CERAMICS WITH NON-UNIFORM MICROSTRUCTURES AND ANISOTROPIC PROPERTIES

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Abstract

Suggesting that materials should have uniform microstructures and properties that are the same in all directions seems attractive. Nonetheless, this reassuring simplicity, which also leads to easy modelling, has strongly influenced materials processing. Recent efforts to produce microstructures with features reminiscent of biological structures may have altered this course, but despite prevalent research on composites or multiphase materials with these special microstructural features, few authors provide detailed quantitative information on size, shape, spatial, and orientational descriptions of the materials investigated. Perhaps a great deal of the challenge is an inability to describe and interpret the real three-dimensional nature of materials, but without useful information on the microstructure, 'design' of new materials is compromised. This paper discusses efforts to quantitatively apply information on microstructures and preferred orientation to understanding properties and property anisotropy.

1. Introduction

In efforts to produce materials with "bio-inspired" microstructures much of the focus has been on hierarchical scaling [1], and not on the inherent anisotropy of constituent materials or on the anisometric microstructural features. If the goal of such investigations is truly capturing the optimal features of biological structures, recognition of the role played by directionality should be incorporated more fully into the processing, characterization, property evaluation and analysis. Processing approaches utilizing materials that are readily oriented on a local scale could be more important than directly reproducing microstructures that have the same appearance as those of biological materials. When such materials are produced, the degree of orientation, and thereby local anisotropy could be critical to understanding the final effects on properties.

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In property evaluations, testing should, whenever possible, explore the degree of property anisotropy. Although optimizing a particular property in a particular direction is a fine goal, recognizing the concurrent decrease in properties in another direction could be critical to many applications. For structural applications, inattention to reductions of strength or fracture toughness in the weak directions may not prepare materials suitable for multiaxial loading. Further, efforts to produce uniform and isotropic ceramics have enabled those tasked with modeling of properties to always begin with such assumptions. Now, even for hierarchical, layered or gradient materials the first models routinely show hierarchical microstructures composed of uniform and isotropic features. Is it not possible to add the hierarchical scaling after introducing non-uniformity and anisotropy? Although some ceramic researchers have recently included anisotropy in models describing material response [see e.g. 2, 3], the prevailing conclusions in fracture investigations focus more on heterogeneity and the sign of residual stresses than on the anisotropy.

In stark contrast, consideration of preferred orientation and its relationship to properties and anisotropy have been the primary emphases for researchers interested in texture of materials. Researchers within this community include primarily metallurgists, a smattering of geologists, and very few polymer scientists and ceramists. As for any small community of researchers, specialized approaches for assessment and representation of information have been developed. Thus, the techniques for measurements of orientation (i.e., pole figures), calculation of orientation parameters or property anisotropy (spherical harmonic or vector method), and representation of data (i.e., pole figures, inverse pole figures and orientation distribution functions), become *de rigueur* for assimilation into the community [see 4, 5]. Despite the potential advantages in understanding the very microstructures currently sought, ceramics researchers readily captivated by qualitative microscopy, traditional powder diffraction (with qualitative assertions on degrees of orientation) and isotropic property tensors seem ill-prepared to adopt these powerful strategies for understanding microstructures.

Defining the critical approaches for inspiring more significant consideration of orientation and directionality in the ceramics community has been difficult. Rather than only focusing on the best examples for relating texture to specific types of properties, it has most often been necessary to do so on materials that have 'important' engineering applications. Thus, work on generating 'textbook' examples is taken with some associated risk. If all efforts on ceramic textures were on fracture of materials with insignificant fracture toughnesses or on electronic materials with less than inspiring properties, few other researchers might be encouraged to take the time to read or hear about the accomplishments. In the area of ceramic textures, individuals with expertise in ceramic processing and property assessment that also can accurately interpret pole figures and orientation distribution functions are quite rare.

This paper consists of examples of texture and anisotropy assessment providing strong descriptive correlations of orientation and properties, descriptions of orientation effects that would not be possible without use of texture analysis and ideas for exploiting quantitative texture analysis in understanding material properties.

