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Short communication

Evaluation of a dry ball-milling technique as a method for mixing boron carbide and carbon nanotube powders

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Abstract

To evaluate the mixing effectiveness of dry ball-milling, multi-walled carbon nanotubes were ball-milled with boron carbide powder, and the resulting mixtures were hot pressed to consolidated tiles. Density, hardness, Young's modulus, and fracture strength of the tiles were measured; all decreased with increasing nanotube content. Microscopic examination revealed that the nanotubes were present in the tiles as micron-sized-and-larger agglomerates. It is concluded that the degree of dispersion of the nanotubes achieved by dry ball-milling was not sufficient to achieve mixing and bonding between the nanotubes and the boron carbide particles.

Keywords: A. Mixing; B. Composites; D. Carbides

1. Introduction

The emergence of carbon nanotubes (CNTs), as well as their microscale mechanical properties, has generated interest in forming composites incorporating the tubes. Because of the prospects for an increase in mechanical toughness, this interest extends to structural ceramics [1–8]. Given the similarities in chemical bonding, boron carbide is a logical choice for a composite with carbon nanotubes. Moreover, the demonstrated growth of nanometer-sized particles of boron carbide on CNTs [9] is evidence of the potential making strongly bonded composites of the two materials.

A challenge to be overcome in fabricating composites will be intimate blending of the nanotubes with ceramic powder. This is expected to be necssary to achieve good bonding. In a study of dispersion and mixing processes, microscopic examination showed that common approaches to dispersion and mixing of powders, such as dry or wet ball-milling, did not result in a good dispersion or mix [10]. To establish a clear correlation between the microscopic evaluation of the dispersion and the mechanical behavior of the resulting composite, we undertook to apply the most effective apparent dispersion and mixing method, dry ball-milling [10], and use it to synthesize composite materials. Evaluation of the mechanical properties of the composites against boron carbide processed in an identical manner allows the effect of adding the nanotubes to be quantified. Microscopic examination of the materials correlates the mixing seen in the micrographs of the blended material with the distribution of the tubes observed in the composite.

2. Experimental procedures

Powder composed of multi-walled carbon nanotubes was mixed with boron carbide (HC Starck, Grade HS). As a sintering aid, one weight percent (1 wt.%) 100 m^2/g alumina (Johnson Matthey, stock #10459) was added to all batches. The powder mixtures were loaded in a Nalgene bottle into which alumina milling media were added. A typical powder charge was 250 g in a 1000-cc bottle, with 5 pieces of 5-g

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Table 1
Carbon-nanotube content and Archimedes-method density values for consolidated tiles

CNT content (wt.%)	Density (kg/m^3)	Density (% theoretical)	Young's modulus (GPa)	$VHN_{1000 \times g}$ (GPa)
0	2510	99.6	435.9	28.17
1	2350	93.2	348.7	23.73
5	2270	90.5	295.2	21.62

media. The bottle was then mounted in a Turbula Type T2C shaker mixer, and agitated for 10 h.

The resulting powder batches were loaded into graphite dies lined with graphite foil. The nanotube content of each batch is enumerated in the first column of Table 1. A Thermal Technology model GRP 2400 hot press was used to consolidate the powders at 1900 °C, under 21 MPa pressure, for 1 h.

Densities of the hot-pressed tiles were determined using the Archimedes method, with water as the displaced fluid. Theoretical density of the tiles was calculated taking the density of the carbon nanotubes to be that of graphite, 2.25 g/cc [1,2].

Tiles were cut into type B (45 mm × 4.0 mm × 3.0 mm) flexure specimens by Bomas Machine Specialties Incorporated of Somerville, MA, in accordance with ASTM C1161. The 1-wt.%-CNT tile yielded 24 specimens; the 0- and 5-wt.%-CNT tiles each yielded 36.

Young's modulus of the flexure bars was determined in accordance with ASTM C1259-98, using a Grindosonic MK5 system. Hardness was measured with a Wilson Tukon B240, using a Vickers indenter and 1000-g load. Flexure strength of each bar was measured in 4-point bending, in accordance with ASTM C 1161, using an Instron Model 1123 with a 5000-N load cell and Series IX software version 8.13.00.

