Oxide Nanocomposites for MEMS Applications

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Abstract – Ceramics offer superior mechanical and chemical properties over the current materials implemented for microelectromechanical systems (MEMS) device fabrication. In spite of this, ceramics robustness must be greatly improved to overcome its anemic fracture toughness. In recent years, nanocomposites have been studied as a means to achieve high fracture toughness values in the realm of ceramic materials, and have been met with some success. However, numerous processing issues must be dealt with when working with nanoscale materials, specifically agglomeration, metastable phase transformations, and grain coarsening. High energy milling and reaction sintering of γ-Al_2O_3 and ZnO (to form $ZnAl_2O_4$) nanopowders were investigated as techniques to alleviate the aforementioned issues. In comparison with as-received γ-Al_2O_3 nanopowder, a 27% increase in theoretical density and conservation of nanoscaled features were obtained when mixed and milled processed γ-Al_2O_3 and ZnO nanopowders were sintered at a heating rate of 15 ^{o}C/min for 1 hr at 1350 ^{o}C.

Introduction

Failure of microelectromechanical systems (MEMS) devices fabricated out of either silicon or metal inevitably involves friction-related component wear and seizure. Furthermore, these materials cannot be easily used for high-temperature applications. Ceramic components could alleviate the friction and temperature problems associated with current MEMS devices, but the inherently brittle nature of most ceramics makes such approaches challenging. Therefore, the fracture toughness of ceramic materials must be improved to render them as a potential material for MEMS fabrication.

Significant increases in ceramic fracture toughness values have been reported through the use of composite processing with nanoscale features – nanocomposites. To date, there have been a number of promising examples of increased fracture toughness with ceramic nanocomposites in comparison to their micro-counterparts through the exploitation of nanoscale features. Mishra et al. [1] reported fracture toughness values in excess of 23 MPa $m^{-1/2}$ for Zr_2O_4-Al_2O_3 nanocomposites, and 14 MPa $m^{-1/2}$ for nanocrystalline TiO_2. Our approach to fabricate a tough ceramic material involves the reaction sintering of ZnO and Al_2O_3 nanoparticles to form a $ZnO/ZnAl_2O_4$ (spinel)/Al_2O_3 nanocomposite. Controlling the spatial extent of the solid-state reaction producing the spinel interphase is the approach to accessing the composite toughening behavior; also, manipulating, via point-defect segregation, the structure and composition of the two composite phase boundaries (i.e., $ZnO/ZnAl_2O_4$ and $ZnAl_2O_4/Al_2O_3$) is an approach to "tune" the frictional response. However, before a tough $ZnO/ZnAl_2O_4/Al_2O_3$ nanocomposite can be fabricated the well-documented problems in sintering nanopowders must be dealt with.

Few ceramic materials, in spite of their mechanical and chemical advantages, are available for MEMS fabrication. The lack in bulk production of nanocomposite materials is due in part to the difficulties associated with fabricating a quality, fully dense material. In general, sintering nanopowders of the reactant species is the main technique implemented for nanocomposite fabrication. However there are major problems connected with the preparation and sintering of nanoparticles that need to be managed and controlled. These tribulations range from deficient green

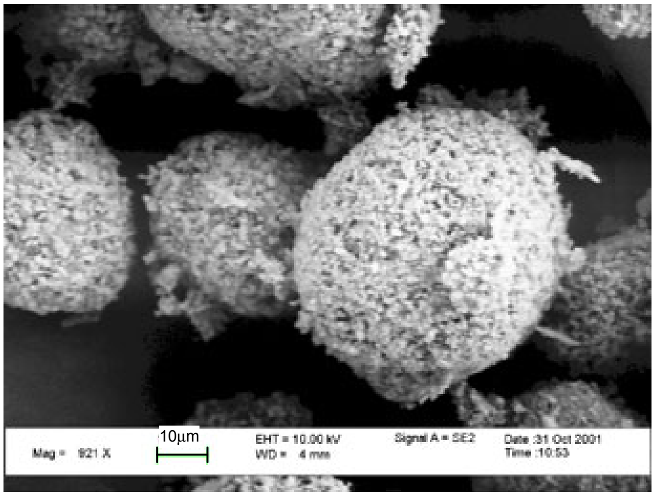

Figure 1. SEM image of agglomerated 100 nm γ-Al_2O_3 nanoparticles

densities (density achieved in presintered powder compact), which stems from particle agglomeration (Figure 1), to innate contamination, metastable phase transformations, and grain coarsening [2]. Therefore many processing issues need to be dealt with when synthesizing composite materials on the nanoscale.