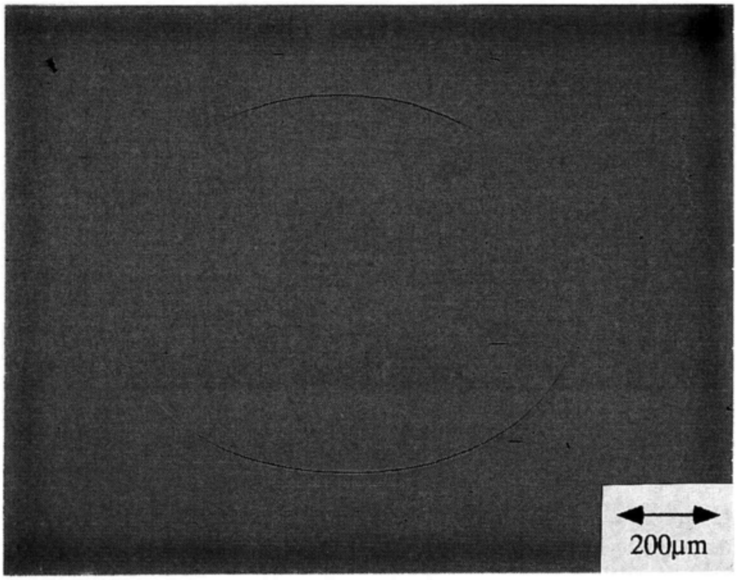


Figure 1 **Indentation of a plane-strain forged, fine-grain silicon nitride material with a 6.35mm tungsten carbide ball. The horizontal direction is the direction along which the grains are aligned with a maximum of approximately six times random.**

2. Anisotropy: Spherical Indentors give Elliptical Cracks

Recent investigations of the damage surrounding spherical indentations in materials by Lawn and coworkers [6-8] have brought to bear increased interest in contact damage and contact fatigue in ceramic materials. We have used this technique to probe anisotropy effects [9,10] in silicon nitride ceramics possessing strong textures [11]. As an example consider the early stages cracking visible in the oriented silicon nitride material shown in Figure 1. For this micrograph, the needle-like silicon nitride grains run predominantly horizontal, with more than six times the grains running in this direction as in a random material. These fine grain silicon nitride materials are pre-disposed to cone-cracking rather than extensive damage below the indents, and the anisotropy effects are quite clear. Since the ratio between the maximum and minimum fracture toughness in such materials is typically two to three, it is not surprising that the crack geometry is not circular. Ultrasound results on similar materials indicate that elastic anisotropy is small, thus the