The tiles, as well as the surfaces of selected flexure bars, were photographed with a Nikon DXM 1200 digital camera. Scanning electron microscopy was conducted with a Hitachi S4700.

3. Results

All three powder batches were consolidated to densities of at least 90% of the theoretical value for the powder, as illustrated in Table 1. Table 1 also includes values for Young's modulus and Vickers hardness, both of which can be seen to decrease with increasing carbon nanotube content.

Fig. 1 illustrates the surface appearance typical of the flexure bars of each batch. The actual dimensions of the sections are 4 mm × 45 mm. Dark surface features appear in the samples into which the nanotube powder was introduced, and their areal density increases with increasing nanotube content. Fig. 2 exhibits scanning secondary electron micrographs of the 5-wt.%-CNT bar, with the bottom figure being a 15,000× study of one of the dark spots on the bar

Fig. 1. Photographs of sections from tiles with no added nanotubes (top), 1 wt.% nanotubes (middle), and 5 wt.% nanotubes (bottom).

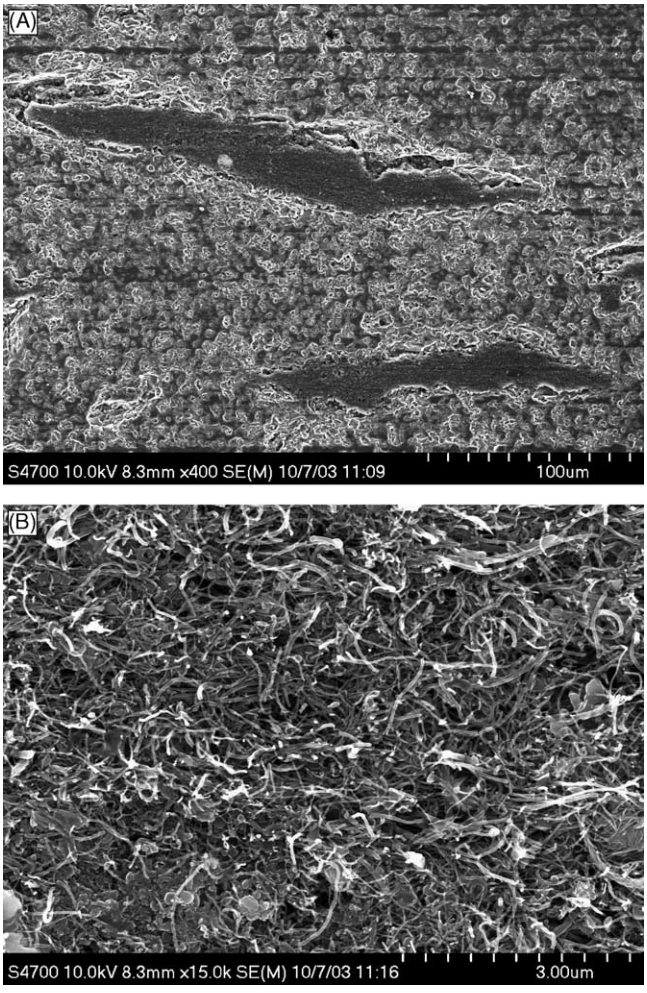

Fig. 2. Scanning electron photomicrographs of the dark spots visible in the 5-wt.%-CNT tile. Photos were taken at 400× (A), and 15,000× (B). Note the tangle of submicron features in the 15,000× image.

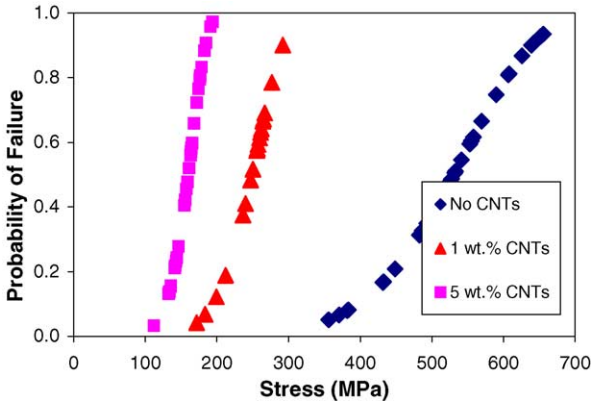

Fig. 3. Failure probability plots for bend bars cut from each tile, determined using the Weibull distribution function.

surface. Rather than being dispersed throughout the structure, the nanotubes are agglomerated into regions with dimensions as large as 100 μm.

