Processing Nanostructured Structural Ceramics

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ABSTRACT

The processing of ceramic nanopowders into components has been investigated via a series of research projects, each focusing on a different stage of the manufacturing route. As a result of the work performed, progress has been made into the ability to control the agglomerates present in the powder resulting in the production of a free-flowing and crushable powder for die pressing; the formation of low viscosity but high solids content suspensions that enable wet green forming routes to be used that yield homogenous and high quality green bodies and finally, the ability to achieve fully dense ceramics with average grain sizes of just 65 nm by pressureless sintering. All the work presented here is based on yttria-partially stabilised zirconia ceramics; an additional observation for this material is that the level of dopant required appears to be significantly reduced compared to 'conventional' submicron grain sized ceramics.

1.0 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, 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 potential 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. For example, one could envisage that a device as small as a wrist watch could contain a telephone, camera, GPS system and hand-held computer. 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 will probably be the long-term solution, these may 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 manufactured without loosing 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].

Focusing on ceramic systems, there are three main challenges to achieving the goal of fabricating engineering components from nanopowders [1], viz:

The low cost production of large quantities of nanopowders with controlled agglomeration: Of these three requirements, the first two will inevitably be solved provided demand is sufficient, however, the presence of significant agglomeration due to the very high surface energies associated with ultrafine particles has significant consequences on the pore distribution in 'green' (i.e. unfired) compacts. It is

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generally bimodal, consisting of large inter-agglomerate and small intra-agglomerate pores. The removal of the former by vacancy diffusion requires higher sintering temperatures and/or longer sintering times, promoting grain growth. Hence a small and uniform pore population is desired; this is associated with very weak agglomerates and a high green density [3,4,5]. The extensive characterisation of many different nanopowders at Loughborough University has shown that those delivered as suspensions tend to be significantly more tractable for subsequent processing since wet green forming routes can be used which avoids having to dry out the powder with the consequent formation of the agglomerates. However, since the majority of advanced ceramic components are currently produced in industry by dry pressing, it is also important to learn how to create large but exceptionally weak agglomerates that flow and crush readily.

The compaction of the particles to achieve flawless, dense packing prior to sintering (i.e. avoiding cracks, pores and density gradients): Decades of research have shown that the degree of homogeneity of particle packing in the green body has an enormous impact on sintering characteristics. In this regard, nanocrystalline powders are at a severe disadvantage, both due to the effects of agglomeration outlined above and because the finer the powder the poorer the flow characteristics as a result of the large number of particle-particle contacts. The combination means that wet forming techniques offer distinct advantages over dry pressing routes, viz. the ability to sediment out hard agglomerates and the potential for much more homogeneously packed green bodies due to the greater ease with which particles can slide over one another and rearrange in the wet state. In addition, and very importantly, the surface chemistry of ceramic particles in suspension can be systematically altered to encourage the particles to arrange themselves in orderly, packing efficient configurations. The primary disadvantage for wet forming routes is the very high viscosities that arise even at low solids contents due to the short interparticle distances and the resultant strength of the interparticle forces.

The maximisation of densification and minimisation of grain growth during sintering: Whilst similar densification phenomena occur as for conventional micron-sized powders, the temperatures required are consistently lower; sintering may start at ~0.2 of the absolute melting point (T_{mpt}) compared to ~0.5 T_{mpt}. This generates many potential benefits, including the avoidance of undesirable phase transformations and interfacial reactions, the elimination of the need for sintering aids and the opportunity to produce bonded or graded materials from combinations incompatible at high sintering temperatures, e.g. ceramics and low melting point metals. The specific challenges related to the high reactivity of the powders include the potential for contamination and grain coarsening. Success in avoiding the latter is related to control of the competition between densification and grain growth, something that is extremely difficult because the driving forces for both are proportional to the reciprocal grain size and hence comparable in magnitude. Successful approaches that have been developed include:

The addition of solutes or 2nd phase particles that reduce grain boundary mobilities or pin them; however this is limited to additives that do not negatively affect the desired properties of the final product [6,7] and so is a major limitation for many ceramic systems.