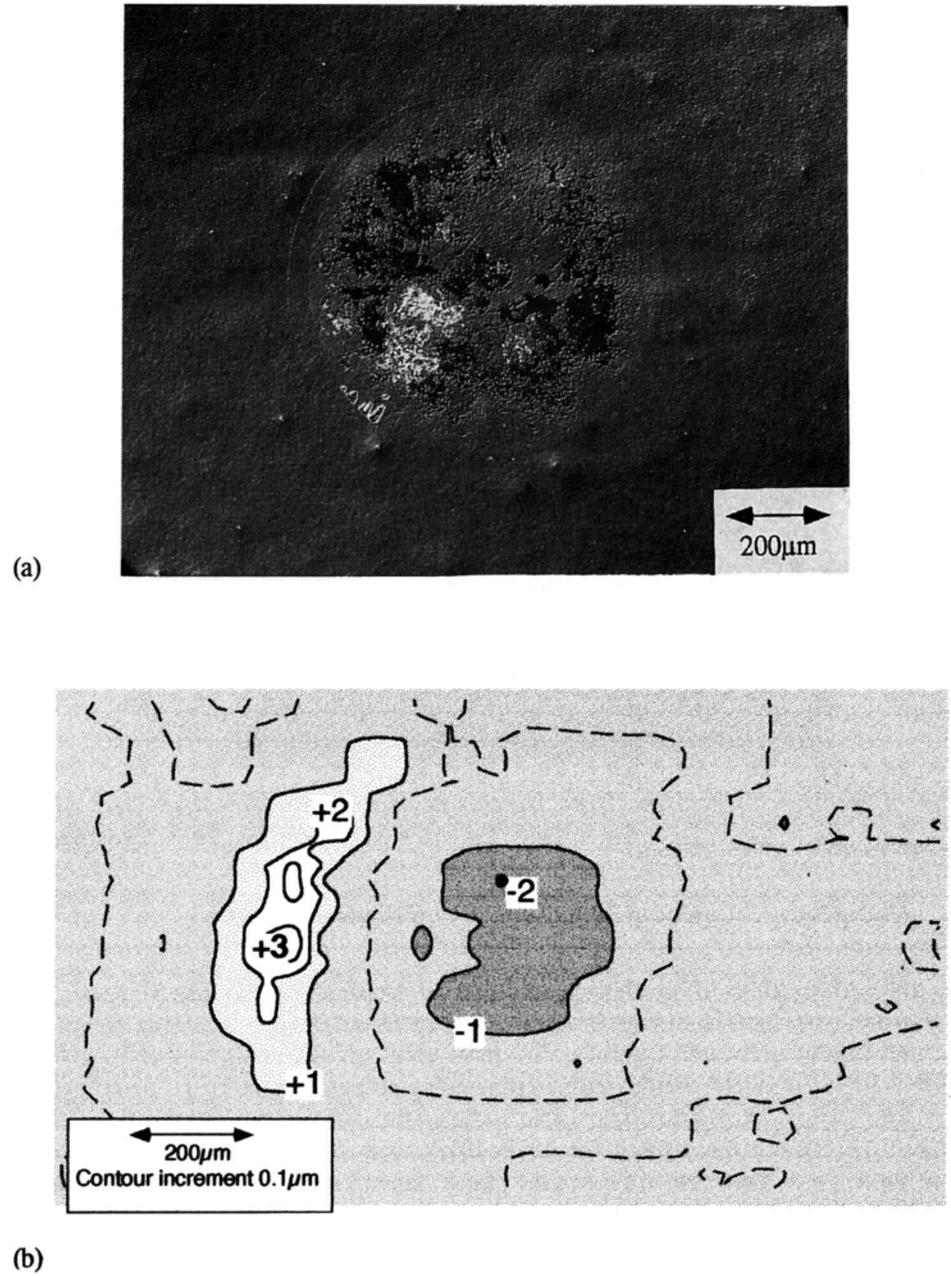


Figure 2 A fine-grain with silicon nitride grains canted at a 45° angle to the surface of the specimen shows cracking (a) on the left-hand-side wherein the cracks can go between the grains. At this same location surface uplift associated with shear damage to the surface can be observed.

crack geometry can be ascribed primarily to the alignment of the silicon nitride grains [9]. Calculation of expected elastic anisotropy is difficult since β-silicon nitride single crystal elastic constants are not available, although orientation models could also be used to infer the single crystal elastic constants.

Further quantification of the indentation process is necessary to better understand the contact process, but thus far the focus has been on damage observations from micrographs. In an effort to introduce some quantitative aspects to analysis of indentation, our recent work has employed profilometry. Through evaluations of oriented and unoriented silicon nitride materials with several toughness levels moderated by control of grain size, it is apparent that in addition to stark uplift near cracks, uplift can be resolved up for distances of several indent diameters. An example of anisotropy effects in spherical indentation is shown in Figure 2. The micrograph in Figure 2(a) shows the surface crack adjacent to an indent in fine-grain silicon nitride sample with grains aligned at 45° to the indent surface. The crack that is apparent on the left-side of the indent runs mostly within the boundaries between the individual grains. The shear nature of the indent is clearly seen in a profilometry contour map (Figure 2(b)). Similar specimens that have been tested with grains aligned 45° to the surface have demonstrated strong anisotropies in the directionality of friction and wear [9]. In such specimens a change in the direction of sliding across the surface results in quite different cracking behavior. The profilometry results shown here provide insight into the strong asymmetry found in wear evaluations on similar surfaces.

A summary of microstructure effects on profilometry traces across indents in materials with different microstructures is shown in Figure 3. The very deep indent is that for a hot-pressed silicon nitride with a coarse grain size that shows only very abbreviated cone cracks. The indent, and the associated uplift near the indent, are clear. Note, that the uplift surrounding the indent does taper off to zero well away from the indent to nearly produce volume conservation. Investigations on such materials with anisotropic microstructures are anticipated to add insight into the indentation process.

