

R. Deformation Processes for the Next-Generation Ceramics

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Objectives

- Assess the plastic deformation behavior in nanocrystalline oxide ceramics and applicability to fabrication of complex shapes.
- Characterize thermal and mechanical properties to assess influence of nanocrystalline microstructures for gaining improved performance for wear and other components.

Approach

- Collaborate with members of the Pennsylvania State University task on Synthesis of Nanocrystalline Ceramics, develop advanced colloidal technology-based processing to fabricate monolithic bodies and sintering technology to be able to fabricate dense monolithic nanocrystalline (i.e., grain sizes <100-nm) bodies.
- Characterize the potential for enhanced plasticity in ceramics resulting from reducing grain size below 100 nm and with the application of applied electric fields with regard to mechanical behavior improvements and applicability to forming and surface finishing technologies.

Accomplishments

- Expanded the fabrication of powder compacts to include granulation technology, which can readily produce larger samples and more complex geometries. The recent sintering studies of granulated compacts were sintered to >92% of theoretical density and exhibited grain sizes of 6 to 140 nm. However, these bodies contained mainly monoclinic phase, which was attributed to a loss of yttria during powder synthesis. This is now being addressed in the Pennsylvania State University task.
- Observed electric field effects on deformation to exhibit a temperature dependence that apparently is altered by the mechanism dictating the plastic flow. Above 1200°C, the reduction in yield stress increases with decrease in temperature. At 1200°C, the field effect becomes more sensitive to the strain rate, which suggests a shift from grain boundary sliding to a dislocation-related process.

Future Direction

- Develop a two-step sintering profile to be able to optimize the microstructure of large compacts produced by the granulation process. Room temperature fracture and wear properties will be examined to seek approaches for developing ceramics with greater wear resistance.
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Introduction

In addition to lower specific weight, ceramics have a number of attractive properties for application as components in various heavy-vehicle systems. However, many heavy-vehicle components require ceramics with complex shapes as well as function. Furthermore the demanding service conditions necessitate improved mechanical reliability together with fracture and/or wear resistance. Underlying the performance and use of ceramics is their tendency to fail in a brittle fashion except at temperatures generally well above 1000°C. Complex shape forming processes for ceramics are relegated to approaches based on powder processing as a result of the excessive temperatures for hot forming. On the other hand, metallic alloys can be hot worked at temperatures below 1000°C to not only form the desired shape but also to enhance their properties. The ductility (>20% plastic strain) of metallic alloys at temperatures below 500°C is the source of their 10- to 100-fold greater fracture toughness as compared to that of ceramics.

In ceramic systems, one needs to combine processing to tailor microstructures with novel concepts that offer the potential to enhance deformation. One such concept that has seen considerable interest is that of superplastic deformation of submicron-grain-sized ceramics above 1000°C.¹ Recent studies suggest that reducing the microstructure to achieve grain sizes <100 nm could lead to permanent/plastic deformation in ceramics at quite modest temperatures.^{2,3} Recent studies have shown that the application of electric fields can reduce the yield stress or increase the creep rates of ceramic systems.⁴ To date, this has not been exploited to determine the effects on the deformation of nanocrystalline oxides. The present study seeks to examine the influence of true nanocrystalline microstructures on the mechanical properties of ceramics, as well as approaches to economically fabricate nanocrystalline ceramics monoliths.

Hardness values generally obey the Petch-Hall behavior with the hardness rising as the grain size is reduced. However, results show that when the grain size is ~20 nm, the room temperature hardness then decreases as the grain size continues to be decreased.^{1,5} This behavior has two important implications for applications of interest here. One is that some permanent deformation might be achieved in ceramics with grain sizes <30 nm, and this might

offer improved reliability. More likely of interest is the fact that ceramics with grain sizes below 100 nm but above the softening point will be extremely hard, and that offers substantial advantages in overcoming wear problems in rolling stock. In addition, surface roughness of as-sintered ceramics decreases as the grain size decreases. In fact, the as-sintered surfaces of alumina substrates with grain sizes <500 nm exhibit a mirror-like finish without any surface preparation. This feature should be applicable to the fabrication of low-friction components.