Very rapid firing; however this requires a) extremely homogeneous green compacts since local variations in green density lead to regions of the same compact being at different locations on the sintering curve and b) physically small-sized components. Both of these can be considered to be significant limitations.

Pressure-assisted techniques; however these routes, which include hot pressing, hot isostatic pressing and the mis-named spark-plasma sintering, bring with them the major disadvantages of high processing costs combined with limited component shape capability.

Two-step sintering; this exploits the difference in kinetics between grain boundary diffusion and migration [8] and combination with microwave heating is particularly successful [9]. More detail on this approach will be provided later in the paper.

2.0 EXPERIMENTAL AND RESULTS

The research discussed in this paper focuses on three separate aspects of the processing of nanostructured ceramics, viz.

- The production of a flowable and compactable dry nanopowder suitable for use in the die pressing of ceramics since this is the favoured green forming route by industry;
- The production of low viscosity but high solids content nanosuspensions that are stable and can be used in wet forming routes such as slip or gel casting; and
- The pressureless sintering of green bodies to yield components with densities in excess of 98% of theoretical but retaining average grain sizes of <100 nm.

Whilst a range of different ceramic nanopowders are being investigated at Loughborough, the work discussed all relates to the processing of yttria partially stabilised zirconia (YSZ) nanpowder with an average particle size of ~19 nm, figure 1. The powder is produced by MEL Chemicals in the UK and is available as aqueous suspensions of approximately 27 wt% solids content.

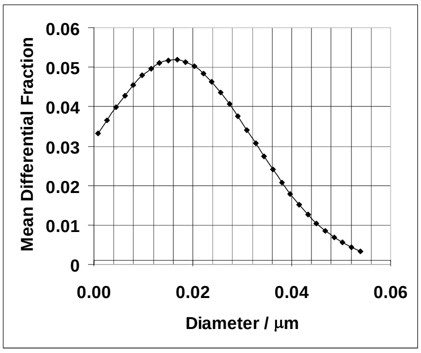
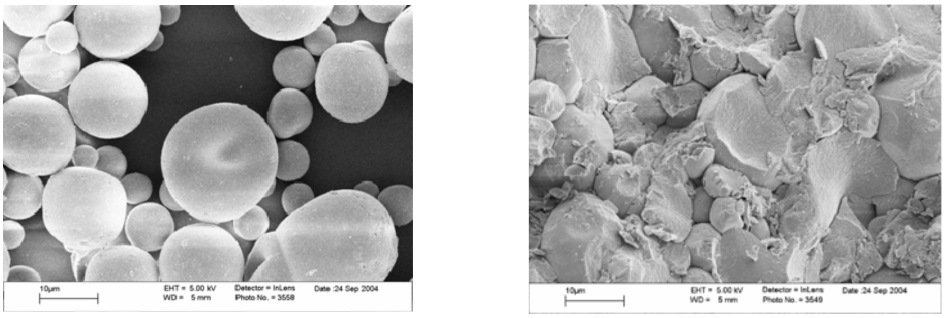


Figure 1: Average particle size distribution for the precursor YSZ powder.

2.1 Control of powder agglomeration

As indicated above, the primary green forming route currently used by industry is die pressing. This relies on compacting a dry powder within a rigid die via the application of uniaxial pressure and hence one of the key variables is the ability of the powder to flow swiftly and uniformly into the die. As a result, nanopowders are at a major disadvantage since they generally don’t flow unless they are agglomerated into large aggregates; typically these need to measure 20 – 60 µm in diameter. However, to generate the required quality in the green body, these large agglomerates must crush during compaction to release the individual particles. If any agglomerates are retained they will have a locally higher density than the rest of the component and hence will be further up the sintering curve, resulting in abnormal grain growth and hence a poor final microstructure.