3. Seeding: Microstructural Gardening

Intentional seeding of microstructural features into a material has recently been demonstrated in ceramics [see e.g. 12-18], but has long been practiced in the metal casting industry wherein seed particles with compatible crystal structures have been used to refine the size scale of secondary phases (graphite in cast iron and primary silicon in high silicon-aluminum alloys). The significant distinction for many ceramic materials is that the goals can include the arrangement and the spatial distribution of the microstructural features (see next section). This form of microstructural arrangement might best be called *microscaping*. Seeding of ceramics produced from non-ceramic

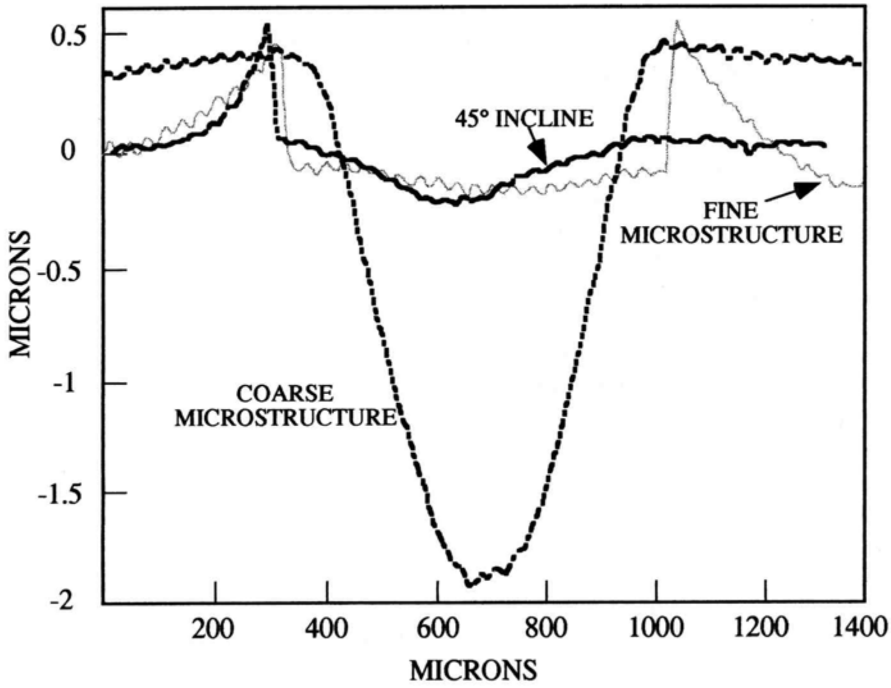


Figure 3 Indent profilometry for three different silicon nitride materials.

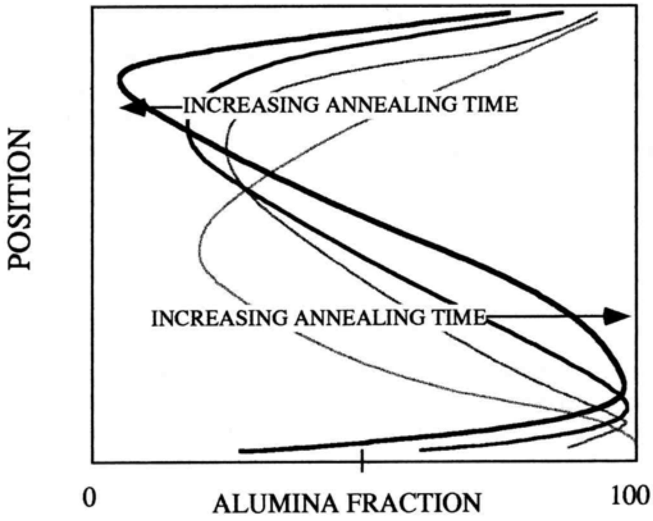


Figure 4 Redistribution of alumina in a zirconia-alumina gradient material wherein 12.5 volume percent of the material was initially alumina platelets, 37.5 volume percent was initially alumina powder and the balance was ceria-zirconia powder (after [22]).

precursors has been employed to alter the final product in the contexts of processing difficulty, shrinkage reduction and microstructure [12-15, 20]. Oriented microstructures are readily produced wherein grain growth permits the process to occur from anisometric grains oriented during green processing [16-19]. These materials permit introduction of only a small fraction of the larger,oriented grains in green state processing. Subsequent grain growth can increase the fraction of oriented phase, thereby reducing the negative consequences of sintering materials with a large fraction of the oriented phase. Annealing studies by Roeder et al. on zirconia-alumina composites containing alumina platelets demonstrate that it is possible to not only have seeded orientations, but phase re-distribution in materials with gradient microstructures driven by grain size distributions (see Figure 4) [21,22]. The potential for inheriting preferred orientation from polymer precursors [23,24], nucleating orientations with transient phases [e.g. 25], and seeding (or grafting for heterophase materials) with a second material that is available in a suitable anisometric form may lead to greater innovations in microscaping.

