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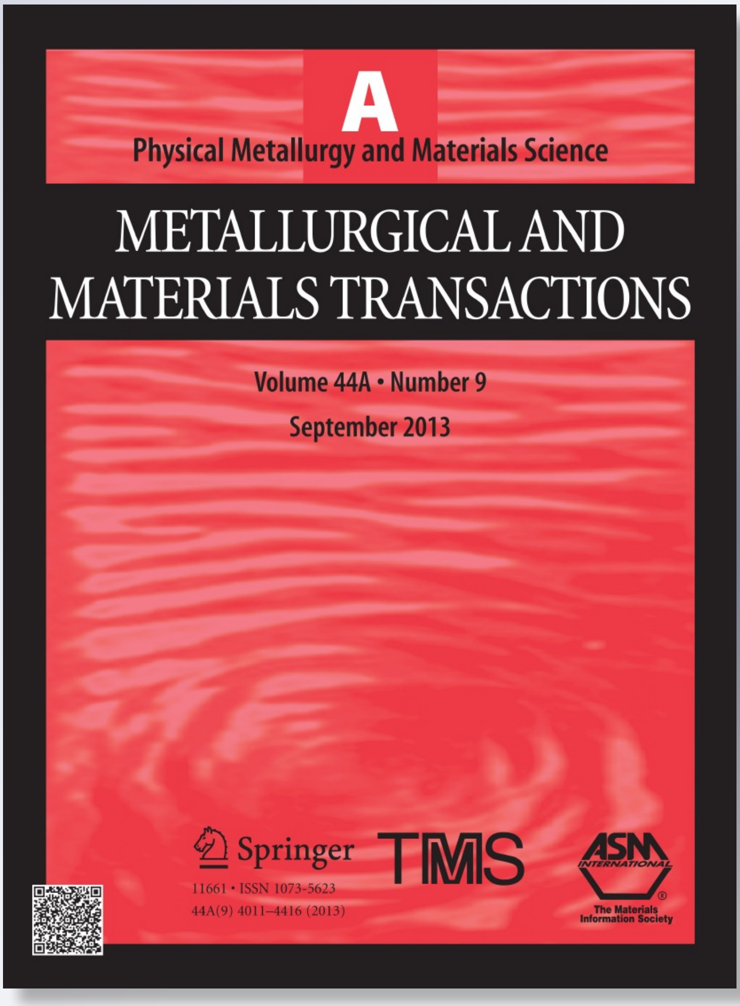

Fabrication of Dense ZrO_2/CNT Composites: Influence of Bead-Milling Treatment

GUSTAVO SUÁREZ, BYUNG-KOOG JANG, ESTEBAN F. AGLIETTI,
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Highly concentrated zirconia-carbon nanotube (CNT) water suspensions were prepared using an advanced milling technique. The bead-milling operation parameters were optimized for this system and used to prepare zirconia-stabilized water-based suspensions with different CNT contents. The effects of different milling conditions were studied. The particle dispersion was evaluated by SEM observations on dried suspension. Green's density and SEM observations of compacts were used to follow the colloidal dispersability of the composites. Materials of tetragonal zirconia and CNTs were prepared with a high concentration of CNTs (1, 5, and 10 wt pct CNT). The homogeneous dispersion and distribution of the fibers in the bulk material after slip casting of the suspension were examined. The samples were sintered using spark plasma sintering (SPS) at 1473 K (1200 °C) and finally, fully dense materials were obtained. The mechanical properties were evaluated using the Vickers indentation technique.

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I. INTRODUCTION

THE first publications on carbon fibers appeared from 1889 to 1890.[1,2] In 1952, the concept of tubes was introduced by Radushkevich *et al.*[3] who observed the hollow structure of carbon formed by thermal decomposition. However, it was in 1991 that, through a report in *Nature* by Iijima,[4] carbon nanotubes (CNTs) were promoted as a new field of study, and since then their fields of application, as well as the number of reports concerning this material, have increased exponentially.

