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13. ABSTRACT (Maximum 200 words)

Alumina based ceramic nanocomposites were investigated with the objective of improving fracture toughness. Specific focus during processing was directed at the retention of nanocrystalline microstructures in the matrix of the composites while still achieving full density. Second phases were added to the alumina matrix to investigate the applicability of toughening mechanisms that have been developed earlier for microcrystalline ceramics.

The use of spark plasma sintering technique allowed the retention of ultrafine grain size of alumina due to lowered sintering temperatures and shorter sintering times. Very attractive improvements in fracture toughness were noted in Al2O3/Nb, Al2O3/carbon nanotube, Al2O3/SiC whisker, and Al2O3/Nb/carbon nanotube composites. The results were analyzed in the context of effective toughening mechanisms in these nanocrystalline matrices.

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FUNDAMENTAL INVESTIGATION ON PROCESSING OF HIGH PERFORMANCE COVALENT CERAMIC NANOCOMPOSITES BY POLYMER PRECURSOR PYROLYSIS

FINAL PROGRESS REPORT

ARO GRANT #DAAD19-00-1-0185

FOREWORD:

This is the Final Progress Report of the ARO Grant on improving the mechanical properties of ceramic nanocomposites. Ceramics have many attractive attributes, e.g., chemical inertness, abrasion, and erosion resistance, high temperature strength, etc. However, they all, in general, lack adequate values of fracture toughness.

In this investigation, we have succeeded in raising the fracture toughness of single-phase alumina by almost four or five times by taking advantage of ductile-phase toughening, fiber-toughening, transformation-toughening, and a combination of ductile-phase and fiber-toughening.

The results have been published in several peer-reviewed archival journals and have been presented in national and international conferences. The University of California has also filed five patent applications in the related subject areas.

STATEMENT OF THE PROBLEM STUDIED:

The goal of this project was to gain a fundamental understanding of the processing and properties of ceramic nanocomposites. Specific focus during processing was directed at the retention of nanocrystalline microstructures in the matrix of the composites while still achieving full density. Alumina was chosen as the base matrix material to obtain general understandings that might also be applicable to other ceramic systems. Second phases have been added to the nanocrystalline alumina matrix to investigate the applicability of toughening mechanisms that have been thoroughly developed in microcrystalline ceramics. The mechanisms of interest were ductile-phase toughening, fiber toughening, and transformation toughening.

One of the drawbacks of toughening conventional ceramics is the decrease in strength and hardness that typically accompany the introduction of second phases into the base material. Nanocrystalline matrix ceramic composites can overcome this obstacle through the balancing of the softening/weakening effect of the second phases through the increases in hardness and strength that accompany refinement of grain size into the nanoscale.

The materials systems investigated were as follows:

Ductile-phase toughening:
- -- Alumina-Niobium

Fiber toughening:
- -- Alumina-Silicon Carbide Whiskers
- -- Alumina-Carbon Nanotubes

Transformation toughening:
- -- Alumina-Zirconia
- -- Alumina-Barium Titanate
- -- Alumina-Neodymium Titanate

SUMMARY OF RESULTS:

MATERIAL PREPARATION & CONSOLIDATION

High-Energy Ball-Milling:

Mechanical attrition (high-energy ball-milling, HEBM) as a refinement technique has been widely used for preparation of nanocrystalline metallic materials. This method has now been applied to preparation of ceramic nanopowders. HEBM is known to be able to bring about a number of effects on oxides, which greatly enhances solid-state phase transformation. The effect of milling on the phase transformation and microstructural development can be postulated as follows. First, HEBM can lead to higher green density of the compacts due to pore collapse from the high compressive and shear stresses during the milling. Second, the high energetic level and highly localized internal energy distribution of the HEBM powder might provide additional nucleation energy to overcome the phase transformation barrier. The residual stress induced by HEBM is likely responsible for this broadening of the XRD peaks seen in Figure 1. All these effects along with the effect from electric-field-assisted-sintering, lead to the optimized condition for forming of nanocrystalline alumina nanocomposites.

Typical powder processing for the composites in this study included the as-received γ-Al_2O_3 nanopowder being first mechanically milled using HEBM (in a Spex 8000 mixer mill in a WC ball and vial) with one weight percent polyvinyl alcohol (PVA), a dry milling agent, to prevent severe powder agglomeration. Milling was followed by a vacuum heat treatment at 350°C for 3 hrs, for the removal of the PVA.