Approach

This project involves two major thrusts. The first is a collaborative effort with researchers in the Synthesis of Nanocrystalline Ceramics task at Pennsylvania State University in the processing and sintering of nanocrystalline ceramics. The goal being to develop the technology to form “green” (unfired) bodies of nanocrystalline particles with densities well in excess of 50% of the theoretical density to allow one to devise pressureless sintering profiles to produce dense monolithic bodies with grain sizes <100 nm (see Ref. 6 for a review of processing of nanocrystalline ceramics). This is aimed at finding approaches to produce sizeable monolithic bodies for subsequent evaluation. The second thrust focuses on the mechanical and friction and wear behavior of nanocrystalline ceramics and the influence of external parameters [e.g., stressing rate, temperature, environment (e.g., air, vacuum)], and electric fields on the plastic deformation behavior.

Synthesis, Evolution, and Stability of Nanostructures in Bulk Materials

Outstanding challenges in particle processing to form bulk, dense nanograin-sized materials include the dispersion of the nanosize particles and control of gas evolution from the very high surface area compacts during sintering. Typically, nanometer size particulates suffer from a high degree of agglomeration, which results in poor particle packing (green densities <40% of theoretical), which inhibits sintering and promotes undesirable grain growth. Two routes to obtaining well-dispersed powders include comminution and colloidal processing.^{7,8} By optimizing colloidal processing approaches, one should be able to produce “green” bodies with densities in excess of 60% of theoretical

by control of interparticle forces through appropriate chemical additives to suspensions of nanoparticulates combined with filter pressing or pressure casting of the high-solids-content slurries. By controlling the packing of nanoparticulates one should be able to control the porosity to achieve the narrow size distribution necessary, which then will enhance densification.

Densification of nanocrystalline ceramics has typically involved the use of applied pressure to achieve dense sub-100-nm grain sized samples.⁹ In those few cases where pressureless sintering has been employed successfully, long hold times at the sintering temperatures were required to achieve densities $\geq 95\%$ of theoretical, which allows undesired grain growth to proceed.¹⁰ Heating to a temperature sufficient to achieve densities of $\geq 75\%$ of theoretical followed by rapidly lowering the temperature to a level to obtain sufficient boundary diffusion to remove pores trapped on boundaries while minimizing grain growth have been only partially successful because long hold times at the lower temperature were still required.¹¹ Here we seek to optimize the processing of the “green” bodies and utilize modified sintering cycles to achieve dense sub-100-nm grain size oxides.

Deformation Behavior in Nanostructured Materials: Baseline deformation data will be established through studies of high purity, dense sub-micron grain size zirconia ceramics in order to evaluate the influence of nanocrystalline microstructures. These studies will then be extended to <100-nm grain sized ceramics. This will include (a) nanostructured ceramics to explore for the softening effects observed in nanocrystalline metals by evaluating both the creep response over a range of temperatures and applied stresses, and the yield stress as a function of strain rate and temperature, and (b) the influence of external factors (e.g., electric fields) that have been shown to enhance deformation processes in ceramics with micrometer grain sizes. Modeling studies will be conducted to describe the deformation behavior and to address such phenomenon as space charge/solute segregation coupled with electric field effects. Additionally, the fracture, hardness, and wear response of nanocrystalline oxides will be evaluated to assess their application in wear components.

Results

Sintering

The Synthesis of Nanocrystalline Ceramics task recently expanded the powder processing method to include granulation to more readily produce large powder compacts. In the granulation step, the chemically derived particulates are dried and treated to form granules, which are basically large, soft agglomerations. These then could be pressed to form bodies of various dimensions to densities of 50 to 55% of theoretical density! The process is very amenable to commercial manufacturing. The ORNL studies have focused on exploring the densification of compacts based on the granulation process approach. Sintering trials at ORNL showed that these granulated compacts could then be densified to greater than 90% of theoretical density, while achieving grain sizes <200 nm. Subsequent characterization revealed that the sintered materials consisted of primarily monolithic zirconia rather than the tetragonal phase. The monoclinic phase is a result of the martensitic transformation from the tetragonal phase upon cooling from the sintering temperature. Transformation to the monoclinic phase involves a volume expansion of ~4%, which is quite large and the associated stress state results in extensive microcrack formation. Such microcracking leads not only to a decrease in density but also to damage and loss of structural intensity.