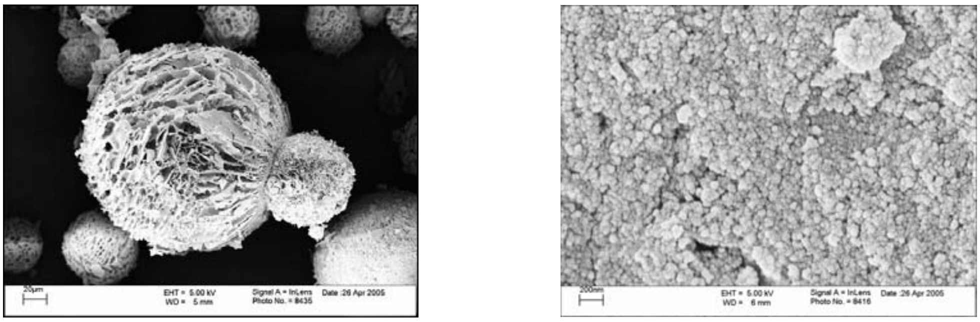
One of the most common approaches to the production of ceramic powders for die pressing is spray drying; a slurry of the powder is fed into a hot gas stream that causes the liquid medium to evaporate yielding largely spherical agglomerates, figure 2a. However, when this technique is used for nanopowders, the extremely large surface area of the particles leads to very high surface forces and hence the agglomerates formed can be too strong to crush during compaction resulting in a very inhomogeneous green microstructure, figure 2b.



a. b.

Figure 2: a) Spray dried agglomerates, b) their retention in the microstructure after pressing.

An alternative powder processing route involves spray freeze drying; in this process the slurry is sprayed into a bath of a cryogent, often liquid nitrogen. This instantaneously freezes the droplets and the solvent is then removed by sublimation at low pressure. The agglomerates formed can be similar in size and shape to those produced by spray drying, and hence the flow characteristics are often not very different, however the lack of a raised temperature results in much weaker interparticle bonds and hence the agglomerates are significantly more friable, figure 3a. The green bodies formed consequently have a much more homogeneous and uniform microstructure, figure 3b.



a. b.

Figure 3: a) Spray freeze dried agglomerates, b) a more uniform green microstructure as a result of the agglomerates crushing.

The agglomerates shown in figure 3a were produced by spray freeze drying a 27 wt% aqueous nanozirconia suspension produced by MEL Chemicals in the UK without binders into liquid nitrogen and then subliming the ice from the mixture at -30^{o}C at ~0.2 millibar. Whilst the green microstructure is still not optimal, hence further work is ongoing, the resultant powder flows almost as well as a commercial submicron zirconia powder that is being used as a benchmark and crushes sufficiently to avoid agglomerates being retained in the microstructure.

2.2 Rheology of nanosuspensions

Although die pressing is a fast and cheap green forming route, and hence the most common method used by industry for the manufacture of advanced technical ceramics, it is by its very nature limited in its ability to yield truly high quality materials. Far superior microstructures can be produced using wet forming routes such as tape, slip and gel casting in which the green body is formed directly from suspensions, albeit at significantly slower production rates. This is because of the greater ease with which particles can slide over one another and rearrange. However, since the key to successful wet forming is usually the ability to produce a well dispersed, high solids content, low viscosity suspension, nanopowders are again at a significant disadvantage. When the particles in a suspension approach within ~2 nm of each other the interactions are such that the force required to move them past each other increases substantially, i.e. there is a significant increase in the viscosity. Now, for a given solids content, the finer the particles the closer they will approach one another and so as particle size decreases, higher viscosities are experienced. As an example, whilst it is possible to achieve a viscosity of ~1 Pa s for a 60 vol% suspension of 1 μm zirconia particles, a suspension of 50 nm zirconia particles would have a similar viscosity at only ~20 vol% solids content. With the exception of electrophoretic deposition, a wet forming route used to produce coatings, this limits the maximum solids content that can be used to typically <20 vol%. The consequence is that it is very difficult to obtain high green densities, which, in turn, limits severely the ability to retain a final average grain size of <100 nm after sintering.

