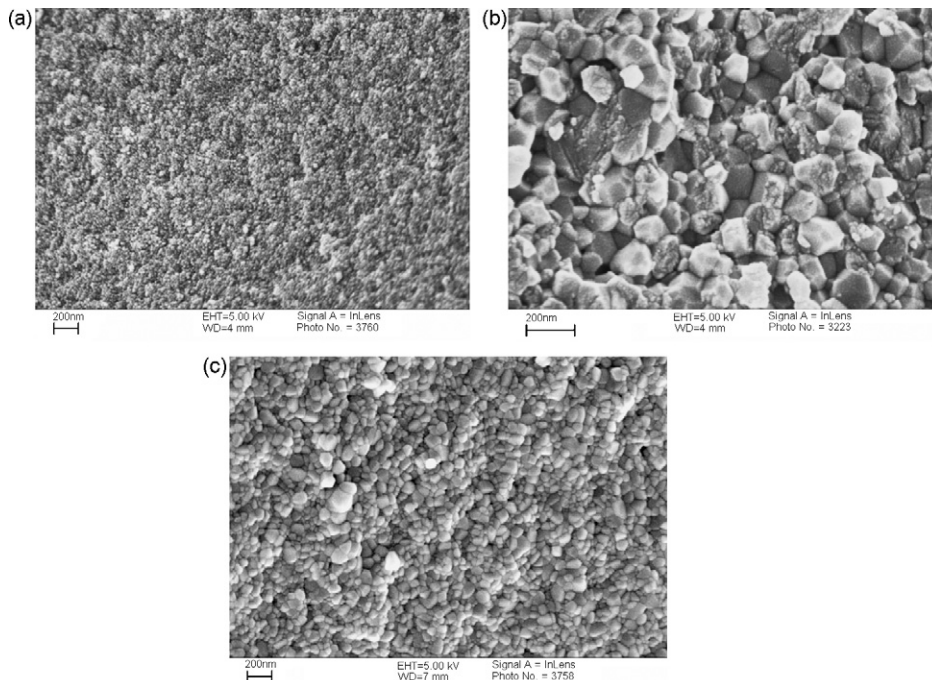


Fig. 7. Micrographs of fracture surfaces of the YSZ ceramics corresponding to the points marked a, b and c, respectively.

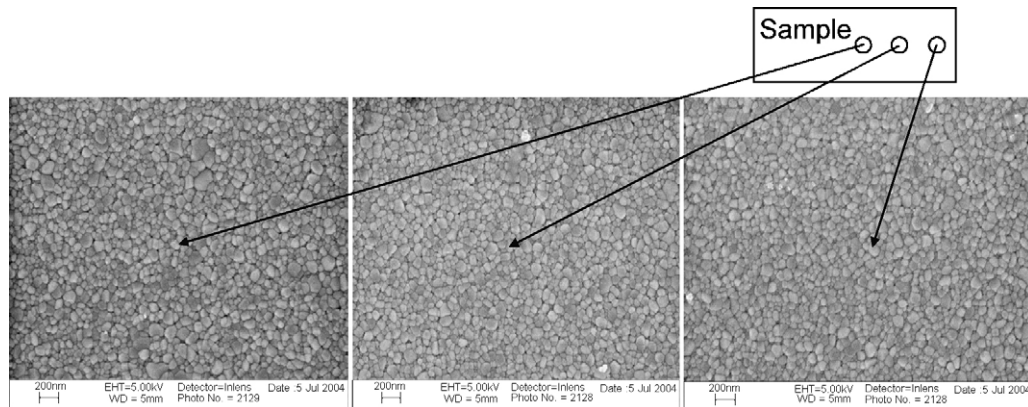


Fig. 8. Sintered nanostructure at three different locations of a slip cast 3YSZ nanoceramic. The density was $\sim 99.5\%$ of theoretical and the average grain size 64 nm throughout the component.

With radiant heating, there was a steady increase in grain size up to around 90–95% of full density when there was a sharp increase in grain size. This fits with the closing of the porosity, when grain growth generally becomes significant. The use of two stage sintering, however, clearly reduced grain growth whilst allowing densification to continue occur, confirming the results proposed by Chen and Wang⁵ using nano Y_2O_3 powder. Their argument was that the suppression of the final-stage grain growth was achieved by exploiting the difference in kinetics between grain-boundary diffusion and grain-boundary migration and that the particle network became ‘frozen’ during the second sintering stage. Like them, it was observed that to succeed in two-stage sintering a density $\geq 75\%$ of theoretical had to be obtained during the first stage. It is believed that the benefit arising from this level of densification was actually related to the pores, which became subcritical and so unstable against shrinkage, rather than the density value itself.

The use of hybrid heating can be seen to have resulted in a much finer average grain size at all densities. Although recent results from Loughborough have now confirmed the existence of the so-called ‘microwave effect’ during ceramic sintering,⁸ it is believed that the major effect influencing these results is

that a much faster heating rate was used. Due to the volumetric nature of the hybrid heating, $20^\circ C \text{ min}^{-1}$ could be used without risking any damage to the samples from thermal stresses, whilst the radiant heating was limited to only $7^\circ C \text{ min}^{-1}$. At higher heating rates the bodies were found to crack as a result of thermal expansion mismatch between the surface and centre of the bodies due to the low thermal conductivity in these materials. Since, as indicated by Chen and Wang,⁵ the bulk of the grain growth that occurs during two stage sintering is during the initial heating to T_1 , the faster this stage can occur, the smaller the amount of grain growth overall.