A number of studies have focused on various approaches that may be implemented to enhance the fabrication of nanocomposites, which may ultimately lead to optimized mechanical properties. Materials with an initially high green density tend to exhibit relatively high final densities after sintering. This may be due to the decreased amount of initial porosity in the system, which leads to an increase in the amount of particle-to-particle contacts. Unlike micron sized powders, high green densities are difficult to obtain with nanoparticles due to interparticle adhesion and increased dominance of interparticle friction. The effects of interparticle friction are important at the nanoscale because of the high surface area to volume ratio. Green densities of compacts pressed from nanoparticles of alumina often do not reach more than 60% theoretical density when pressed at room temperature and pressures less than 1GPa [3]. Lin and De Jonghe [4] have achieved 60% relative green densities of 180 nm α-Al_2O_3 particles via cold isostatic pressing under a pressure of ~1.28 GPa.

In addition, controlling phase transformation kinetics during sintering is a key factor for obtaining relatively high dense nanocomposites – as this is the case for sintering nanoparticles of alumina. γ-Al_2O_3 is the metastable polymorph making up nanoparticles of alumina. The thermodynamically stable alumina phase at common sintering temperatures, however, is the hexagonal form α-Al_2O_3. It has been found that if proper pretreatments to γ-Al_2O_3 nanopowders are not taken before sintering that full theoretical densities are almost impossible to achieve, due to the formation of a vermicular structure [1,5]. Control of the $\gamma \rightarrow \alpha$ phase transformation is critical for sintering to high relative densities. It has been established that enhanced sintering kinetics are achieved with mechanically treated, ball milled, γ-Al_2O_3 powders [6].

Experimental Procedure

In the present study γ-Al_2O_3 and ZnO nanopowders were used to examine the effect that high-energy milling, dispersants, and two phase mixtures have on the theoretical density and final grain size achieved after sintering. The nanopowders used in this study are NanoTek® Aluminum Oxide, 99.5+%, which is γ-Al_2O_3, and NanoTek® Zinc Oxide, 99+%, produced by Nanophase Technologies Corporation. The nanoparticles' size range is between 50 to 200 nm. The γ-Al_2O_3 particles are roughly estimated as spherical shaped; the ZnO particles have an aspect ratio of roughly 3:1, as seen in Figure 2.

Five sample types were used in this study as seen in Table 1. Sample A was the as-received γ-Al_2O_3 with no processing prior to sintering – a standard for comparison with the processed powders. Samples B and C were γ-Al_2O_3 and a 2:1 molar ratio of γ-Al_2O_3 and ZnO, respectively, made into low-solids-content mixtures with the organic dispersant

Table 1. Percent theoretical density

Sample	Processing	Phases	% ρ_{th}
A	As-received	Al_2O_3	57
B	Shatterbox w/ 2,MOE	Al_2O_3	63
C		Al_2O_3 / $ZnAl_2O_4$	65
D	Shatterbox dry	Al_2O_3	84
E		Al_2O_3 / $ZnAl_2O_4$	83

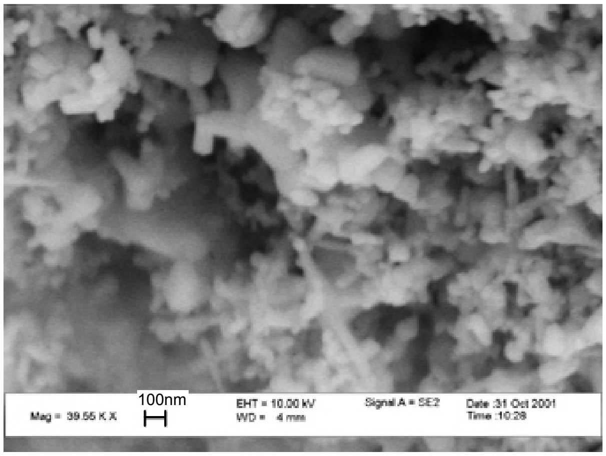

Figure 2. SEM image of as-received NanoTek® ZnO with an aspect ratio of ~3:1.