In an effort to overcome this problem, work at Loughborough has focused on examining the role of a range of different surfactants on the rheology of nanoceramic suspensions. The first observation has been that the natural pH of nanoceramic suspensions can be quite different to that for submicron particles of the same composition due to the different synthesis routes used. Therefore, 'industry-standard' dispersants can cause flocculation rather than dispersion. However, in work that has recently seen a patent application submitted a route has been identified to the production of low viscosity, high solids content suspensions, figure 4.

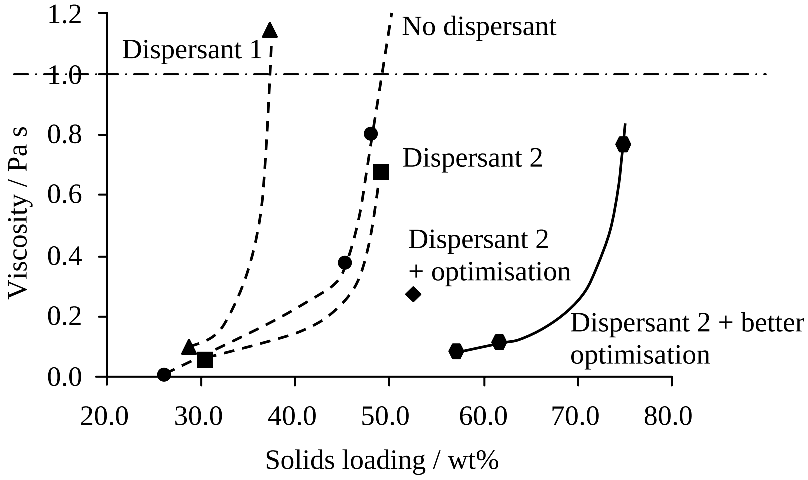


Figure 4: Effect of different dispersants and processing conditions on the viscosity of zirconia nanosuspensions. When optimised, it has been possible to achieve a solid content of ~75 wt% whilst keeping the viscosity to <0.8 Pa s (typical limit for processing is ~1 Pa s).

Although the experimental details of this route are still confidential, the results of the work to date have been the ability to concentrate an as-received zirconia nanosuspension that had a solids content of ~27 wt% and a viscosity of ~0.1 Pa s into one with a solids content of ~75 wt% whilst keeping the viscosity below about 0.8 Pa s. The key significance is that ~1 Pa s is a practical upper limit for many wet forming routes. Currently, suspensions formed by this route with solids contents greater than ~56 wt% are unstable, the viscosity increasing with time over a period ranging from a few days (~60 wt%) to a few hours (~75 wt%). However, at 56 wt% the suspensions have been observed to be stable for periods lasting a week or more, figure 5.

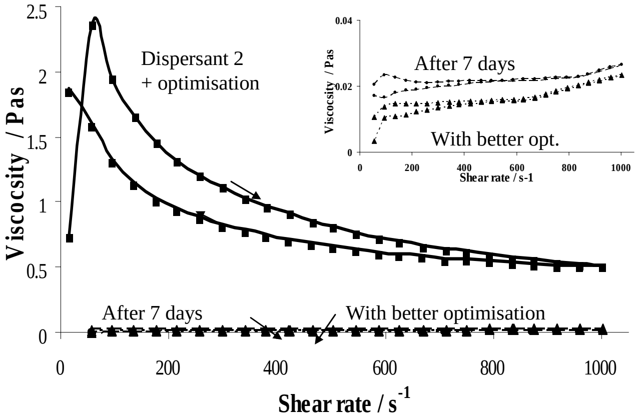
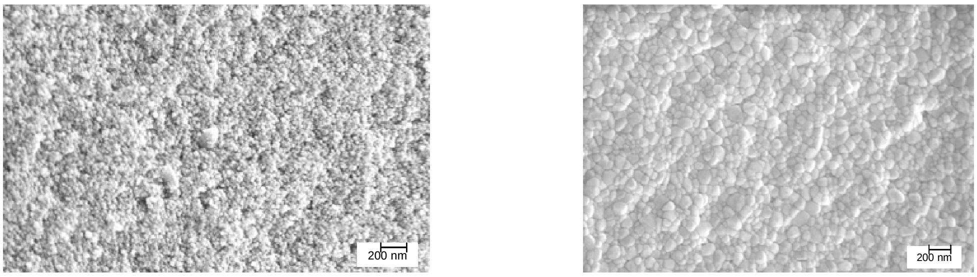


