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Nanostructured ceramics: a review of their potential†

Markys Cain* and Roger Morrell
Centre for Materials Measurement and Technology, National Physical Laboratory, Teddington, Middlesex, TW11 0LW, UK

The driving forces for the recent development of nanoscale features in conventional ceramic materials for both mechanical and functional reasons are discussed, and the causes of some of the resulting property enhancements are identified. Examples from the technical literature are examined, and the potential for future applications is assessed in terms of the tradeoff between enhanced properties and the added costs and difficulties of processing ultrafine powders. © Crown copyright 2001. Reproduced with the permission of Her Majesty's Stationery Office. Published by John Wiley & Sons, Ltd.

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1 INTRODUCTION

For practical purposes, if we define 'nanoscale' as being of dimensions of less than say 100 nm, compared with 'microscale', which typically implies dimensions between 100 nm and 100 μm, we can argue that nanostructured materials are definitely not new in the ceramic field. Many of the features of clay-based ceramics, which have been with us for millennia, are on a 'nanoscale'. Figure 1 shows an example of a long-standing technical ceramic, electrical porcelain, in which the matrix of the microstructure between the large quartz grains comprises a network of mullite needles surrounded by glassy phases. Even if no special 'nanoscale' control has been intended, the nature of the minerals employed in formulating the porcelain has resulted in 'nanoscale' features in the microstructure, particularly the clay particles. A more recent development has been glass-ceramics. Bulk crystallization in a glass relies on incorporating species into the composition that will provide a high density of nuclei to initiate the development of small grains. This can be either through homogeneous nucleation, initiated typically by two-phase separation of the glass on a nanoscale followed by crystal growth in regions of modified composition, or through heterogeneous nucleation, in which a precipitate of a species of limited solubility is first developed, typically also on a nanoscale, on which a different major crystalline phase grows. Figure 2 shows an example of a β-spodumene (lithium aluminosilicate) glass-ceramic

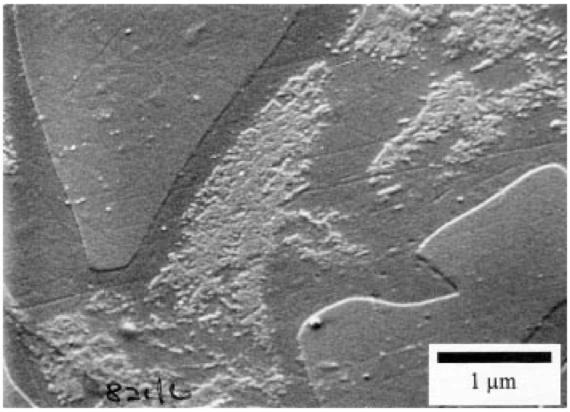

Figure 1 Scanning electron micrograph of the microstructure of a quartz-based electrical porcelain showing a nanoscale mat of interlocking mullite crystals originating from the clay particles in the original batch, surrounded by glassy material from the fluxing component. The large grains are quartz.

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* Correspondence to: M. Cain, Centre for Materials Measurement and Technology National Physical Laboratory, Teddington, Middlesex, TW11 OLW, UK.
E-mail: markys.cain@npl.co.uk