In the last decade, CNTs have attracted great interest especially of those researchers working with composite ceramics, and these materials are considered to be promising as reinforcing elements for structural composite materials because of their remarkable physical and mechanical properties.[5–7]

The use of CNT-reinforced ceramics has been drawing great interest because of the high mechanical, thermal, and electric properties of these fibers.[7] Owing to the small diameter, large aspect ratio, and surface characteristics of the nanotubes, it is difficult to obtain a good mixture of the two phases before the sintering process, especially while using aqueous suspensions. Some success has been achieved with conventional milling techniques, primarily with the use of low-to-moderate nanotube volume fractions.[8–11]

Previous reports on CNT-reinforced ceramics have shown conflicting results. Some of them present results with an increment in fracture toughness due to the incorporation of CNTs.[12–14] Some others found no improvements in their mechanical properties.[6,8,15]

Some researchers present the reinforcement mechanisms of the matrix as a result of the bridging and the pull-out effect[15,16] of the nanotubes on the fractures produced by indentation. Sun *et al.*[17] reported that the CNT agglomerates at grain boundaries, and weak bondings between CNTs and zirconia are responsible for the decrease in the hardness and lack of improvement in other properties.

At present, contradictory results are available in the literature regarding mechanical properties. One reason could be the use of different processing methods, and another, the differences in the measurements of the mechanical properties.

We present a processing route for homogeneous CNT dispersion in a zirconia matrix and show the full densification of the composite and Vickers hardness and fracture toughness values.

Several processing routes have been identified, and different sintering techniques have been used to prepare ceramic/CNT composites in the literature: direct mixing,[9] CNT coating ceramics,[18] or surface modification.[19] Peigney *et al.*[20,21] developed a technique to synthesize CNTs in situ to obtain CNT/metal oxide composite powder. In spite of the success achieved in some studies reporting improved mechanical or electric properties, some difficulties in dispersing CNTs homogeneously remain.[8,18,22] Until now, it has not been possible to prepare more than 6 wt pct of CNT loading in ceramic-CNT composites with no presence of agglomeration.[14,23–25]

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Water-based mixing of CNTs in composites dispersed with a polymer by a mechanical force, such as a shear-intensive force or ultrasonication,[26,27] is one of the most convenient techniques for dispersing CNTs in ceramic suspensions; however, it is unsatisfactory for moderate or high concentrations of nanotubes.

A dispersion technique called bead milling was previously used for complete deagglomeration of different ceramic systems, leading to an improved final product.[28–31]

In the current study, the bead-milling treatment was used to prepare fully dispersed and deagglomerated tetragonal zirconia suspensions containing high concentrations (up to 10 wt pct) of CNTs. The suspensions were slip-cast, and homogenously dispersed CNT-zirconia composites were obtained. Finally, SPS sintering was performed,[32] and high-density ceramic composites were obtained with a high CNT concentration.

The mechanical properties were also measured, and an analysis of the effect of the processing route was also conducted.

II. EXPERIMENTAL PROCEDURES

A. *Materials*

A commercial grade powder of 3 mol pct Y_2O_3-doped tetragonal ZrO_2 (3YTZ, Tosoh Co., Tokyo, Japan) with a mean particle size of 65 nm (BET surface area of 15.3 m^2/g) and commercial grade multiwall CNTs with a 2.1 g/cm^3 density were used. The physical characteristics of the material is shown in Table I.

Table I. Physical Characteristics of the CNTs

Fiber Diameter (nm)	150
Average Length (μm)	44 to 105
Aspect Ratio	10 to 500
True Density (g/cm^3)	2.1
Specific Area (m^2/g)	13.0

B. *Sample Preparation*

1. *Colloidal processing*

Aqueous suspensions were prepared with a total solid content of 10 vol pct (39.3 mass pct). The powders were dispersed by adding the ZrO_2 powder into distilled water containing 1.5 wt pct of the polyelectrolyte dispersant (polyammonium carboxylate, ALON A-6114, Toagosei Co., Tokyo, Japan).