Figure 5: Viscosity of the suspension produced with dispersant 2 and better optimisation compared to that with the original level of optimisation. Inset shows how the viscosity has hardly changed after seven days, indicating stability.

These suspensions have subsequently been used to produce ceramic components by the process known as slip casting. This is a technique that was originally developed for the traditional ceramics industry; it is relatively slow but yields high quality components. Figure 6 shows the uniformity of the microstructure, both before and after sintering.



a. **b.**

Figure 6: a) Green and b) sintered microstructures of slip cast nano suspensions produced with dispersant 2 and optimisation. The green body was ~50% dense whilst the sintered body was ~98% of theoretical density after 2-stage sintering using a conventional furnace. The average grain size was ~80 nm.

2.2 Sintering of nanostructured ceramics

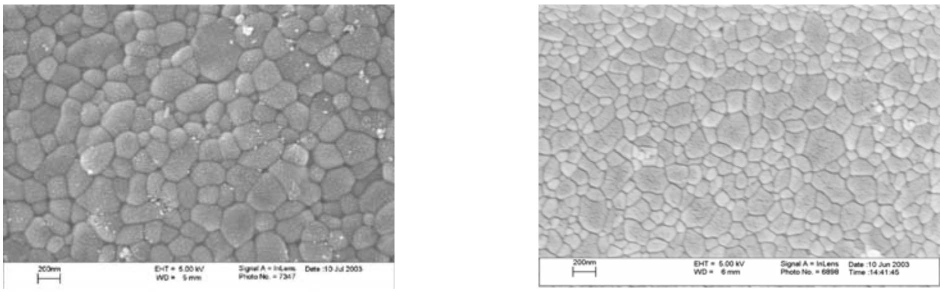
The 56 wt% concentrated nanozirconia suspension was used to produce green compacts by slurry casting and also vacuum dried at room temperature prior to being micronised (a very high shear grinding technique) and then die pressed into green compacts at compaction pressures ranging up to 500 MPa. With both routes, the green bodies were discs 10 mm in diameter and about 6 mm thick; the green densities were in the range 52 - 62% of theoretical.

Three different types of sintering experiments were performed using a furnace capable of operating in pure conventional, microwave and hybrid modes (manufacturer C-Tech, UK); this enabled direct comparisons to be made under otherwise identical experimental conditions. The first set of experiments involved the standard, single stage ramp and hold heating approach, the sintering temperature being varied in the range 1100 – 1300°C and the soaking time from 30 – 120 mins, depending whether microwave or radiant energy source was employed. In the second set of experiments, sintering was deliberately performed at only 900 and 1000°C to ensure that full density was not reached, but *exactly* matching time-temperature profiles were used whilst the fraction of microwave and conventional power was varied. The aim was to investigate the effect of the amount of microwave power used on the degree of densification achieved. In the third series of experiments, the samples were sintered using a two stage approach; the samples were first heated to an initial temperature, T_1, before being cooled rapidly to a lower temperature, T_2, where they were held for varying periods of time, t, following the procedure developed by Chen and Wang [10]. T_1 was varied from 1000 – 1200°C, T_2 from 900 – 1000°C and t from 10 to 30 hrs. Temperature was measured using optical thermometry (Orbis Technologies, USA), which previous work has shown is capable of measuring temperatures to ±3°C [11]. Morphological characterisation of the green and sintered ceramic disks was carried out using a field emission gun scanning electron microscope (FEG-SEM) that allows high magnification images to be obtained even on unfired ceramic green bodies. Sintered densities were measured by the Archimedes method using de-ionised water.