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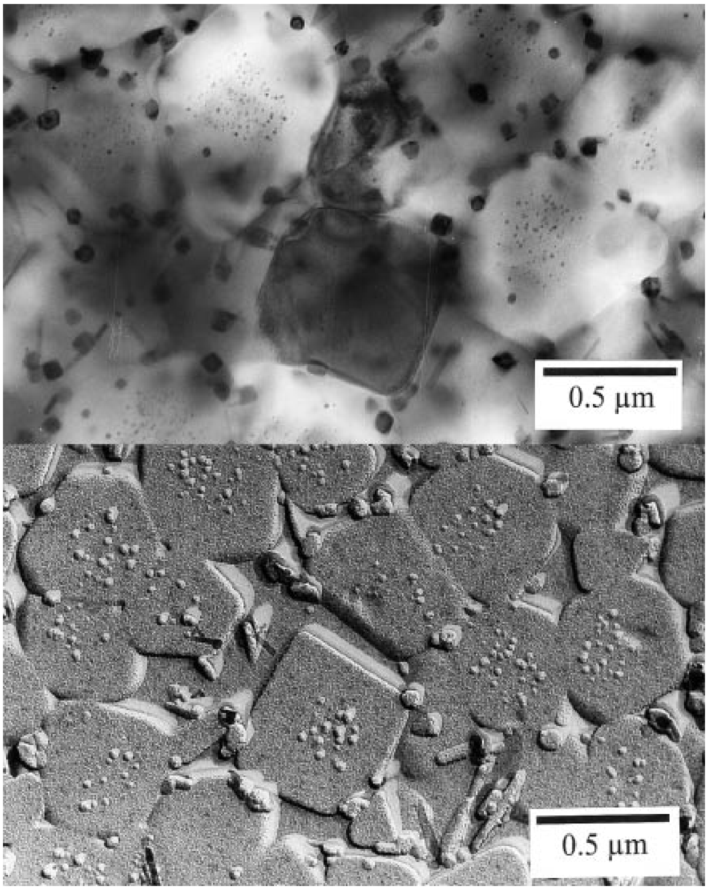

Figure 2 Transmission electron micrograph of the microstructure of a β-spodumene glass-ceramic containing TiO_2 nanoscale nuclei within grains and with larger grains swept to boundaries with grain growth: (upper), transmission electron micrograph; (lower), transmission electron micrograph of a gold–palladium shadowed replica of an etched surface.

heterogeneously nucleated with TiO_2, which appears initially on a nanoscale. The TiO_2 particles are clearly less than 30 nm across at this stage of heat treatment.

The essential differences between these examples of ceramic products with nanoscale microstructures and some of the more recent developments is in the way in which the raw materials are handled to make dense products. Both the above examples do not require the handling of submicrometre powders. In the case of porcelain, the starting particle sizes are 1 –100 μm. In the case of glass-ceramics, the raw materials used for the glass batch may be even coarser. In the more recent, deliberately engineered nanoceramics, such as yttria partially stabilized zirconia (Y-TZP) and Al_2O_3/SiC nanocomposites, the scientific emphasis has been on improving performance[1,2] whereas the technical difficulties to be resolved have mostly concerned handling of nanoscale powders.

Ceramic materials in nanoscale powder form have also been available and have been used for many years. Cerium oxide has long been used as a polishing medium (rouge), which has the great advantage of progressively breaking down to become finer and finer. γ-Alumina has been available for more than half a century with a particle size of less than 50 nm, and is also used for polishing. Transparent silica structures known as aerogels, and produced by the removal of moisture from silica gel, have microstructures on the nanometre scale, and have found applications such as in insulation in double glazing. Nanoscale carbons, and other materials such as TiO_2, are used as stiffening fillers in rubber and plastics. In many respects, nanotechnology started with ceramics!

Table 1 Feature size for significant changes in properties (after Kamigaito[3])

Technical change in properties	Feature size at which changes might be expected (nm)
Catalytic activity	<5
Making hard magnetic materials soft	<20
Producing refractive index changes	<50
Producing superparamagnetism and other electromagnetic phenomena	<100
Producing strengthening and toughening	<100
Modifying matrix dislocation movement, hardness and plasticity	<100

So where are nanoceramics leading? This paper reviews the state of the art, looks at the technical possibilities, the potential advantages and disadvantages, and tries to draw some conclusions for the future.

2 NANOCERAMICS — THE STATE OF THE ART

2.1 Why nanoscale?

Kamigatio[3] has suggested that nanoscale microstructures may result in changes in properties when the feature size is less than a particular level, as listed in Table 1. Such potential changes in properties are what has driven research in nanoceramics over the last decade, particularly in view of the limitations in properties and performance of existing conventionally processed materials.