The aqueous ceramic suspensions were dispersed in an ultrasonic stirrer (Nissei model USS-1) with 35W (Nihonseki Kaisha, Ltd., Japan) for 15 minutes. CNTs were added to the zirconia suspension to obtain 1, 5, and 10 wt pct (3, 13, and 24 vol pct, respectively). The obtained slurry was exposed to an ultrasonic homogenizer (Nissei 1200T) at a frequency of 19.6 kHz (Nihonseki Kaisha, Ltd., Japan) for 10 minutes to redisperse the agglomerated particles.[33]

For breaking heavy agglomerates present in the suspension, we used a bead-milling treatment (Ultra Apex Mill Type UAM-015, Kotobuki Industries Co., Ltd., Kure, Japan). This equipment requires ZrO_2 beads with diameters of 50, 30, or 15 μm at a speed of 4000 rpm, as described elsewhere.[29] The volume of the vessel was 320 cm^3 with a wall and stirring disks made of zirconia. To evaluate the dispersion of the suspension, SEM (JSM-840, JEOL, Tokyo, Japan) observations were conducted, and the particle size distribution was measured using a particle-size analyzer (UPA-UT151, 0.8 to 6500 nm *NANOTRAC*® equipment, Nikkiso, Japan).

The suspension obtained after 60 minutes of bead-milling was used for probe conformation as is explained below.

2. *Probe preparation*

The suspension after 60 minutes of bead-milling was outgassed in a desiccator to eliminate air bubbles and slip-cast in plaster molds with a Teflon film of 0.2 μm pore size, separating the slurry from the mold to avoid contamination. The slip-cast samples were slowly dried in air for 48 hours to avoid cracking and cold-isostatically pressed at 392 MPa. Finally, samples were dried at 383 K (110 °C) for 24 hours. The green density was determined by the Archimedes method in kerosene. The microstructure of the sintered bodies was observed by high-resolution scanning electron microscopy (SEM) on the fracture surface.

C. *Sintering and Characterization of the Sintered Samples*

Green samples were sintered in SPS at 1473 K (1200 °C) for 10 minutes under a pressure of 150 MPa. The samples were covered inside the die, top, and bottom, with carbon powder to avoid cracks due to the system geometry and sample resistance. The sintered density was measured by the Archimedes method in water. To calculate the sintered relative density, the following values were employed: for tetragonal zirconia, 6.059 g/cm^3, and for the CNTs, 2.1 g/cm^3. The microstructure of the sintered bodies was observed by high-resolution SEM on the fracture surface.

D. *Mechanical Properties*

Mechanical properties were measured for the different processing routes and different CNT concentrations.

Vickers hardness was measured by the indentation method at loads of 0.5 and 1 kg applied to the sample for 15 seconds. The fracture toughness was calculated by the indentation method at a load of 10 kg for 15 seconds using Vickers indentation and Shetty[34] equation hardness and fracture toughness.

III. RESULTS AND DISCUSSION

A. *Dispersion*

The use of high-energy milling, referred to as bead milling, is an effective technique for the full dispersion of ceramic suspensions.[29,30,35,36] To achieve an appropriate efficiency of this equipment, it is necessary to study the effect of different dispersion media and the final dispersion obtained. For this reason, it was necessary to test the effect of the bead size on the CNTs-ZrO_2 suspension.

Figure 1 shows the effect of the bead size on the average particle size of suspension containing ZrO_2 and CNTs. It is proper to recall that standard model for calculation of particle size distribution is designed for spherical particles. Therefore, only zirconia particles can be certainly measured. However, it is considered that agglomeration of any type can be observed by this technique and represented in the particle size distribution.

This figure proves that ultrasonication is insufficient to obtain a fully dispersed suspension. The initial particle size according to the specifications is 65 nm, and the average particle size shown in Figure 1 is near 180 nm, indicating a high rate of agglomeration. In addition, the CNT content does not seriously affect the final particle size with this treatment. Similar results were obtained for the three CNT concentrations.