To successfully accomplish an oriented microstructure of a ceramic that is derived from an organic precursor it is necessary to retain the orientation derived from prior processing through to the final ceramic. One strategy would be to seed the precursor and another is to have the precursor have orientation attributes that would be retained from directional processing. The latter case is that practiced in the manufacture of graphite fibers from previously oriented polymer fibers [e.g. 26]. For such a process to be viable with ceramic fibers derived from a polymer precursor (see Figure 5), it is essential that attributes of the monomer be suitable and are at least somewhat retained during pyrolysis. As demonstrated by Laine et al. [20] differences in the architecture of monomer units can strongly influence microstructure development during pyrolysis of ceramics. In our research on production of tetragonal fibers [23, 24], the tetragonal phase, which has a quite similar relationship to the central portion of the difunctional zirconium alkoxide utilized in this investigation, can be retained in undoped materials if oxygen activities during pyrolysis are kept quite low. Unfortunately, efforts to orient the initial organic fibers have been unsuccessful due to the low molecular weights of the alkoxide and a probable cycloid morphology of the macromolecules. Thus, although in this instance the monomer unit is apparently suitable, oriented fibers have not been produced.

In the preparation of lead zirconate titanate (PZT) films for ferroelectric applications preferred orientations that are optimized with respect to crystal structure are very important. For optimum ferroelectric switching, the desired orientation for tetragonal phase films is with 001 poles normal to the film and the desired orientation for rhombohedral films is with 111 poles normal to the film (see Figure 6). Chen and Chen have proposed that in some cases the orientation process can occur through the presence of oriented transient phases during pyrolysis [25]. Although some conflicting results [e.g. 27,28] cast doubts regarding the specifics of the orientation process, the proposed mechanism is very attractive. The potential for phases to be consumed or disappear after facilitating preferred orientation may make a broader range of orientation control possible.

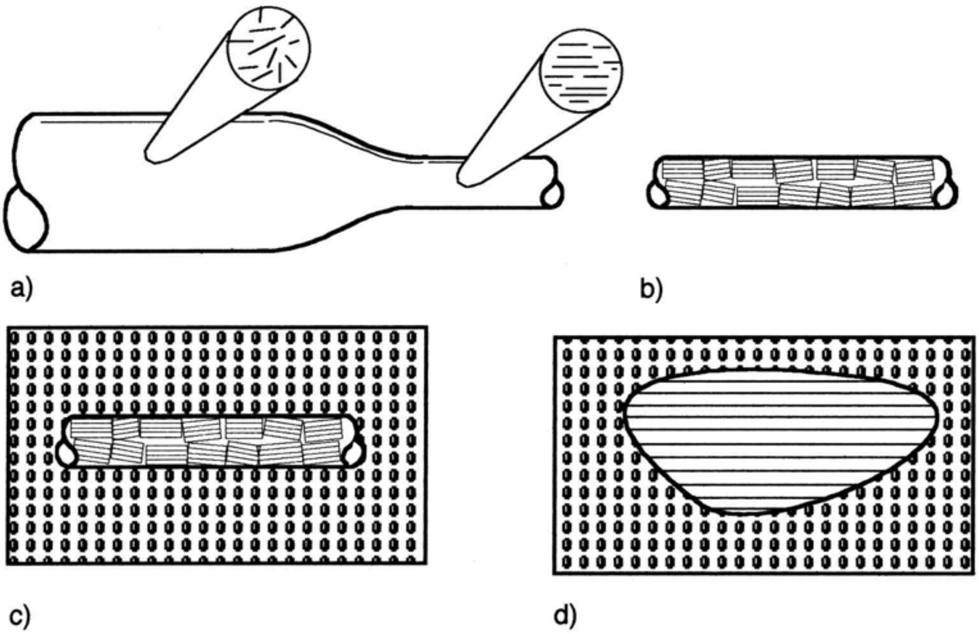


Figure 5 Illustration of orientation selective processing using a polymer-derived seed. In this approach, a) drawing a zirconium-based polymer will align polymer chains in the axial direction. b) During pyrolysis, orientation is retained, thus forming oriented, polycrystalline zirconia fibers. c) These fibers, or seeds, are then annealed in a fine-grain zirconia matrix such that d) the larger, oriented seed consumes the smaller grains, inducing a local orientation.