From the first sintering experiments, it was found that >97% of theoretical density could be achieved after only 30 mins at 1250°C with microwave sintering, table 1. This was 4 times faster than with conventional sintering and 150 – 200°C lower in temperature than for conventional sub-micron zirconia ceramics. In addition, the average grain sizes of the conventionally and microwave sintered MEL samples were found to be ~210 nm and ~140 nm respectively, figure 7.

Table 1: Sintered densities as a function of sintering technique.

Sample	% Sintered density	
	Conventional 1250°C/120 mins	Microwave 1250°C/30 mins
Vacuum dried, die pressed compact	95.2	98.6
Slurry cast compact	96.6	99.0



a. b.

Figure 7: FEGSEM Microstructure of the a) conventionally and b) microwave sintered slurry cast compacts. The average grain sizes were ~210 nm and ~140 nm respectively.

The results from the second series of experiments, when the fraction of microwave power used to achieve single stage sintering was varied from 0 to 1000 W whilst the temperature/time profile was kept constant by varying the amount of conventional power, are shown in figure 8. N.B. the temperature gradients across the samples were found to be <15°C. The degree of densification was found to increase with increasing microwave power used, more than 12% density enhancement was observed when 1000 W of microwave power was used compared to pure conventional even though the specimens were subjected to *identical* thermal histories. Interestingly, the effect was more dominant in the early stages of sintering, a result that has been observed before [12]. These results suggested that the use of microwave sintering would be beneficial for achieving higher densification whilst retaining finer nanostructures, a result that was subsequently observed, table 2 and figure 9.

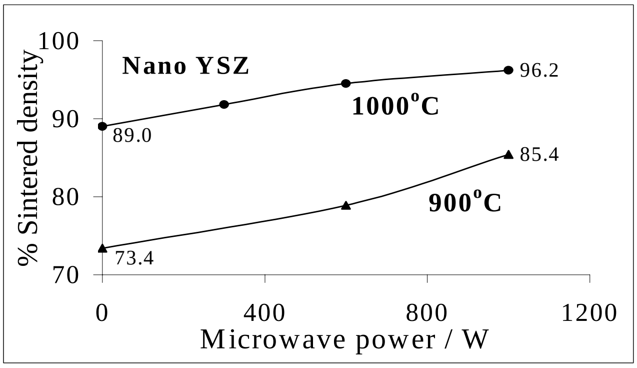


Figure 8: Density enhancement in nano 3-YSZ ceramics as a function of microwave power, for *identical* time-temperature sintering profiles.

Table 2: Sintered densities and grain sizes for 2-stage sintered nanozirconia ceramics.

Experimental conditions	% sintered density	Avg. grain size / nm
Conv. T_1 1150°C; T_2 1000°C; t 30 hrs	97.5	93
Hybrid T_1 1150°C; T_2 1000°C; t 3 hrs	>99	<65

