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In situ bend testing of niobium-reinforced alumina nanocomposites with and without single-walled carbon nanotubes

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Abstract

Alumina-based nanocomposites were fabricated and consolidated via spark plasma sintering. The effect of single-walled carbon nanotube (SWCNT) and niobium additions to nanocrystalline alumina was examined by in situ bend testing. The addition of 10 vol.% niobium to nanocrystalline alumina provided substantial improvement of fracture toughness (6.1 MPa $m^{1/2}$)—almost three times that of nanocrystalline alumina. Observation of cracks emanating from Vickers indents, as well as bend specimen fracture surfaces, reveal the operation of ductile phase toughening in the Nb–Al_2O_3 nanocomposites. Further addition of 5 vol.% SWCNTs to the 10 vol.%Nb–Al_2O_3 revealed a more porous structure and less impressive fracture toughness—having an indentation and bend fracture toughness of 2.9 MPa $m^{1/2}$ and 3.3 MPa $m^{1/2}$, respectively.
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Keywords: Spark plasma sintering (SPS); Al_2O_3; Nb; Nanocomposites; Carbon nanotubes; Fracture toughness

1. Introduction

Recently, controversy has grown over whether the addition of carbon nanotubes to nanocrystalline alumina (Al_2O_3) benefits the brittle ceramic's mechanical properties, specifically its fracture toughness [1–4]. However, it is clear that the addition of carbon nanotubes can add electrical and thermal conductivity to an otherwise insulating material. The carbon nanotubes that primarily exist at the grain boundaries of alumina provide an effective matrix of conducting pathways [5]. If the fracture toughness can be improved, ceramic matrix composites (CMCs) hold great promise for use in structural and load bearing applications. CMCs possess superior chemical inertness, higher hardness, and lower densities than metals and their alloys. Furthermore, CMCs with nanocrystalline matrices have superior strength and hardness properties over their microcrystalline counterparts. Unfortunately, the monolithic fracture toughness of the nanocrystalline ceramic matrices is significantly less than those in the microcrystalline regime. For example, microcrystalline alumina has an intrinsic fracture toughness of ~3.3 MPa $m^{1/2}$—as compared to about 2.3 MPa $m^{1/2}$ for nanocrystalline alumina [6].

The addition of ductile phases such as metals to ceramic matrices has been proven to be an effective toughening mechanism [7]. Energy is dissipated from the propagating crack through two different phenomena: crack blunting at the ductile particle and/or absorption of energy through the deformation of the ductile phase. Both phenomena relieve the stress field around the crack tip.

The addition of fibers to a brittle ceramic matrix can improve the fracture toughness by means of fiber bridging. Toughening is achieved when the fibers either shed load from the crack tip while remaining intact, debonding between the fiber and the matrix followed by fiber pullout, and/or fracture of the individual fibers followed by energy absorption through pullout of the broken fiber. Another toughening mechanism that is quite common in fiber-reinforced composites is crack deflection [8]. This occurs in situations in which the fiber is significantly stronger than the matrix and the fiber is favorably oriented as to allow for the crack propagation direction to proceed away from the axis of highest

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stress. Commonly, the crack deflects to a less efficient cleavage plane directed by the longitudinal direction of the fiber. This scenario leads to increased fracture energy through increased surface area and lower driving forces due to the reduced resolve normal stresses at the crack tip [9].

The present work examines the mechanical properties of nanocrystalline alumina reinforced with niobium with and without single-walled carbon nanotubes (SWCNTs). Mechanical bend testing conducted within an SEM, as well as indentation testing, was used to reveal the extent of ductile phase toughening produced by the addition of 10 vol.% niobium to nanocrystalline alumina. In addition, these same methods were used to study the nature and extent of failure mechanisms present when 5 vol.% SWCNTs was introduced to the Nb-Al_2O_3 system.

2. Experimental procedures

2.1. Powder processing of Nb/alumina and Nb/SWCNT/alumina nanocomposite powders

The following powders were mixed by hand prior to high-energy ball milling (HEBM): as-received alumina powder (α and γ phases, 45 nm, Baikowski International Corp.), the appropriate amount of 90 wt.% Nb (99.85% purity, 74 μm, Goodfellow)-10 wt.% Al (99.5% purity, 45 μm, Johnson Matthey Electronics) alloy to yield a 10 vol.%Nb/alumina composition, and 1 wt.% polyvinyl alcohol (PVA). Aluminum was added to reduce the surface oxide of the niobium particles and PVA was added to prevent severe powder agglomeration. This powder mixture was placed in a tungsten-carbide (WC) vial and HEBMed for 24 h using one WC ball. The composite powder was heat treated (at 350 °C for 3 h in vacuum) to remove the PVA before further processing was performed.