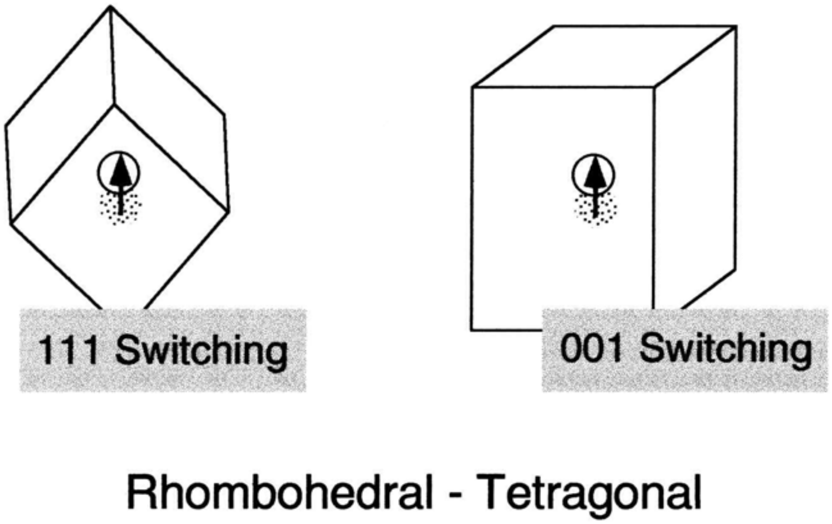


Figure 6 Schematic figure showing the switching directions for ferroelectric materials with different crystal structures.

4. Forces of Nature: Enhanced Gravity and Artificial Fields

Efforts to produce aligned microstructures of ceramics most often take place using powder processing routes that produce desirable orientations. Green state processing with anisometric grains has been widely practiced. Routes to introduce preferred orientation with tape casting, slip casting and pressure filtration processes do, however, suffer serious limitations if parts with non-planar geometries are desired. Processing techniques to produce preferred orientations in useful components with non-planar geometries (both on a local and non-local basis) can be facilitated by applying direction fields that interact with the ceramic particles during green state processing. Three approaches that have this character, centrifugal slip casting (enhanced gravitational fields combined with fluid separation) [21,22,29-40], magnetic alignment [41-44] and electrophoresis [45-47] have been successful in introducing oriented, and some cases layered or gradient, microstructures.

Centrifuging, the approach used to produce specimens for the microstructural studies of zirconia-alumina materials described in the previous section, is quite successful in producing oriented, layered or gradient materials, it imparts an inherent limitation on geometry. As shown in Figure 7, producing parts with the more complicated geometry of a gear by centrifuging results in parts wherein the layered microstructure might not be very beneficial. On the other hand, by combining both the directionality of centrifuging with the fluid transport available in slip casting, called centrifugal slip casting, parts with layers that follow the part shape can be produced. Other work on centrifugal processing also discusses the benefits of centrifuging with regard to green body fabrication, final properties and aspects of microstructure development [33-40]. A number of applications for centrifugal slip casting are suggested in Figure 8.

Both magnetic field [41-44] and electric field [45-47] routes to producing oriented ceramics do find a common thread in the long-practiced 'poling' of ferroic materials. The difference is that rather than applying a large field to produce a favorable state of ferroic domains within the material, the orientation process can take place before firing. Although both possess limitations on the extent to which they can be applied to any material, and in particular to composites, intriguing examples have been demonstrated. Magnetic field-induced textures of Fe_2TiO_5 by Faber and coworkers have demonstrated vacuum filtration and gel-casting within magnetic fields. The intriguing potential of such work is that under such circumstances it is possible to manipulate orientation by tensorial properties that are not necessarily correlated with other critical aspects like grain anisometry, elastic anisotropy or thermal expansion anisotropy. Processing with these techniques can result in green state textures without a requirement of anisometric grains [41,42]. Research by Nicholson and coworkers [45-47] on electrophoresis has been successful in introducing both layered and oriented microstructures. Since in electrophoresis the particles are driven to the electrode, the use of small and mobile electrodes permits patterning on the scale of the microstructure [48]. Thus, non-planar layers and gradients are possible.