Particularly with regard to mechanical ceramics, there has been a drive over the last three decades to improve strength and toughness, and thus make ceramics more amenable to and reliable in engineering applications. The understanding of strength σ_f in terms of Griffith 'flaws' related to grain size g, as embodied in the Hall–Petch relationship, $\sigma_f \propto g^{-1/2}$, suggests that finer grain sizes can lead to stronger materials. This is certainly happening in the hardmetal industry, but in ceramics, the strength seems to be limited by surface flaw size due to machining or handling, which becomes no longer simply related to grain size, with the damage extending several grain depths. However, fine grain size can be useful for other reasons:

- the firing temperature can be reduced, saving energy and ensuring removal of residual porosity;
- optical properties are changed; in particular, transparency can be improved because light scattering is reduced;
- microcracking due to crystallographic thermal expansion anisotropy can be reduced;
- surfaces can be better polished.

Strength is also related to fracture energy, or toughness, which restricts the propagation of small flaws. Practically, reducing the grain size has little effect on toughness, and may even reduce it. However, toughness changes can be produced by modifying internal microstructural stresses (tesselated stresses), and hence crack paths, using second-phase particles (so-called nanocomposites). This is perhaps the most important area of development, and has led to some very high claimed strengths.[4,5] The exact toughening mechanisms are still subject to debate, and some are discussed below.

Such microstructural modifications also affect other properties, notably wear resistance and surface finish, through changes to the surface deformation and material removal mechanisms. Technical advantages of such products are currently being explored, e.g. in cutting tool applications.

Finally, it may be possible to develop phase assemblages and properties that are not available in coarser-grained versions. The prospects are probably best in the electroceramic field, e.g. where domain structures may be influenced strongly by fine grain size.

2.2 Different types of nanostructured ceramic

It is instructive to identify some of the types of nanostructure that might be targeted. Figure 3 shows three basic types, described as 'nano' (single nanophase), 'nano/nano' (two nanophases), and 'micro/nano' (the nanophase dispersed in the

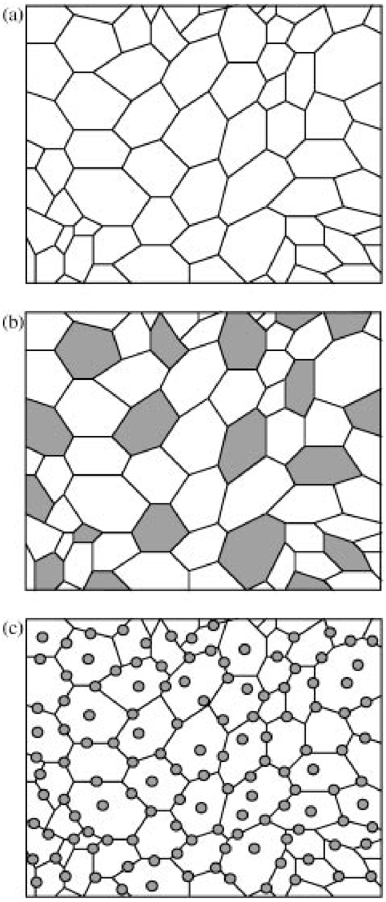

Figure 3 Basic types of nanoceramic: (a) all-nano, single phase; (b) all-nano, two phase; (c) micro/nano, two-phase type with the nanophase dispersed both within grains and at all places along grain boundaries.

microphase). Other subtypes can also be identified, e.g. different spatial relationships between the phases. In the case of the 'micro/nano' type, the dispersed nanophase component could be distributed along grain boundaries of the microphase (i.e. swept along with grain growth in sintering), in the bulk of the grains (i.e. left behind by grain growth), at grain boundary junctions only, or in all positions. Technical properties might well be different for these different subtypes.

It is clear from these geometries that, in order to obtain technical gains in bulk material, close attention must be made to obtaining:

- an understanding of interactions between species during processing of mixed-species materials;
- an understanding of how the internal stress distribution will be changed by adding additional species;
- uniform fine particle size, in order to obtain uniform grain structure;
- good dispersion of the species in mixed-species materials;
- minimal agglomeration, which might lead to large residual pores.

If not then inhomogeneity, poor density, and residual defects will occur, defeating the objectives of nanoscale microstructural manipulation.

2.3 Manufacturing issues

Before performance improvements can be achieved, a number of manufacturing hurdles have to be overcome in a cost-effective manner. This is the key to exploiting these microstructural aims. Consideration must be given to the following.