Earlier work demonstrated that colloidal processed ZrO_2 -1.7 mol % Y_2O_3 bodies could be sintered to densities >95% of theoretical density (TD) when held at 1150°C for only 5 min. These were fully tetragonal phase and had grain sizes <100 nm. Even with 200- to 400-nm grain sizes, ZrO_2 -1.7 mol % Y_2O_3 bodies were fully tetragonal. On the other hand, granulated compacts sintered at 1125°C for 5 min had densities > 90%TD but were composed of 75% monoclinic and 25% tetragonal phases even though the grain size was below 100 nm. Because the grain size is well below 200 nm, the formation of monoclinic phase must be attributed to an insufficient yttria solute content, which is added to stabilize the tetragonal phase. Current synthesis efforts are addressing steps to control and maintain the yttria levels in the as-synthesized powders.

Deformation studies

Collaborations with Prof. Hans Conrad and Dr. Kang Jung of North Carolina State University are assessing the reduction in flow stress in zirconia ceramics due to the application of an applied direct current (dc) field. In this case, the chemical/ electrochemical potential associated with vacancy flux can be altered by both an applied stress and an applied electric field:

$$\mu^* = \mu^o + Ze\phi_i - \sigma\Omega - Ze\phi_a \quad (1)$$

where μ is the potential (superscript o for the standard state, superscript * with electric field); Z is the valence of the ion; e is the charge in coulombs; σ is the stress; Ω is the atomic volume; Φ_a is the applied electric potential (= EX_{SC}); E is the applied electric field; X_{SC} is the width of the space charge zone at the grain boundaries; and Φ_i is the local potential. Thus, one can enhance the flow of vacancies needed for material transport and dislocation motion by applying stress and an electric field. The direction of the vacancy flux is a function of the sign of the applied stress (i.e., vacancies flow to regions under compression). This applies locally to vacancy flow in the deformation of a polycrystalline ceramic where vacancies move from grain boundaries under tension to those in compression while ions/atoms move in the reverse direction. As a result, one can then reduce the applied stress required to deform the material by applying an electric field:

$$\Delta\sigma_E = ZeEx_{SC}/\Omega \quad (2)$$

where $\Delta\sigma_E$ represents the reduction in the flow stress due to the applied field.

The width of the space charge zone is related to the Debye length of the material:

$$X_{SC} = \beta\lambda \quad (3)$$

where it is a proportionality factor in the range of 2 to 5. Theoretical treatments show that the Debye length (δ) in ionic solids increases as both the bulk solute content and temperature are decreased.^{12,13} In addition, δ must be much less than the distance between opposite space charge zones (i.e., \ll grain size). The influence of temperature and solute content on the Debye length in alkali halides is shown in

Figure 1. The increases in the Debye length due to decreases in temperature and solute content will be reflected as increases in the space charge width [Eq. (3)]. One should then expect that the decrease in flow/yield stress brought about by application of an electric field would increase as the temperature decreases [Eq. (2)]. This is indeed the case found for polycrystalline MgO and ZrO_2 -3 mol % Y_2O_3 ceramics (Figure 2).

Initial studies on the influence of an electric field on the yield stress in compression of tetragonal zirconia ceramics containing 2 and 2.5 mol % yttria with grain sizes of 350 to 400 nm were conducted at 1200°C to determine a lower temperature limit for such effects. At 1200°C, the electric field effects apparently are much more sensitive to strain rates as analysis of the results indicated the field effects increase with decrease in strain rates. Analysis of the data reveals the stress exponent at 1200°C is ~ 4 in the zirconia with 2 and 2.5 mol % yttria. On the other hand at $\geq 1400^\circ C$ the stress exponent is 2 both for the zirconia containing 2 and 2.5 mol % yttria ceramics without an applied field and the zirconia-3 mol % yttria with an applied field. As a result, the field effect just begins to be indicated at strain rates of $10^{-4}/s$ at 1200°C, which is the limit of the test facility available for the field effect tests. Studies are now under way to examine the effects of the electric field on the yield stress of the zirconia with 2 and 2.5 mol % yttria at 1450°C. This will allow us to test the effects of solute content on the predicted space