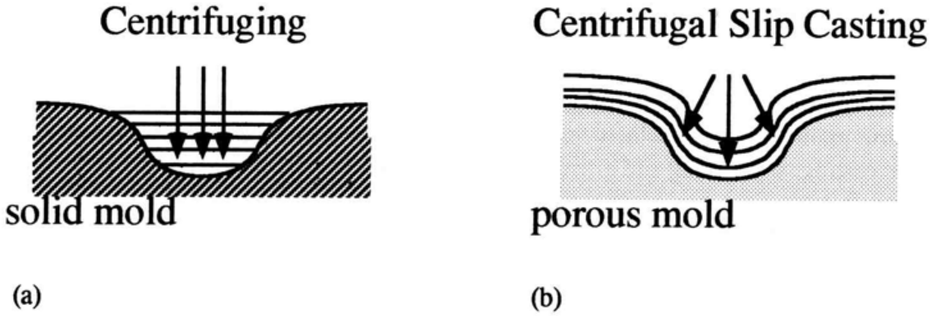


Figure 7 Centrifugal processing with (a) solid molds for centrifuging and (b) porous molds for centrifugal slip casting show different potential for the layers or gradients in composites to follow the part shape.

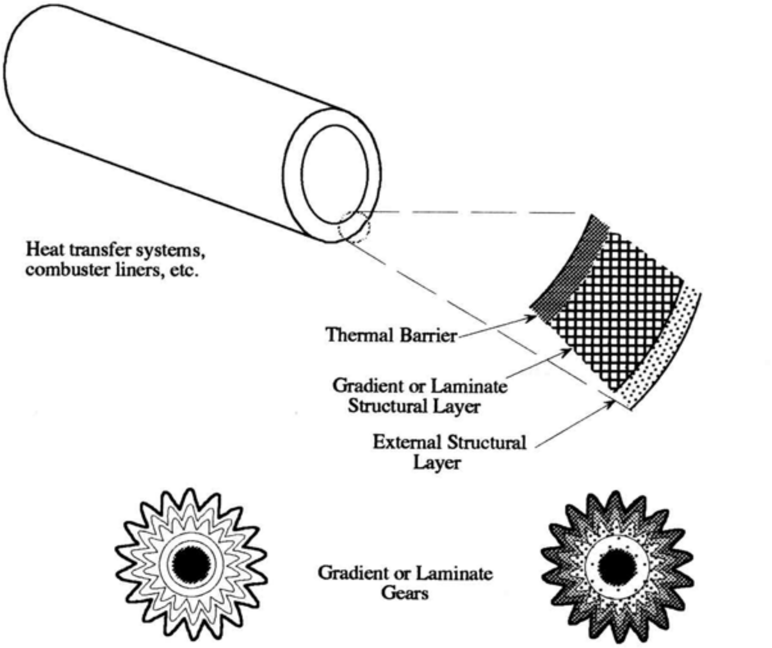


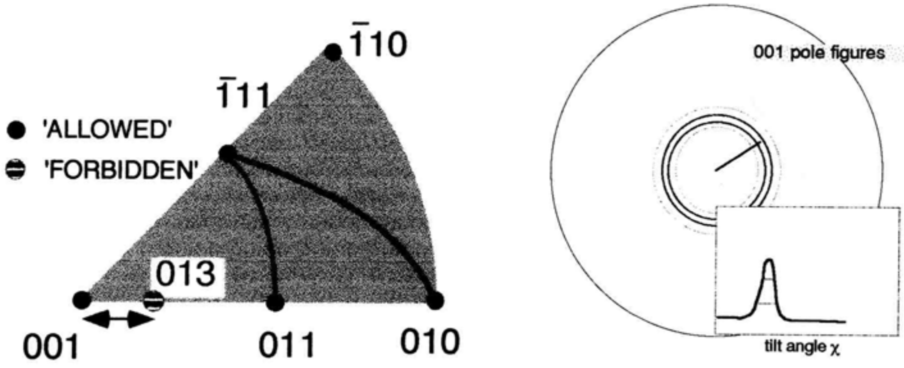
Figure 8 Potential applications for centrifugal processing of ceramics and ceramic composites.

5. Texture Gages: Quantification of Phenomena and Mechanisms

Beyond methods to attain desired properties or evaluate incidental effects of directional processing, texture analysis can also be used to assist in understanding mechanisms, provide critical information for modeling of physical phenomena and resolve problems that escape those employing conventional approaches. The efforts in the texture literature to correlate slip, twinning and recrystallization mechanisms with deformation are designed to translate understanding of single crystal behavior into polycrystalline materials. In engineering applications, models for the plastic anisotropy that should result for particular textures are employed to determine the suitability of particular steels for a forming operation. Additionally, relationships between microstructure, texture and anisotropy for tensorial properties such as elasticity and magnetism have been intensively investigated within the texture community [see 4,5]. These properties are routinely correlated with orientation coefficients derived from texture measurements. Considering the importance of other tensorial properties such as thermal conductivity, thermal expansion, electrical conductivity, ferroelectricity and piezoelectricity, ceramic literature containing models correlated with texture and property anisotropy remains scarce.