Fig. 3 presents the results of the flexure strength measurements after analysis using the Weibull distribution function. The probability of failure at a given stress increased with increasing carbon nanotube content. Also, the Weibull modulus, as indicated by the increase in slope with increasing nanotube content, increased.

Fig. 4 exhibits an SEM examination of the carbon nanotube powder at low and high magnifications. The low-magnification study clearly shows a particle 50–100 μm in size. The high-magnification study of the particle clearly shows that it is composed of carbon nanotubes. Note the apparent high degree of agglomeration of the tubes.

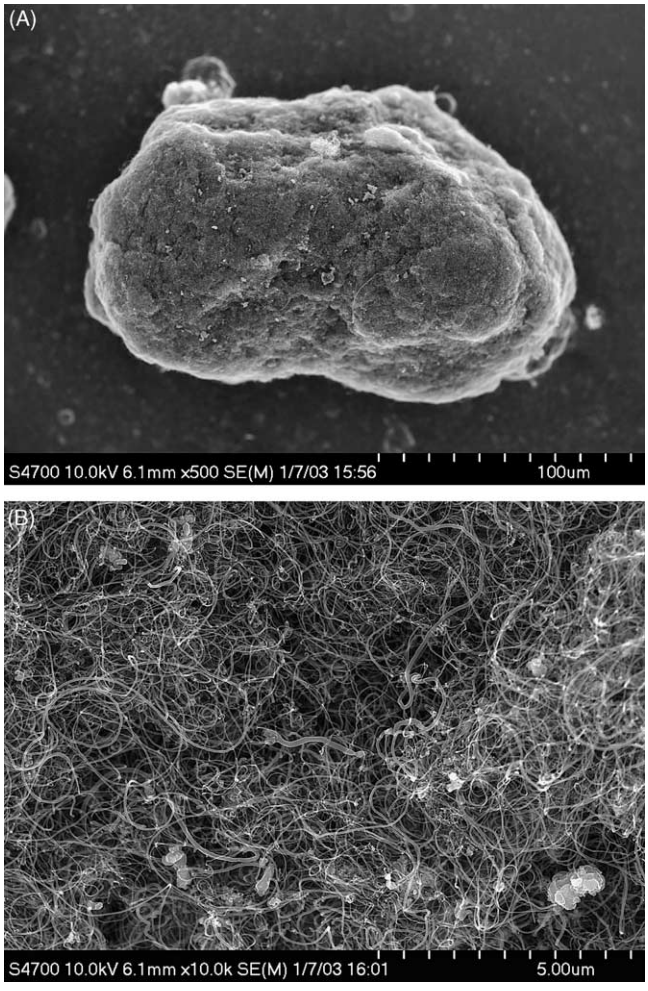

Fig. 4. Scanning electron photomicrographs of as-received carbon nanotubes.

4. Discussion and conclusion

Decreases in density, hardness, Young's modulus, and fracture strength with increasing carbon nanotube content are all consistent with the nanotubes not having been dispersed and well-mixed with the boron carbide powder, and therefore not having been well-bonded to the boron carbide. Microscopic examination provides direct evidence that the nanotubes are incorporated into the tiles in micron-sized agglomerates. The dry-blending procedure under evaluation here did not provide sufficient dispersion of the nanotubes, or mixing of the nanotubes and the boron carbide, for load to be transferred to the nanotubes in the composite.

Moreover, microscopic examination revealed that the nanotubes of the starting powder are agglomerated into particles with dimensions as large as 100 μm. The size of the starting agglomerates differed very little from the agglomerates of nanotubes observed in the composites. It is clear that, whatever the efficacy of the ball milling procedure in forcing small particles of boron carbide into the agglomerates, it is ineffective in dispersing the agglomerates. Given the surface forces to be overcome in disentangling agglomerated nanotubes, it is unlikely that dry procedures will work.

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