The cost of nanoscale powders: the cost of bulk technical ceramics is closely related to the cost of the raw materials, and only when this is insignificant compared with the cost of preparing and consolidating components is a strong industrial take-up likely. Currently, the powder costs can be very high: ECU/g being common, whereas industrial targets might be ECU/kg. Cost reduction may come with volume production, but ultrafine powders are always likely to be more expensive than coarser ones.

Powder reactivity: the high surface area leads to enhanced effects of reactions between a powder and its environment, for example hydrolysis reactions between Si_3N_4 and water vapour, hydration of silicates, oxidation of ultrafine non-oxides. Processing may require controlled environments, such as inert liquids or dry atmospheres, and thus add to processing costs.

The problem of agglomeration/de-agglomeration: the finer the powder, the higher the surface area, and the more likely it is for a particle to adhere to its neighbour. Agglomeration leads to poor mixing, inhomogeneous packing, residual porosity and poor density. Obtaining and retaining a good dispersion is not trivial.

Low green density: a consequence of the tendency to agglomerate is that the packing density in pressing a shape tends to be poor. Binder systems may need to be adjusted to suit the high surface area. Poor density in pressing will lead to large size changes in sintering, which will contribute to distortions and hence to poor dimensional control.

Sintering inhibition: particularly in the case where a non-sinter-active addition is made to a sinter-active material (e.g. in a micro/nano material), the sinter-activity of the latter seems to be reduced. Particle rearrangement is more difficult, and shape change probably requires a larger element of bulk diffusion to occur than is usual in sintering the matrix phase alone.

Mechanically assisted sintering: hot pressing or HIPing can clearly overcome a reluctance to sinter to full density, but it adds enormously to the cost of production, especially for complex shapes. Industrial applications for hot-pressed products are currently very limited when the cost-effectiveness is limited.

For these reasons, it is anticipated that process control will be more difficult than for conventional ceramics, and it may take more investment before bringing products to market.

3 NANOCERAMIC CASE STUDIES

3.1 Alumina reinforced with nanoscale silicon carbide

This is perhaps the most widely evaluated micro/nano system, first investigated by Niihara and Nakahira.[4,5] Typically, 5 to 25% of ultrafine silicon carbide is added to a 1 µm particle-sized pure alumina powder, and is hot-pressed. Niihara reported very high strengths for this type of material, in excess of 1 GPa, but the processing and measurement method are not clear. This result has not been repeated by other researchers, e.g. see Ref. 6, who typically find more modest increases in strength, typically to 700 MPa, compared with 400 MPa for a 2 µm grain size unreinforced alumina.

Hot-pressing has generally been used for this material, because sintering tends to be impeded to some extent by the SiC particles, but sintering to near full density has been achieved if inert gas atmospheres are used. SiC also impedes grain growth, which can be a problem in alumina if over-fired. The SiC particles are located typically on both grain boundaries and within grains.

There are a number of citations of changes in properties of this nanocomposite compared with those of alumina alone, even in similar final alumina grain sizes. Abrasive wear resistance has been shown to be greatly improved with a well-dispersed 5% SiC addition,[7] even compared with 1 µm grain size pure (Fig. 4).[8] Surface finish in grinding is much improved,[9] and there is a dominance of plastic deformation over chipping and fracture. The mode of fracture is changed, from intergranular to transgranular.[9]

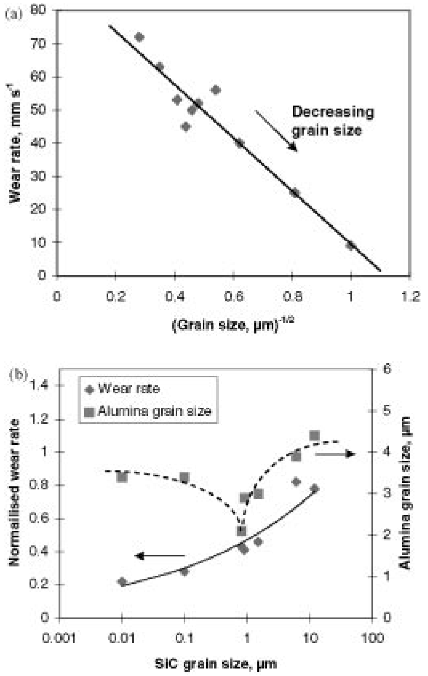

Figure 4 Abrasive wear rates (a) as a function of grain size in aluminas (from data taken from Ref 8), and (b) as a function of SiC particle size added at the 5 is wt% level (from data taken from Ref 7).