After 60 minutes of milling, the particle size reduction shows the effectiveness of bead milling for dispersing the initial agglomeration. It is evident that the 50-micron beads generate the most dispersed suspension, reaching an average particle size ranging from 90 to 100 nm. These results agree with those obtained for the dispersion of pure zirconia suspensions.[30] As a result, the CNTs do not affect the dispersability of zirconia; in addition, the physical characteristics of the fibers do not affect the dispersion observed in the suspensions. The problem of using carbon fibers in composites is related to the heavy agglomeration that is formed mainly within the CNTs. These agglomerates could spontaneously segregate from the bulk of the suspension, and the composites obtained are not homogeneous as a result.

For a direct observation of the system, a drop of suspension was dried and observed by SEM. The dried suspension of slurry containing 1 wt pct of CNTs with and without bead milling using all three bead sizes was studied. As noted above, 50-micron beads were the most effective dispersion media for this system. Three micrographs with no treatment are equivalent. The agglomerates shown in Figure 2 represent the results obtained from the suspension with 10 wt pct of CNT materials, but similar results were observed for 1 and 5 wt pct. It can be seen CNT-CNT, CNT-ZrO_2, and ZrO_2-ZrO_2 aggregation couples, which are very difficult to redisperse. With the milling treatment, many of the agglomerates are broken, but the best results are obtained with 50-micron beads, as observed with the average particle size in Figure 1.

The suspension with 5 wt pct of CNTs also shows that 50-micron beads are the best dispersion media for the system and present the most homogeneous distribution of CNTs and ZrO_2.

In Figure 2, the suspension for 10 wt pct of CNTs can be observed and the results is similar with the one observed for 1 and 5 wt pct of nanotubes content. This concentration of fiber cannot be achieved in aqueous colloidal processing with homogenous and unagglomerated particles within an efficient dispersion process.

The micrograph of the suspension without bead milling shows heavy agglomeration of different kinds. This system leads to a suspension that easily flocculates, showing high segregation. A homogenous compact cannot be achieved from this kind of suspension.

Figure 2 show that the bead-milling treatment is effective in all cases for the dispersion and homogeneous distribution of fibers in the mixture; however, with 50-micron beads, good dispersion is achieved.

The good dispersion generates, in the three CNT concentrations, stable suspensions that can be slip-cast.

The bead-milling treatment induces high friction and impact between the zirconia beads and the suspension particles. No CNT shortening or damage was observed using beads of any size. The effect of the particle size reduction in Figure 1 is similar to that observed for pure zirconia samples in previous study.[29,30] The direct observation of the SEM micrograph shows no CNT reduction or shortening (Figure 2).

The high shear stress that is present in the milling due to the concentration of milling media and the fast

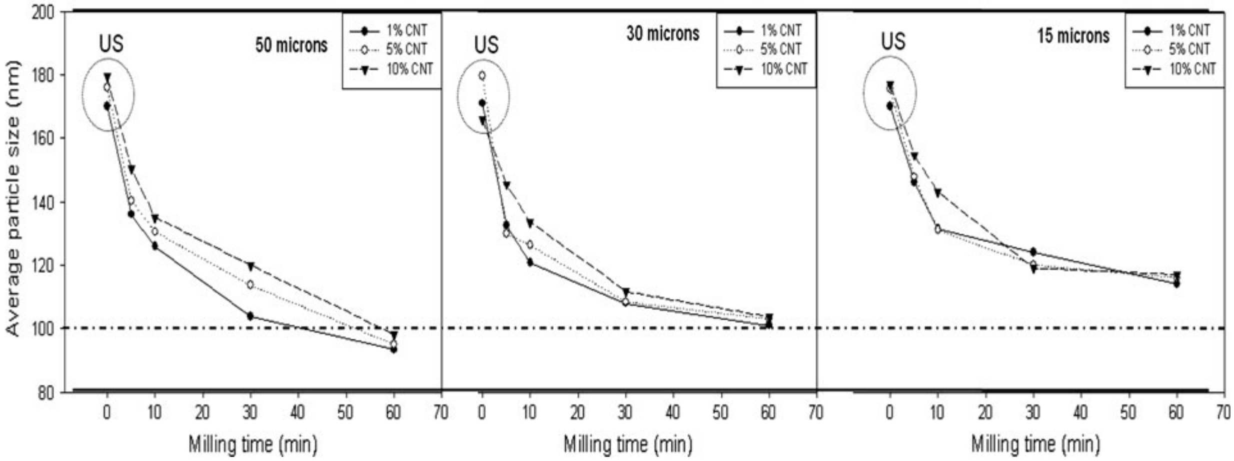

Fig. 1—Average particle size as a function of the milling time for three different sizes of beads (50, 30 and 15 μm) and various CNT contents. US: ultrasonic treatment.