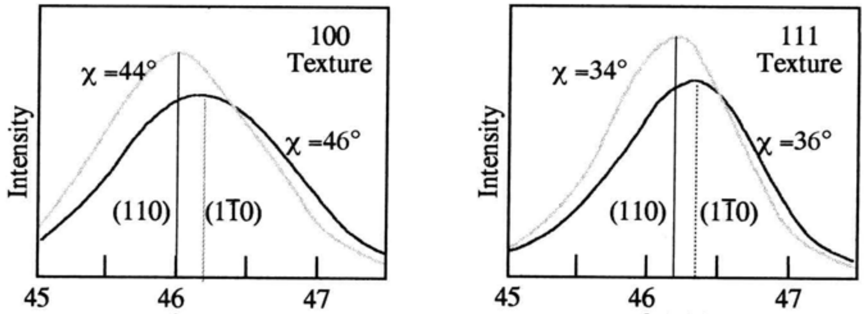
More common to the ceramic literature are examples wherein a very few parameters are employed in techniques derived from conventional diffraction, e.g. the Lötgering [48] or Harris [49,50] methods. These methods suffer from a profound limitations in providing information on phase content and orientation. If the preferred orientation maximum of the specimen relative to the surface chosen as the Bragg plane does not coincide with an allowed reflection, then very little about the character and degree of the texture can be extracted from such a measurement. This has recently been demonstrated in work on $ZrTiO_4$ by Blachere and coworkers [51]. A schematic example describing such a problem is given in Figure 9. For the texture produced by Blachere and coworkers, a 103 pole relative to the plane of a ceramic film, there is no available Bragg reflection. Thus, measurements of pole figures, wherein an axisymmetric ring maximum corresponding to the angle between allowed reflections and 103 poles permit confirmation of the texture intensity and the location of the maximum texture value in orientation space. Input of such data and the symmetry of the crystal into orientation distribution function calculations could then permit modeling of the properties based on the stochastic distribution of specimen orientations.

Research on orientation on the ferroelectric materials barium titanate and lead zirconate titanate (PZT) typically also employs semi-quantitative information inferred from conventional diffraction [e.g. 25, 52]. In recent measurements on PZT, the degree of orientation and extrinsic substrate effects on diffraction could be readily discerned using pole figure measurements [27]. In addition, it is possible to discern shifts in the positions of the individual pole figures wherein it may be possible to access differences between the poling orientations of {100} and {111} for specimens with either texture,



(a) (b)

Figure 9 (a) shows a schematic stereographic section for a hypothetical material with the labeled reflections that are allowed and not allowed. If the texture is such that the texture maximum at the center of symmetry is not one that corresponds to an allowed reflection (e.g. 103), then a (b) pole figuremeasurement can reveal that this is the case. A further calculation of the orientation distribution function could then be used to calculate the 013 pole figure even though it cannot be measured directly.



(a) (b)

Figure 10 (a) shows a two theta scan at two separate tilt angles for PZT with a 100 texture and (b) shows a two theta scan at two separate tilt angles for PZT with a 111 texture.

although distinguishing the effects of the rhombohedral and tetragonal phases of the actual unit cells is difficult. An example showing peak shifts with the specimen plane tilted from the Bragg plane of the goniometer is given in Figure 10. Other routes for assessing domain or transformation effects by texture analysis have been discussed in papers on zirconia ceramics [53,54]. The directional coupling approach applied in these papers could also be applied to ferroelectric, piezoelectric and ferromagnetic materials.

6. Concluding Remarks

The examples given in this paper will hopefully encourage more investigators working on the materials covered to consider ways to introduce quantitative assessment of orientation and anisotropy into their research. Each of the sections provides examples wherein properties are intrinsically tied to processsing. The route to making a microstructure according to a design relies upon understanding all of the important constituents of that design. At this point, the importance of texture and anisotropy in determining optimal properties in ceramics is, for the most part, poorly understood.

7. Acknowledgments

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