The reasoning behind these changes is the modifications in internal stress distribution brought about by SiC particles. Alumina itself has crystallographically anisotropic thermal expansion behaviour, and, on cooling from the firing temperature, stresses are built up between grains of different orientations. These stresses are independent of grain size, but the energy per grain increases with increasing grain size, leading to spontaneous microcracking with grain sizes greater than about 75 µm, a dominance of intergranular fracture, and a tendency for whole grains to 'pop out' during surface contact processes such as abrasive wear or machining. Silicon carbide has a lower thermal expansion coefficient than alumina, which means that an embedded particle in an alumina matrix is subjected to radial compression during cooling from firing, while the immediate surrounding matrix is in radial compression but hoop tension.

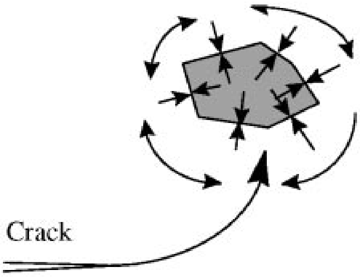

Figure 5 Schematic diagram of the stress field associated with an SiC nanoparticle in alumina, showing how a running crack is attracted to, and pinned by, the particle.

These stresses are much higher than those associated with the alumina crystallographic anisotropy, and so dominate the stress field. The elastic energy associated with each particle is insufficient to initiate and propagate microcracks, but a crack approaching a particle tends to be deflected towards the particle and to be pinned by it (Fig. 5). Particles at grain boundaries thus act as crack stoppers, and alumina grain pop-out by intergranular fracture is impeded.[10] Particles within grains act in a similar way, and more work has to be done to drive a crack through the microstructure. A product of this type seems to have clear technical advantages compared with alumina alone, giving improvements in wear resistance, impact and chipping damage resistance, and surface finish, irrespective of changes in strength and toughness.

3.2 Ceramic cutting tools

The current generations of ceramic cutting tools have a performance limited by toughness (giving impact resistance in interrupted cutting), thermal conductivity (conducting the heat away from the cutting tip and preventing overheating and softening) and chemical interactions with the workpiece material. In certain applications, e.g. in the continuous cutting of cast irons and hard alloys, they possess much greater lifetimes than hardmetals, even when ceramic coatings are applied, because of their higher temperature capability. The drive towards uncooled cutting procedures for environmental reasons, higher productivity and better dimensional tolerances and surface finishes means that further developments of ceramic tooling are needed.

An EC BRITE–EURAM Project ran between 1992 and 1997 to investigate the potential for using nanostructured ceramics for cutting tools.[11] The objectives were to seek whether reinforcement on the nanoscale had any technical advantage in cutting performance, and, if so, how to industrialize the products in a cost-effective fashion. One of the critical issues for the manufacture of bulk components of this type is the need to eliminate expensive hot pressing and to concentrate on cold pressing and sintering to near final shape, permitting minimal machining to obtain dimensions according to ISO standard requirements for indexable inserts. The project additionally addressed a number of issues in the manufacture of such products, including the manufacture and handling of nanopowders in bulk, the additions of temporary binders and lubricants to aid granulation and pressing, the flow of granulated feedstock into automatic presses, and sintering cycles.

The project concentrated on alumina and silicon nitride based materials, and the non-confidential findings of this project can be summarised as follows.