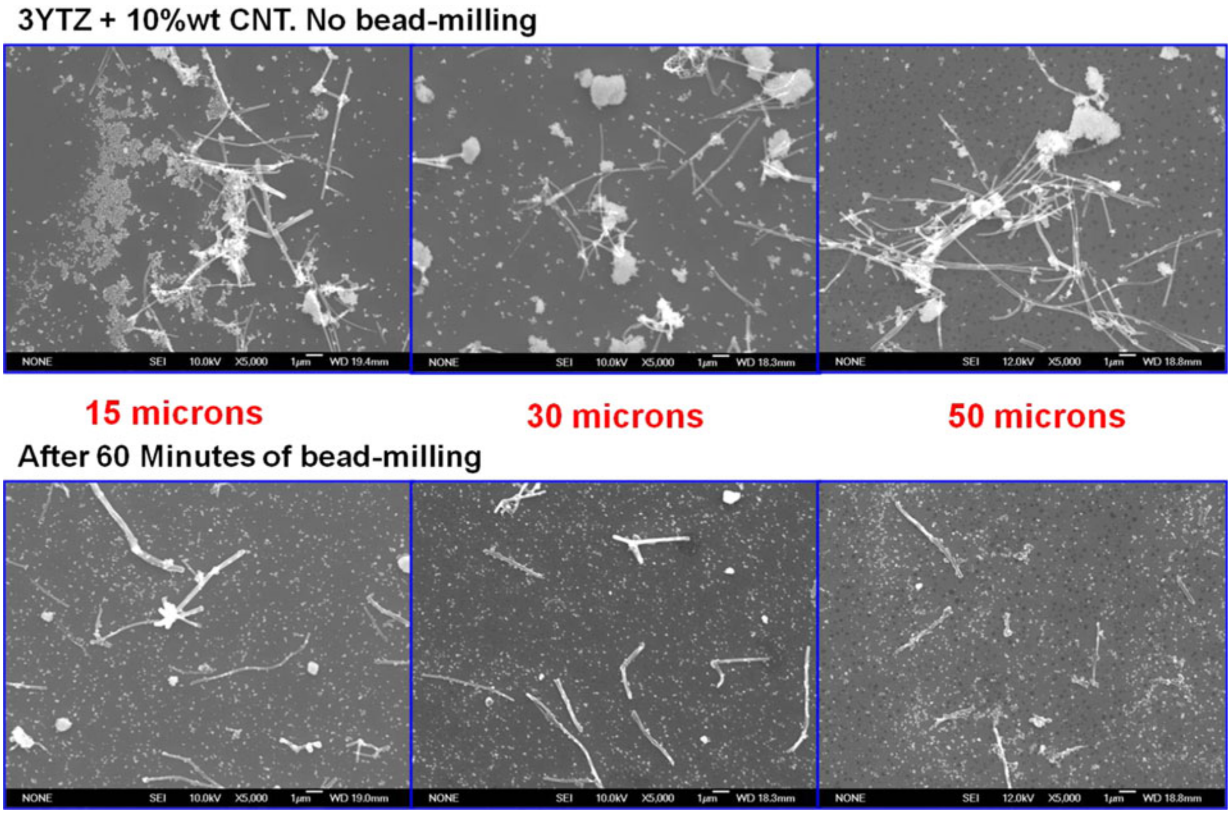

Fig. 2—SEM micrograph of a dried suspension containing tetragonal zirconia with 10 wt pct CNTs without bead milling and after 60 min of bead milling.

rotation of the milling generate highly dispersed suspensions by breaking the agglomeration present.