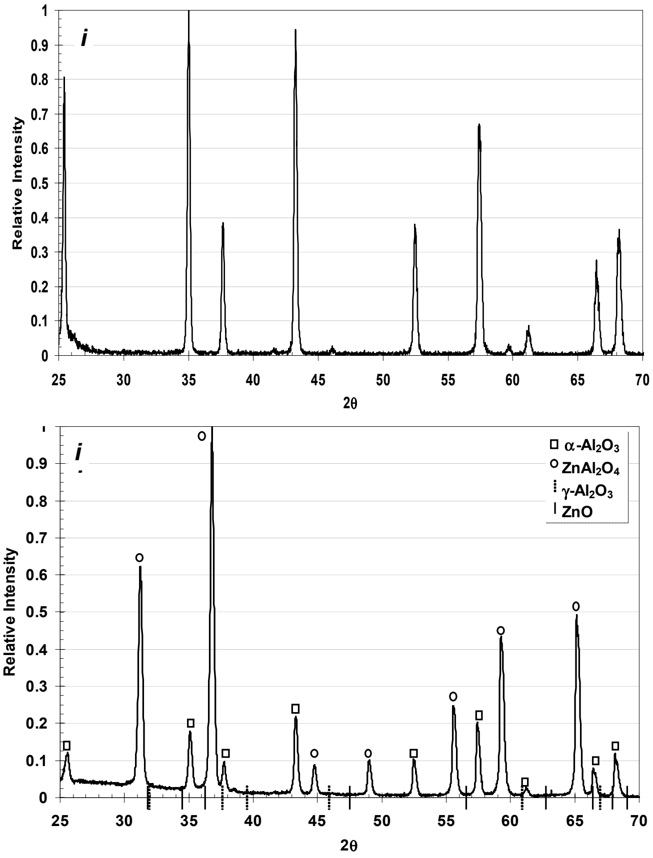

Figure 3. X-ray diffraction pattern of sintered samples (15 °C/min, 1000 °C – 1 hr, 1350 °C – 1 hr) (*i*) sample A, and (*ii*) sample E.

2,methoxyethanol (2,MOE), subsequently subject to 10 min of high-energy milling ("Shatterbox", SPEX Industries, employing alumina media). After milling, samples B and C were heated on a hot plate to boil off all 2,MOE, leaving a dry powder behind. Samples D and E were γ-Al_2O_3 and a 2:1 molar ratio of γ-Al_2O_3 and ZnO, respectively, milled dry in the Shatterbox for 10 min. After the pretreatments, multiple cylindrical samples 6.35 mm in diameter and 1-2 mm in height, of each powder type, were uniaxially cold pressed to a pressure of 200 MPa. Then the pressed samples were placed on coarse $MgAl_2O_4$ powder and sintered in a vacuum tube furnace for an hour at 1000 ^{o}C, to ensure a complete $\gamma \rightarrow \alpha$ alumina phase transformation, and subsequently for an additional hour at 1350 ^{o}C for densification. The furnace pressure was nominally 10 Pa; a heating rate 15 ^{o}C/min was employed throughout the experiment.

Results and Discussion

The sintered samples were analyzed via powder x-ray diffraction (XRD) to observe the phases present after sintering. Figure 3*i* is an XRD scan of sample A and representative of samples B and D, which is indicative of 100% α-Al_2O_3. Figure 3*i* is an XRD scan of sample E and also representative of sample C, which is indicative of α-Al_2O_3 and $ZnAl_2O_4$. The absence of ZnO, whose 2θ positions are labeled as solid lines on the 2θ axis in Figure 3(*i*), in samples C and E indicates that full reaction took place between all the ZnO and half of the Al_2O_3. Therefore, from the reaction equation,

$$Al_2O_3 + ZnO \rightarrow ZnAl_2O_4, \qquad (1)$$

the resulting material is an equimolar ratio of α–Al_2O_3 and $ZnAl_2O_4$.

The samples that were fabricated from powders ground in the Shatterbox with and without 2,MOE before sintering exhibited increased densities relative to their respective theoretical densities over the as-received alumina powder (for reference, the theoretical densities of pure α-Al_2O_3 and 1:1 α-$Al_2O_3/ZnAl_2O_4$ are 3.98 and 4.30, respectively). The theoretical densities of samples B, 65%, and C, 63%, were comparable and about 7% greater than that reached in the control sample A, 57%. The theoretical densities of samples D, 84%, and E, 83%, which were dry milled in the shatter box, exhibited theoretical density 27% greater than the control. The dry milled samples may have a greater theoretical density due to increased mechanical deformation (increased effectiveness of agglomerate elimination) over the samples ground with 2-MOE, which may have acted as a lubricant during grinding.