- A range of ultrafine powders could be made cost effectively in bulk by a variety of methods, including intensive milling, laser pyrolysis, and sol–gel methods, but with reducing particle size they are increasingly difficult to de-agglomerate and disperse, and are increasingly susceptible to hydration effects in storage and handling.
- It rapidly became clear that ultrafine powders are much more difficult to press to a high and reproducible green density than coarser powders, presumably because of re-agglomeration effects. It was necessary to use binder systems specifically developed for the powder, and generally softer than conventional ones. Control of firing shrinkage is therefore less predictable.
- It was found that, with care, some useful nanoscale reinforced materials can be made, but further optimization of the binders is essential to make a flowable but crushable granulate for effective automated manufacturing.
- The properties of the materials developed during the research were excellent, with high hardness and good toughness, and with high strengths being achieved even after relatively coarse grit machining.
- Cutting tool trials using hard alloys, hardened steels and cast irons were performed both on billet material in the laboratory and on the shop floor on real components, such as flywheels, brake discs and calibration rollers. The wear scars on the tools developed at rates similar to those

Table 2 Mechanical reinforcement of matrix ceramics

Matrix	Nanoscale reinforcement
Alumina	SiC, TiC, TiN, ZrO_2, C, TiO_2, spinel, Si_3N_4
Y-TZP	Al_2O_3, TiC
Magnesia	SiC
Cordierite	SiC
Mullite	SiC
Silicon nitride	SiC, TiN, TiC
Silicon carbide	TiB_2
Aluminium nitride	B_4C, SiC
Molybdenum disilicide	SiC
Vanadium disilicide	SiC

> seen in conventional ceramic tooling of similar overall chemical composition These results would appear to imply that tool wear is dominated by the chemistry of interaction with the workpiece rather than tool microstructure. However, the scars were much smoother, and this permitted improved workpiece surface finish and hence longer tool life before the workpiece quality degraded. Increases in the number of components machined per cutting tip leads to reduced overall costs, which include machine downtime to change tips.

Recent publications by Krell *et al.*[12] report on the use of ultrafine-grained pure alumina as a cutting tool. Normally, fine-grained (1–2 μm) pure alumina has neither the strength nor the toughness for versatile machining behaviour. However, these authors report on the use of a substantially sub 0.5 μm fully dense alumina prepared in the form of coarse grinding grit and as cutting tools. In grit form, it was found that the rate of removal of steel from a billet by abrasion was approximately three times greater than conventional brown alumina grit, and about 80% greater than sol–gel-derived sintered alumina. In cutting tool form, tested against hardened steel as a workpiece, the material significantly out-performed conventional alumina and alumina/titanium carbonitride tools. The origins for this excellent behaviour are unclear, but may be related to ultrahigh strength in grit form and, as a cutting tool, to ultrahigh thermal conductivity, possibly with radiation transparency.

In cutting-tool applications, therefore, there seem to be some interesting prospects for using nanostructured ceramic materials for improving tool life, operating under more severe conditions, and eliminating cutting fluids.

3.3 Literature overview

Looking more widely at recently reported research findings, there appear to be many options for mechanical reinforcement of bulk ceramic materials with nanophase hard particulates. These are summarized in Table 2. In many cases it is difficult to find a direct impact of the reinforcement on general technical properties, e.g. toughness measurements, because of inappropriate methods or lack of reproducibility. However, some clear advantages have been found at elevated temperatures, where creep rates have been substantially reduced, e.g. in molybdenum disilicide.[13,14] Pre-

Table 3 Nanomaterial developments for functional devices

System type[a]	Technical focus
Bulk PZT with Ag_n	Mechanical reinforcement
$BaTiO_3$ with Ni_n or Ag_n	Mechanical reinforcement
Bulk PZT with nanoscale oxide additions	Mechanical reinforcement with retained dielectric properties
$BaTiO_3$ with SiC_n	Reduction of slow crack growth in bulk ceramics
MgO with $BaTiO_{3\ n}$	To enhance sinterability of magnesia and to realize a composite possessing ferroelectric properties
Relaxor ferroelectrics	Enhanced dielectric and piezoelectric properties arising from nanostructured phase inhomogeneities
PLZT, etc.	Ferroelectric memories and high dielectric constant materials from nanostructured thin films for silicon integration

[a] The subscript ‘n’ refers to the nanophase component.

sumably, diffusion or dislocation movement is impeded by reinforcing particles, particularly those resident at grain boundaries.