The different bead sizes generate two important effects on the particles in suspension: share stress and bead collision.

For small milling media (15 μm), the free interparticle space among beads is small, and the suspension has high shear stress and little energy due to bead collisions. For the 50-μm beads, the suspension creates more free space among the beads, reducing the shear stress in the milling media and high energy due to the heavier beads and the energy produced by their collision. These results presented in Figure 1 suggest that the effect of collision is most effective for particle dispersion than that of the share stress in this system. In addition, neither the share stress nor the bead collisions generate sufficient energy to produce CNT shortening.

B. *Green Samples*

The treated suspensions with different CNT contents were slip-cast in alumina molds with Teflon filter. Figure 3 shows the fracture surface microstructure of the green compacts obtained by slip casting. The micrographs showed that CNTs present a homogeneous distribution in the bulk compacts. No high-concentration area or segregation was observed in the bulk probe.

The green density was measured as a relative value to the theoretical ones, and the results are shown in Table II.

Table II shows that a better dispersion leads to a better packing system with high green density. The suspensions treated with 50-micron beads always showed a higher green density in accordance with the better dispersion observed in Figures 2 and 3.

The influence of CNT loading in the green density can also be observed (Table II). For higher fiber content, the green density becomes slightly smaller for the same bead size. Composites with higher concentration than 10 wt pct of CNTs in the ceramic matrix would be very difficult to obtain due to agglomerations.

C. *Sintering*

Zirconia-CNT composites were sintered using SPS with vacuum and pressure at 1473 K (1200 °C) for 10 minutes. SEM fracture surface micrographs of sintered samples with 1, 5, and 10 wt pct of CNTs treated with 50-micron beads are shown in Figure 4. Owing to the low contrast of the materials, it is difficult to observe the CNT distribution in the zirconia matrix. For this reason, the fibers are indicated with arrows.

In this way, it is possible to observe the homogeneous distribution of CNTs in the ceramic matrix. Even for a high concentration of CNTs, it is possible to see the homogeneous distribution of the fibers.

The combined effect of bead-milling deagglomeration and low-temperature sintering in SPS leads to the preservation of the integrity of the CNTs. Dense materials with a small grain size are obtained. It is

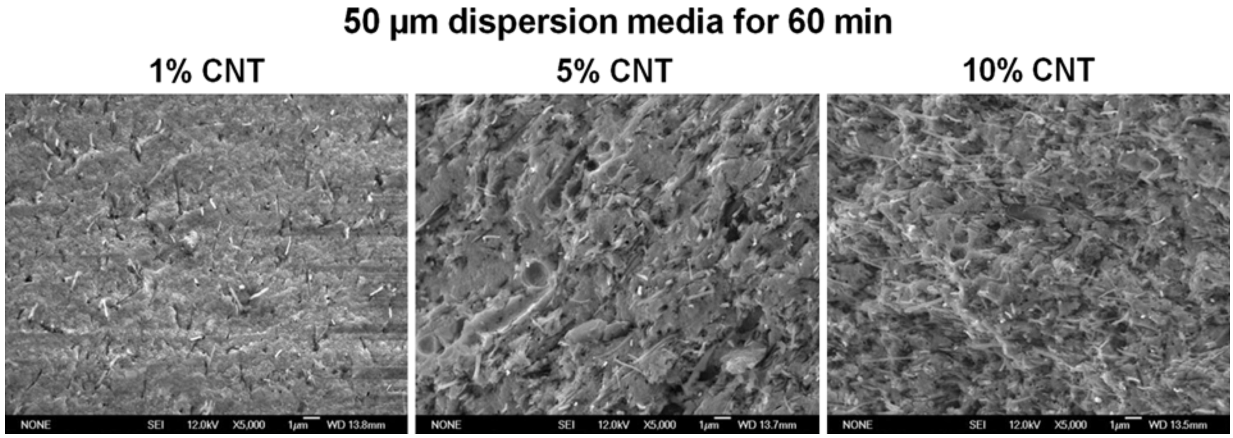

Fig. 3—SEM micrograph of green compacts formed by slip casting with three different CNT contents.