The Nb/alumina composite powder was ultrasonicated for 15 min in 500 ml of ethanol. The slurry was then added to a polypropylene bottle with 280 g (∼1/3 by volume) of zirconia ball media and wet-milled (130 rpm) for 24 h. For the composites containing carbon nanotubes, the appropriate amount of SWCNTs (∼90% purity, Carbon Nanotechnologies Inc., Texas) was weighed out. The SWCNTs were produced by the HiPco process and had diameters of 0.8–1.7 nm and length of up to 1 μm. During final minutes of the previously mentioned wet milling, 8 ml of Nanosperse (an organic surfactant made by NanoLab) was stirred into 150 ml of DI water. The SWCNTs were added to this solution and ultrasonicated for 5 min. The wet-milled slurry was slowly added to the dispersed carbon nanotube solution while ultrasonicating was added back into the polypropylene bottle and wet-milled for an additional 24 h.

In both cases, the Nb/alumina and Nb/SWCNT/alumina slurries were taken off the wet-mill, ball media separated, sieved through a 150 μm mesh, and placed into medium sized glass beaker. A magnetic stir bar was added and the slurry was dried on a stirring hotplate. Once dry, the agglomerates were broken up with a mortar and pestle and sieved through 150 μm mesh. In the case of the Nb/SWCNT/alumina powders, the dispersant was baked off at 450 °C for 4 h.

2.2. Spark plasma sintering (SPS)

Consolidation was performed under vacuum in the Dr. Sinter 1050 SPS machine. The following processing parameters were used: 105 MPa of applied pressure, and "on" pulse of 12 cycles of 2 ms each and a "off" interval between pulses of 2 cycles, a maximum pulse settings of 5000 A and 10 V, and a pressure of 105 MPa. An optical pyrometer was used to measure temperature and a heating rate of 125 K/min was used from room temperature to 600 °C. From 600 °C to the desired final set point (1200–1300 °C in this study), heating rates ranged from 150 K/min to 233 K/min. SPS consolidation yielded fully dense (98 + %TD) samples fit for microstructural characterization and mechanical testing. Density was determined via Archimedes method and consolidated samples had dimensions of 19 mm in diameter and 3–4 mm in thickness.

2.3. Mechanical testing and characterization

Samples were polished to 0.5 μm surface finish and cut into beams having dimensions of 3 mm × 4 mm × 19 mm. The beam samples were pre-notched using a diamond saw, followed by an automated razor blade with 1 um diamond paste to (a/W) ratio of 0.25–0.5. Sample preparation procedures were made in accordance with ASTM STP 1409 presented in reference [10]. The pre-notched beams were three-point bend tested within a Hitachi S-4300SE/N scanning electron microscope using a Gatan Microtest 2000 test assembly. Crack propagation was observed under a 0.55 μm/s loading rate and the breaking load was recorded. The following equations from ASTM Standard E399-90 were used to calculate the nanocomposites' fracture toughness [11]:

$$K_{\mathrm{Ic}} = P\frac{S}{(BW^{3/2})}F\left(\frac{a}{W}\right), \quad F\left(\frac{a}{W}\right) = 3\frac{\left(\frac{a}{W}\right)^{1/2}\left(1.99-\left(\frac{a}{W}\right)\left(1-\left(\frac{a}{W}\right)\right)\left(2.15-3.93\left(\frac{a}{W}\right)+2.7\left(\frac{a}{W}\right)^2\right)\right)}{\left(2\left(1+2\left(\frac{a}{W}\right)\right)\left(1-\left(\frac{a}{W}\right)\right)^{3/2}\right)}$$

where P is the breaking load, S the pin span (in this case 15 mm), B the width, W the height, and a is the notch depth. Fracture surfaces were analyzed in a FEI XL-30 SFEG Scanning electron microscope. For comparison, the fracture toughness of the nanocomposites was calculated using the indentation method using a standard Tukon microhardness tester using a diamond Vickers indenter and 2.28 kN load. A Buehler light microscope and ANALYSIS program was used to measure the cracks emitted from the indentations.

3. Results and discussion

Indents were measured and the hardness and fracture toughness averaged over 10 valid indents. Results from all materials tested are given in Table 1. For comparison, a pure alumina sample (slightly larger grain size of 1.4 μm) was fabricated and tested using identical procedures for a base line comparison. The three-point bend setup is accurate in that it predicted about