4 OTHER NANOCERAMIC SYSTEMS

This paper has concentrated so far on the effects of developing nanoscale structure in mechanically strong systems. In addition, there is a wide range of possibilities in the electrical/electromagnetic fields using ceramic materials, including electro-active materials such as piezoelectrics and thin film devices. Table 3 lists some of the recent reported developments.

$BaTiO_3$, lead zirconate titanate (PZT) and many other ferroelectric and piezoelectric materials are perovskite materials that are used in technologically very important sensor and actuator applications because of their unique electrical and electromechanical properties. Like many polycrystalline ceramics, such materials possess low fracture strength and low toughness. The demands for smaller component sizes and of a higher surface finish are limiting the development of many new sensors and actuators based on these and other piezoelectric ceramics. Ways in which their mechanical properties may be improved are currently being sought.

Higher strengths may be achieved by increasing the sintered density by hot pressing the powders, but this makes for a more expensive end product, and is not suitable for large-volume production.

Recently, various new approaches have been developed using some of the concepts described earlier in this paper. Most of the examples are based on microstructural refinement by additions of second-phase nanosized particles.

Our first example is related to improvements in slow crack growth prevalent in $BaTiO_3$ ceramics. Slow crack growth in this ferroelectric material occurs predominantly along grain boundaries (like in most ceramic materials), and its rate is enhanced in aqueous environments. An approach to modify the grain boundaries using nanoscale SiC particles was successfully demonstrated by Hwang and Niihara[15] in $BaTiO_3/SiC_n$ composites, fabricated by hot pressing $BaTiO_3$ and β-SiC (5 vol.%) powders. The nanoparticles were observed to decorate the grain boundaries of the major phase, which acted to strengthen these interfaces, with the result that slow crack growth was reduced significantly. Additionally, the SiC could effectively deflect crack propagation and lead to transgranular fracture, further suppressing slow crack growth.

Our second example relates to the changes in microstructure of $BaTiO_3$ with additions of nanoscale dispersants of nickel metal.[16,17] Additions of NiO to $BaTiO_3$ reduce to leave nickel metal nanosized particles decorating the grain boundaries of the $BaTiO_3$ grains. This had two effects on the properties of the composites. At only 5 vol.% nickel additions the fracture strength was increased by a factor of 2.5 times that of the monolithic $BaTiO_3$ alone. The toughness was also increased, due to the soft nickel dispersions acting as crack front stress-absorbing sites. The 'dielectric constant' also increased with increasing volume percentage of nickel addition. The average grain size of the $BaTiO_3$ decreased with increasing nickel additions, resulting in a 'Hall–Petch'-type strength enhancement. The nickel particles resided mainly along grain boundaries, but they also segregated at the surface of the composite, effectively *increasing* the dielectric electrode area. The increase in dielectric constant was thus attributed to (i) grain boundary refinement, (ii) the influence of the dielectric field surrounding the nickel metal particles and (iii) an increased electrode area.

Our third example is based on nanophase strengthening of PZT piezoelectric ceramics. The electrical properties of PZT are often very sensitive to solid-solution reactions with neighbouring phases or sintering additives or through the reduction of the ferroelectric phase during sintering. These issues provided the background to the work carried out by Niihara and coworkers,[18] where small additions of nanoparticulate oxides were expected to have a large effect on the mechanical and electrical properties of the ferroelectric material.

Nanoscale dispersions of MgO, Al_2O_3 and ZrO_2 were added to PZT powders and sintered using conventional techniques. The mechanical properties and dielectric and piezoelectric properties were then evaluated. Intergranular fracture was the common failure mode for monolithic PZT, whereas the composites exhibited higher strengths (up to 1.7 times) and higher hardness with failure modes typified by transgranular fracture. The grain size of the PZT, in the composites containing as little as 0.1 vol. % MgO or 0.5 vol. % Al_2O_3, changed from 8 μm to less than 1 μm. The additions of the reinforcement were considered to strengthen the grain boundaries and to reduce the grain size through the solid-solution diffusion of Al^{3+} and