Table II. Density and Relative Density of Slip-Cast Green Samples Dispersed with Different Bead Sizes

CNTs (Weight Percent)	Density (g/cm^3) and Relative Density (Pct)		
	15 Microns	30 Microns	50 Microns
1	3.57 (60.03)	3.67 (61.71)	3.77 (63.39)
5	3.26 (58.88)	3.43 (61.95)	3.44 (62.13)
10	3.03 (59.44)	3.05 (59.83)	3.06 (60.02)

difficult to observe the CNT distribution because of the characteristics of the materials.

Figure 4 shows magnified images of the samples to enable us observe more precisely the location of the nanotubes. It is clear that fibers are located on the grain boundary region without agglomeration of CNTs. Some pores seem to appear because of the carbon fibers being pulled out from the matrix or pulled-out material.

Table III shows the sintered density of samples with different amounts of CNTs. It is clearly seen that the addition of nanotubes affects the final density of the samples. The zirconia samples sintered at 1473 K (1200 °C) in SPS can lead to full densification, as reported by many researchers.[30,37–40] In such a case, CNTs do not seem to interfere with the densification. Even in high concentrations, there is a relative decline in density; however, the ceramics are still considered to be fully dense.

The interface bonding between CNTs and ZrO_2 can be the reason for the decreasing density with a high CNT concentration. The shrinkage generated by densification can form hollows around fibers. This effect can be stronger for higher concentrations, a phenomenon that can be observed in Table III. This effect is confirmed by density measurements, which also shows that 50-micron beads had the best results confirmed by density measurement. In spite of the lack of full densification, the 50-micron beads had the best results for the dispersing CNT-ceramic system.

D. *Mechanical Properties*

Both Vickers hardness and fracture toughness mechanisms in ceramic-CNT composites are under study. The highly favorable mechanical properties of CNT materials allow for their use in composites obtaining lower weight with an improvement of the mechanical properties, seeking to reinforce the fracture mechanism in the structure. Many researchers have studied this aspect of CNT composites and showed different results. Table IV is a summary of results in the measurements of the mechanical properties of different solid-loading ceramic composites containing CNTs.

The table shows different results for ceramics systems without surface modification of CNTs in a zirconia matrix. Some of them present decrements in hardness and fracture toughness, and others show improvements. This is explained by Dusszova *et al.*[6,8] as a consequence of the lack of bonding between the fibers and the ceramic matrix. The explanation for the diminution in the mechanical properties is based on the role of fibers in the ceramic matrix. Fibers can act as a pore with the direct consequence of decreasing the mechanical properties. Other researchers[14] have demonstrated improvements in mechanical properties in their studies.

The current study presents both results: slight improvements for a low concentration of CNTs and decrements of the hardness and fracture toughness for CNTs with a high concentration.

Figure 5 shows the values of the mechanical properties of the sintered samples. The measured Vickers hardness (H_v) in our study is in concordance with the literature[31–34] (13 to 16 GPa) for three different fiber contents. Moreover, it can be observed that the addition of 1 wt pct of CNTs presents an increment in the Vickers hardness of the zirconia composite. This observation can be seen only with the 50-micron bead treatment. In addition, processing 1 wt pct of nanotubes with different bead size does not improve the mechanical properties, as can be seen in Figure 5.

With the increment in the CNT content to 5 or 10 wt pct in the zirconia matrix, the H_v decreases independently of the bead size used. This behavior is the opposite of that of the projected results for fiber reinforcement in the composite. It was anticipated that better mechanical properties would be obtained with a larger addition of CNTs. Duzova *et al.*[6,8] also observed a decrease with an addition of CNTs of 1.07 wt pct.