Samples D and E have comparable theoretical densities however the composite sample, E, retained its nanoscale features, as seen in Figures 4*ii* and 4*iii*. Sample D experienced extensive grain growth during sintering, reaching a final grain size of about 1 μm (Figure 4*i*). The nanoscale features retained in sample E had a bimodal size distribution of distinctly different grain sizes, 400 – 600 nm and ~100 nm. Tzing and Tuan [7] observed the same Al_2O_3 and $ZnAl_2O_4$ grain growth restriction on the micron scale, and also a significant fracture strength increase from 241 MPa for monolithic Al_2O_3 to 377 MPa for an $Al_2O_3/ZnAl_2O_4$ composite with parallel processing. The phase of each grain

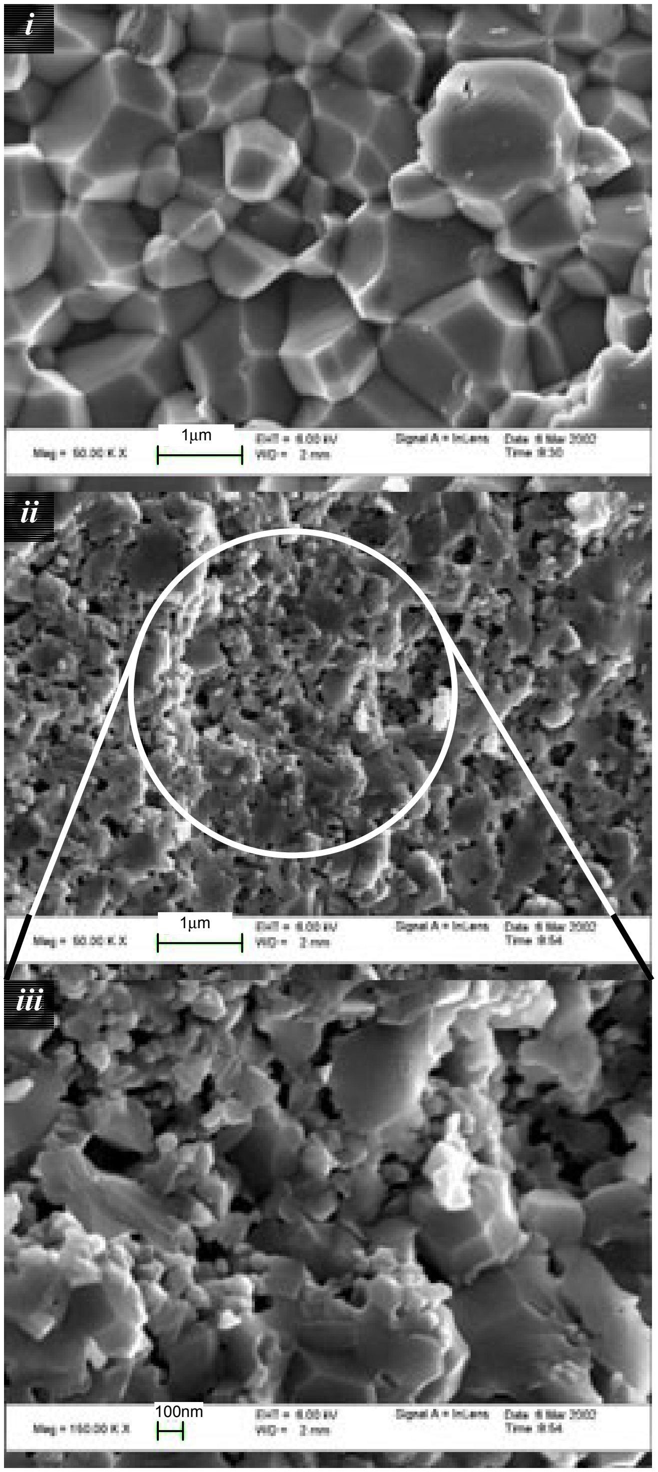

Figure 4. SEM images of samples D (*i*), and E (*ii* & *iii*), which were subjected to dry grinding in the shatter box (sintering parameters: 15^{o}C/min, 1000^{o}C – 1 hr, 1350^{o}C – 1hr). Notice sample D's extended grain growth and the retainment of nanoscale features in sample E, due to its duplex phase structure.

size class in the nanocomposite has yet to be determined; however initial indications are that the larger grains are α-Al_2O_3 and the 100 nm grains are $ZnAl_2O_4$.

Summary

The present study has established that high-energy milling of nanopowders prior to sintering is a practical method in achieving a relatively dense α-Al_2O_3/$ZnAl_2O_4$ nanocomposite, resistant to grain growth. The enhanced sintering kinetics caused by the milling may be attributed to a number of effects such as deagglomeration of clustered nanopowders and/or the optimization of the Al_2O_3 $\gamma \rightarrow \alpha$ phase transformation. Supplementary research must be done to determine the mechanism(s) for increased sinterablility, and the sintering conditions needed to obtain a denser nanocomposite, >98% theoretical density. In addition, the nanocomposite's fracture toughness must be also tested and controlled by the fine tuning of its nanostructure. These results are encouraging, indeed, in the development work required to make viable ceramic components for MEMS devices.

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