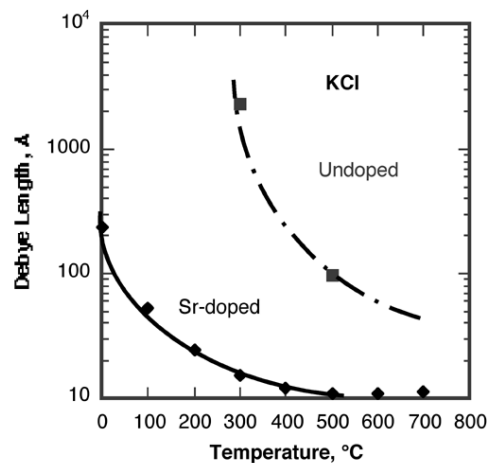


Figure 1. The Debye length is predicted to increase as either the temperature or the solute content decrease as shown for the case of potassium chloride.¹²

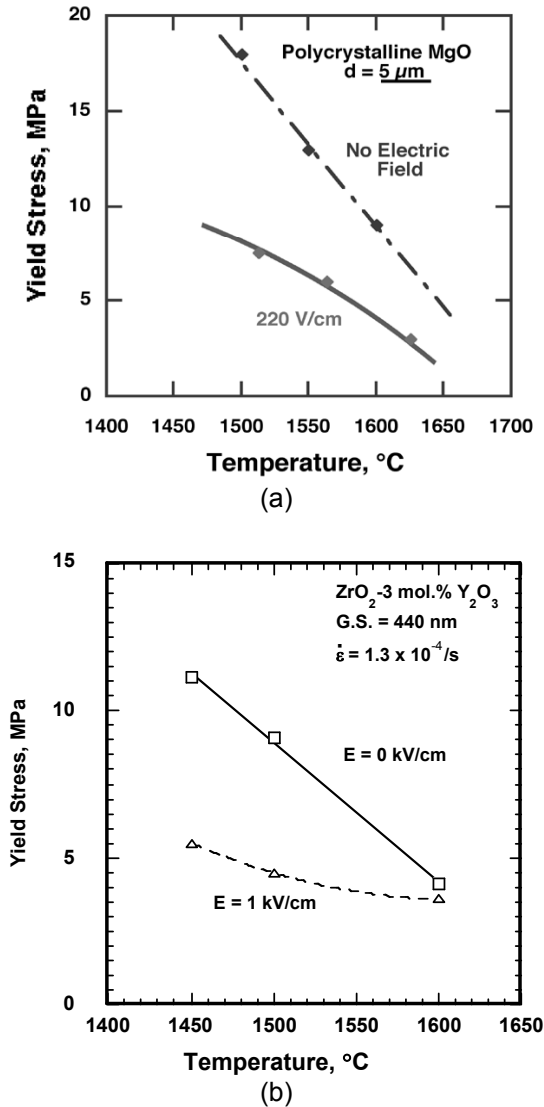


Figure 2. The effectiveness of the application of a dc electric field in decreasing the tensile yield stress increases as the temperature in the range of 1650°C to 1450°C in the case of both cubic magnesia (a)¹⁴ and cubic zirconia containing 3 mol % yttria¹⁵ (b) ceramics.

charge zone size and the role of the space charge zone on the yield behavior.

Conclusions

The fabrication of powder compacts was expanded to include granulation technology, which can readily produce larger samples and more complex geometries. The recent sintering studies of granulated compacts were sintered to >92% of theoretical density and exhibited grain sizes of 6 to

140 nm. However, these bodies contained mainly monoclinic phase, which was attributed to a loss of yttria during powder synthesis. This is now being addressed in the Pennsylvania State University task.

Electric field effects on deformation were observed to exhibit a temperature dependence that apparently is altered by the mechanism dictating the plastic flow. Above 1200°C, the reduction in yield stress increases with decrease in temperature. At 1200°C, the field effect becomes more sensitive to the strain rate, which suggests a shift from grain boundary sliding to a dislocation-related process.

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