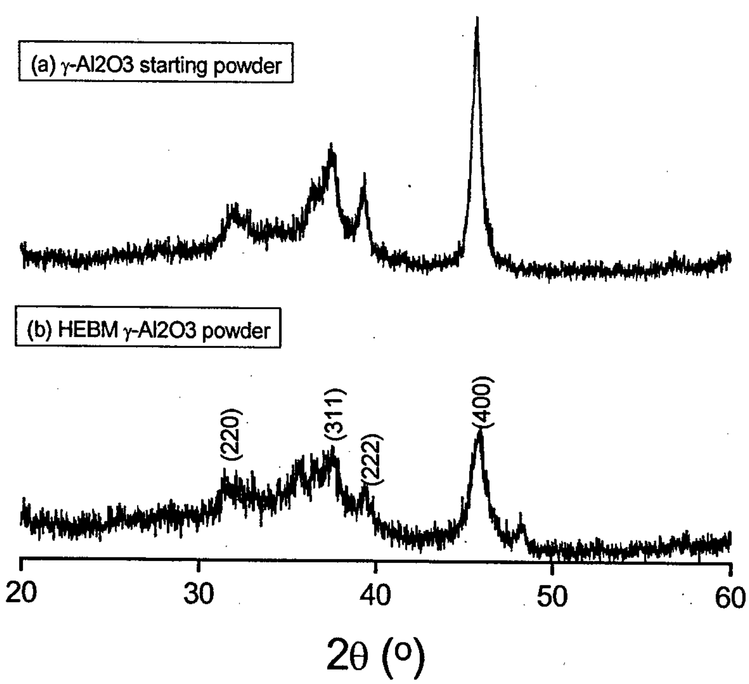

Figure 1. XRD profiles for (a) as-received γ-Al_2O_3 and (b) HEBM γ-Al_2O_3 nanopowders.

Spark Plasma Sintering:

One of the main difficulties to the sintering of nanocrystalline ceramics is the ability to retain a nano-scale grain size and still obtain full density. The advanced consolidation technique employed in the present study to overcome this hurdle is spark plasma sintering, SPS. It is a pressure-assisted sintering method based on the supposition of the presence of high temperature plasma (spark plasma) momentarily generated in the gaps between powder particles by electrical discharge during DC pulsing. SPS can rapidly consolidate powders to near theoretical density through the combined effects of rapid heating rate, pressure application, and electrical pulsing. In the present study, powder consolidation was carried out under vacuum in a Dr. Sinter 1050 SPS apparatus. The processing parameters used in the present study were as follows: an applied pressure of 80 MPa, an "On" pulse of 12 cycles of 2 ms each and the "Off" interval between pulses of 2 cycles, and maximum pulse parameters of 5000 A and 10 V. After applying the given pressure, samples were heated to 600 °C in 2 minutes and then ramped to their sintering temperature using heating rates ranging from 150 °C/min to 500 °C/min.

<u>*MATERIAL Parameters and the Resultant Properties*</u>

- Al_2O_3-10 vol.% Nb ductile phase toughened composite[i]:
  - ⇒ Using consolidation parameters of only 3 minutes and 1100 °C by SPS this material has been consolidated to full density.
  - ⇒ The alumina matrix grain size is ~200 nm and the niobium grain size is ~20 nm.
  - ⇒ This composite has a hardness of 22.5 GPa (slightly higher than pure alumina) and a fracture toughness of 7.0 $MPam^{1/2}$ (more than twice that of pure alumina).

- Al_2O_3-20 vol.% SiC_w fiber toughened composite[ii]:
  - ⇒ The consolidation of this composite dramatically demonstrates the effect of HEBM on sintering kinetics. In only 3 minutes at 1150 °C by SPS, HEBM powders were consolidated to 100% TD. Non-HEBM powders achieved only 80% TD under the same sintering conditions (100% TD required 1250 °C).
  - ⇒ The HEBM specimen also retained a finer alumina grain size, 146 nm.
  - ⇒ The resulting mechanical properties were a hardness of 26.4 GPa and a fracture toughness of 6.0 $MPam^{1/2}$.

- Al_2O_3-10 vol.% SWCN fiber toughened composite:
  - ⇒ The alumina-single walled carbon nanotube (SWCN) composite was consolidated to full density by wet ball-milling followed by SPS at 1150 °C for 3 minutes.

- ⇒ This material retained a hardness of 16.1 GPa while demonstrating a fracture toughness of 9.7 $MPam^{1/2}$.
- ⇒ Due to the electrically conducting nature of the SWCN the composite is 13 orders of magnitude more conductive than pure alumina, 1510 S/m.

➢ Al_2O_3-20 vol.% 3Y-TZP transformation toughened composite[iii]:
- ⇒ The HEBM powders for this composite were successfully consolidated to full density by SPS at 1100 °C for 3 minutes.
- ⇒ Grain growth in this composite was limited to such an extent that the consolidated grain size was only 96 nm.
- ⇒ This material also exhibited a remarkable fracture toughness of 8.9 $MPam^{1/2}$.

➢ Al_2O_3-5 vol.% Nb-5 vol.% SWCN synergistically toughened composite:
- ⇒ Using consolidation parameters of only 3 minutes and 1150 °C by SPS this material has been consolidated to full density.
- ⇒ This material retained a hardness of 13.8 GPa while demonstrating a fracture toughness of 14.2 $MPam^{1/2}$.

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Fundamental Investigation on Processing of High Performance Covalent Ceramic Nanocomposites by Polymer Precursor Pyrolysis
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