Mg^{2+} into the PZT lattice, thus changing the surface and grain boundary energetics. The low reactivity of zirconia and PZT meant that the zirconia additions had little effect on the microstructures developed. The effects of the additions on the dielectric properties were less dramatic. Dielectric constants decreased with increasing nanoparticle additions and, following poling (ferroelectric domain orientation under a high voltage gradient), the nanocomposites exhibited no net increase in dielectric constant. The influence of the nanoparticles on the domain reorientations that normally occur during the poling process were considered responsible for this effect. The electromechanical coupling coefficient (a very important parameter when choosing materials for actuator design) showed little change in the 0.1 vol. % MgO nanocomposite compared with the monolithic PZT, making these composites suitable for high reliability piezo-actuators.

Our final example relates to the addition of nanophase particles of $BaTiO_3$ into an MgO matrix, to realize a composite possessing ferroelectric and piezoelectric properties whilst retaining good mechanical properties.[19] $BaTiO_3$ enhanced the sinterability of the MgO, driving sintered densities from ~80% theoretical to near theoretical density. The grain size of the sintered MgO decreased with increasing $BaTiO_3$ second phase. The $BaTiO_3$ particles, dispersed in the MgO matrix, acted to suppress grain growth, thereby improving the composite mechanical strength. Increasing the $BaTiO_3$ content even further (and also by increasing the sintering temperature) resulted in the particles segregating at grain boundaries as well as within the MgO grains. This results in strengthened grain boundaries and changes in fracture modes.

The examples given above are aimed at describing how the microstructure of electro-active materials may be altered by additions of nanoscale second phases. This has the overall aim of providing materials scientists, engineers and designers with new materials with enhanced properties for applications in severe and demanding environments.

5 CONCLUDING REMARKS

There are many exciting facets to the development of nanoscale features in ceramic materials, both in bulk and in thin film form, but a number of important factors and criteria are emerging, which the authors can summarize as follows for bulk materials.

- In designing a material there has to be a clear concept of the functionality being targeted. Consideration must be given to factors such as thermal expansion mismatch between the phases, the role the various phases will play in the internal stress distributions, and the effect there will be on properties not necessarily directly related to the desired target. Special characteristics that derive solely from fine particle size may not be predictable with confidence.
- The benefits of fine microstructures are readily outweighed by heterogeneities, pores or other features common in ceramic manufacture, particularly where mechanical properties are critical. It is essential to keep the system as clean as possible to avoid adventitious contamination, and to control interactions between the component materials and the atmosphere.
- In multicomponent systems involving species with differing sintering behaviours, there will be a mismatch in rates of sintering that may inhibit densification. Filling of gaps between non-sintering particles by a sinterable matrix does not necessarily occur, and may leave ultrafine porosity. Hot pressing can clearly overcome this, but may not give a cost-effective product. Reactions between species can produce side effects, e.g. oxide layers on non-oxides can modify behaviour significantly.
- Powder handling seems to be the critical issue. For each system it is necessary to learn how to create and maintain dispersion and to prevent, or at least limit, agglomeration, which otherwise prevents good packing density in the pressing of shapes. Binder systems may need to be modified compared with conventional particle size materials, purely to function in an appropriate fashion through granulation, to collapse in pressing, to lubrication of die parts, to achieve an appropriate green density, and to minimize spring-back effects on ejection from a pressing die. Experience to date suggests that powders with average sizes much less than 50–100 nm cause unacceptably severe problems compared with coarser particles.
- Handling of ultrafine powders may represent a health hazard, as yet not quantified. Retention of the powders as liquid suspensions may be the best option at present.
- Understanding cost/benefit ratios for nanostruc-

tured materials is important. This applies particularly to bulk materials with low sale value, where even with scale-up and elimination of production difficulties the ratio may be marginal compared with existing products for small increments in performance. Good cost/benefit ratios are more likely to be obtained in the functional materials area, where the quantities of materials are much smaller, and typically have higher potential value.

- It remains imperative to balance the advantages given by nanoparticle additions to electro-active materials to the potential loss in electrical performance. The application must be most prominent in the minds of the materials scientist.

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