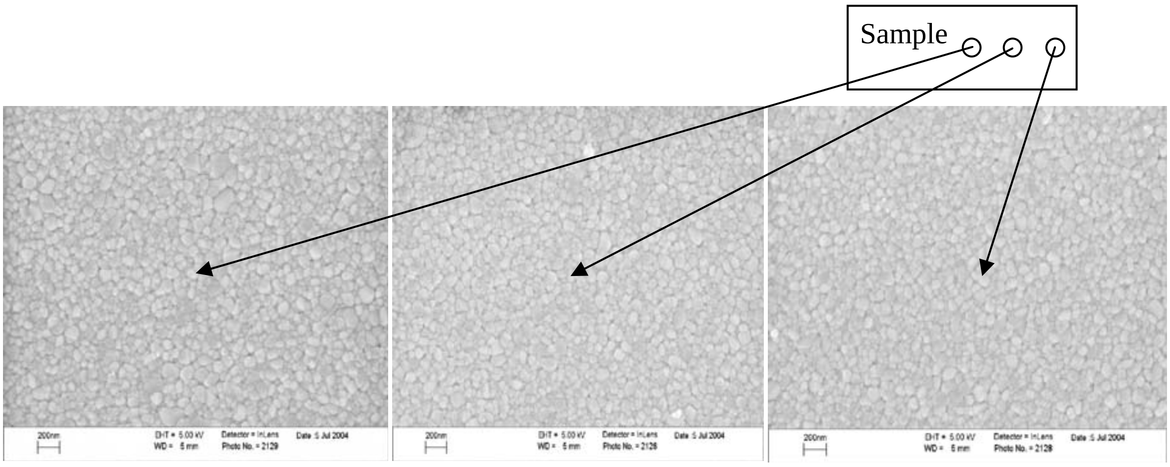


Figure 9: FEG-SEM images of the sintered slurry cast zirconia nanoceramic. The density was >99% of theoretical and the average grain size <65 nm throughout the component.

It is believed that it is the first time that fully dense zirconia ceramics have been produced with average grain sizes as fine as 65 nm by pressureless sintering when starting with an initial grain size of 20 nm, i.e. grain growth was limited to just a factor of ~3.

Although characterisation of the resultant ceramic properties has only just begun, preliminary results are somewhat disappointing. In common with reports in the literature, the values for both hardness and toughness for 3 mol% yttria partially stabilised zirconia (3-YSZ) were no higher than for conventional, micron-sized material of the same composition. However, detailed crystallographic characterisation results have suggested a grain size dependent shift in the phase boundary composition for nano YSZ ceramics leading to 'over stabilisation' at any given yttria content, a view apparently confirmed by hardness values that showed a maxima at around 1.9 mol% yttria content. This will not only have significant implications for achieving the peak mechanical and electrical performance but may also lead to a redrawing of the phase diagrams for other nanostructured advanced ceramics. Further work is planned at Loughborough to explore this effect in detail.

3.0 CONCLUSIONS

The research outlined above has yielded four key developments, viz.:

- The production of a flowable and compactable dry nanopowder suitable for use in the die pressing of ceramics since this is the favoured green forming route by industry, though further work is still required to optimise it as well as trials using high speed die pressing equipment;
- The production of low viscosity, <0.8 mPa s, aqueous suspensions of YSZ nanoparticles with solids contents as high as 76 wt%; the current state-of-the-art is for the viscosity to be excessively high for practical application at solids contents as low as ~30 wt%. Whilst not stable for long periods of time at solids contents >56 wt%, the development is the subject of a patent application [13].
- Provided the YSZ green bodies formed have a density ≥55%, they can be pressureless sintered using microwave two-stage sintering to >99% of theoretical density whilst retaining the final grain size at <100 nm [9]; the limit to date is 65 nm for a powder with an average particle size of 19 nm. The only existing techniques that can match this require the use of pressure, e.g. hot pressing, hot isostatic pressing and 'spark plasma sintering', which are very expensive and have limited shape capability.
- The level of dopants required to achieve given phases in nanocrystalline YSZ ceramics has been found to be different compared to their microcrystalline counterparts, supporting earlier work [14]. This suggests that work performed to date on 3 and 8 mol% yttria-doped nano YSZ, for mechanical properties and ionic conductivity respectively, has been based on sub-optimal yttria levels. Work is required to investigate this further and determine the optimum levels for both mechanical performance and ionic conductivity.

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