As for the radiantly heated samples, the rapid increase in grain growth began at densities of 90–95%; achieving full density resulted in average grain sizes ≥ 160 nm. However, the combination of hybrid heating with the two stage sintering technique clearly resulted in the ability to retain a final grain size in the range 60–80 nm whilst achieving densities in excess of 99%. Fig. 8 illustrates the homogeneity that was achieved across the entirety of a sample. The density was $\sim 99.5\%$ of theoretical and the average grain size was 64 nm.

In the original work of Chen and Wang,⁵ Fig. 9, the curve representing the second stage of sintering was horizontal; it was this that gave rise to their claim that the microstructure was ‘frozen during the second stage of sintering. In the current work it can be seen that it is curved in a similar manner to the single stage sintering data but with a significant increase in average grain size occurring at densities above about 97% of theoretical. This suggests that the operative mechanism during two stage sintering may be essentially the same as during conventional sintering but the densification curve is pushed to the right by the samples effectively having a much higher green density than would be normal for ceramic sintering. Further work is needed to clarify this situation, since, if the present work is correct then this casts doubt on the mechanism proposed by Chen et al.

4. Conclusions

It has been possible to concentrate commercial, low solids content aqueous nanosuspensions consisting of ~ 16 nm 3YSZ powder particles up to ~ 32.5 vol% solids content whilst retain-

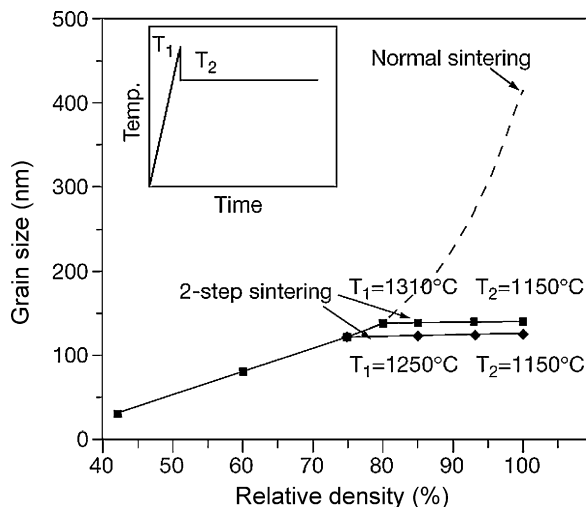


Fig. 9. The two-stage sintering process, after Chen and Wang.⁵

ing a viscosity as low as 0.2 Pa s using a new process; a patent application has been submitted. These nanosuspensions have subsequently been slip cast using standard plaster of Paris moulds to yield green bodies that are very uniform and homogeneous. Significant problems with cracking on drying for the samples made from the nanosuspensions with solids contents greater than ~ 12 vol% have been at least partially overcome by the use of humidity drying. This allowed suspensions with solids contents up to ~ 20 vol% to be slip cast without any evidence of cracking; these yielded green bodies with densities of $\sim 54\%$ of theoretical.

The green bodies could be sintered to $>99\%$ of theoretical using a two stage sintering technique whilst retaining a final average grain size of <100 nm. When a hybrid microwave-conventional approach was used, the resulting average grain size was finer; the best sample to date had a value of just 64 nm whilst being $\sim 99.5\%$ dense. It is believed that the primary advantage offered by the hybrid heating approach is the ability to use a much faster initial heating rate, $20^\circ\text{C min}^{-1}$ versus just 7°C min^{-1} , since the bulk of the grain growth observed using this approach occurs during heating to the first sintering temperature, known as T_1 . The nanostructure was also very uniform throughout the sample.

Unlike the work of Chen and Wang,⁵ who developed the two stage sintering process, the nanostructure did not remain ‘frozen’

during sintering at T_2 . Instead, a relatively small amount of grain coarsening was observed at densities above about 97% of theoretical. This suggests that the mechanisms taking place during the second stage of the sintering process are similar to those occurring conventionally but shifted to higher densities. Further work is clearly needed and is underway at Loughborough.

References

1. Mayo, M., Processing of nanocrystalline ceramics from ultrafine particles. *Int. Mater. Rev.*, 1996, **41**(85), 1743–2804.
2. Groza, J. R., *Int. J. Powder Met.*, 1999, **35**(7), 59.
3. Santacruz, M. I., Annappoorani, K. and Binner, J. G. P., Preparation of high solids content nano zirconia suspensions. *J. Am. Ceram. Soc.*, in press.
4. Binner, J. G. P., Santacruz, M. I. and Annappoorani, K., Aqueous nanosuspensions, International patent application Publ. No. WO 2006/136780 A2, Publ. Date 28/12/06.
5. Chen, I. and Wang, X.-H., Sintering dense nanocrystalline ceramics without final-stage grain growth. *Nature*, 2000, **404**, 168–171.
6. Binner, J. G. P., Vaidhyanathan, B. and Wang, J., A comparative study of temperature measurements during microwave processing. In *Proceedings of the 9th International Conference on Microwave and High Frequency Heating*, 2003, pp. 477–480.
7. British Standards, Advanced Technical Ceramics – Monolithic Ceramics – General Textural Properties, Part 3, p. 10, *BS EN 623-3* (2001).
8. Wang, J., Binner, J., Vaidhyanathan, B., Joomun, N., Kilner, J., Dimitrakakis, G. and Cross, T. E., Evidence for the microwave effect during hybrid sintering. *J. Am. Ceram. Soc.*, 2006, **89**(6), 1977–1984.