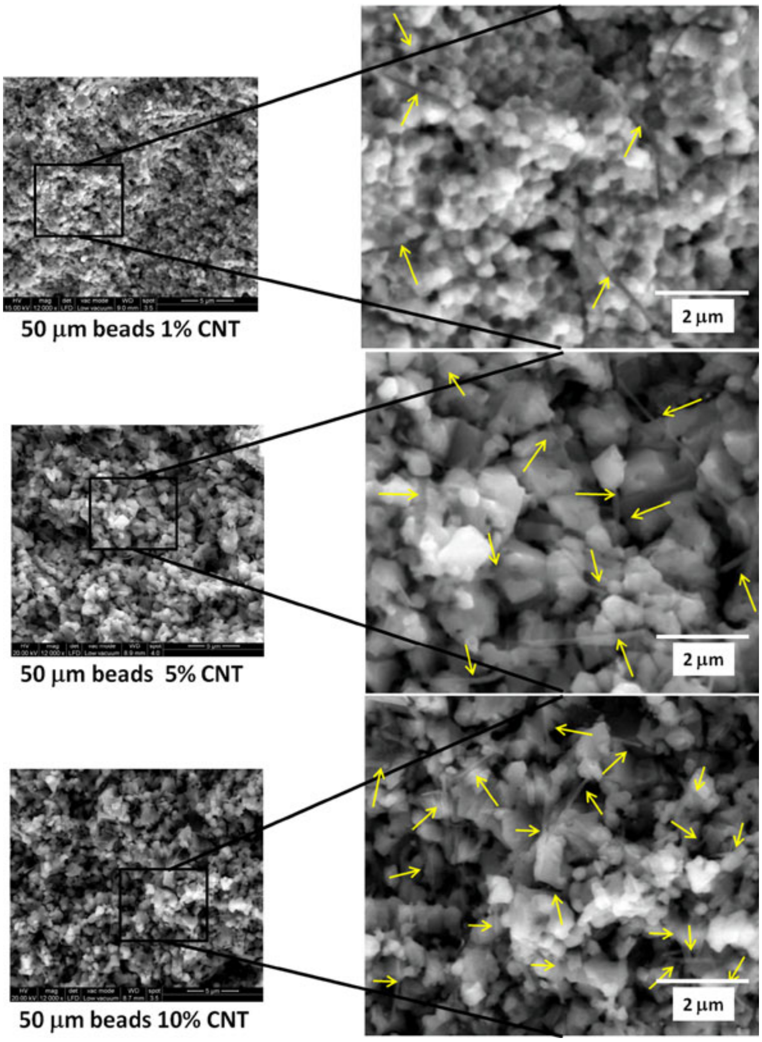

Fig. 4—SEM micrograph of SPS-sintered samples containing 1, 5, and 10 wt pct of CNTs with amplification.

Table III. Density of Sintered Samples in SPS for Three Different CNT Contents and Bead Sizes

	Density (g/cm^3) and Relative Density (Pct)		
CNTs (Weight Percent)	15 Microns	30 Microns	50 Microns
1	5.77 (97.03)	5.79 (97.36)	5.91 (99.38)
5	5.26 (95.00)	5.39 (97.34)	5.49 (99.15)
10	4.83 (94.74)	4.96 (97.29)	5.05 (99.06)

Table IV. Mechanical Properties of Different Studied Ceramic Composites Without Surface Treatment of Fibers

Matrix	CNTs (Weight Percent)	CNT Treatment	Sint. Temp. [K (°C)]	H_v (kg/mm^2)	K_{IC} (Mpa,m^{0,5})	Author
3YTZ	0	no	1473 (1200)	15.5	6	Suárez *et al.*[29]
3YTZ	1.07	no	1573 (1300)	8.3	5.6	Duszova *et al.*[8]
3YTZ	0.5	no	1523 (1250)	12.2	6.8	Mazaheri *et al.*[14]
3YTZ	1.5	no	1523 (1250)	12.3	9.2	Mazaheri *et al.*[14]
3YTZ	3	no	1573 (1300)	12.6	10.1	Mazaheri *et al.*[14]
3YTZ	5	no	1623 (1350)	12.8	10.9	Mazaheri *et al.*[14]
3YTZ	1	no	1473 (1200)	16.0	5.1	Suárez *et al.*[30]
3YTZ	5	no	1473 (1200)	10.9	7.0	Suárez *et al.*[35]
3YTZ	10	no	1473 (1200)	11.0	5.4	Suárez *et al.*[36]

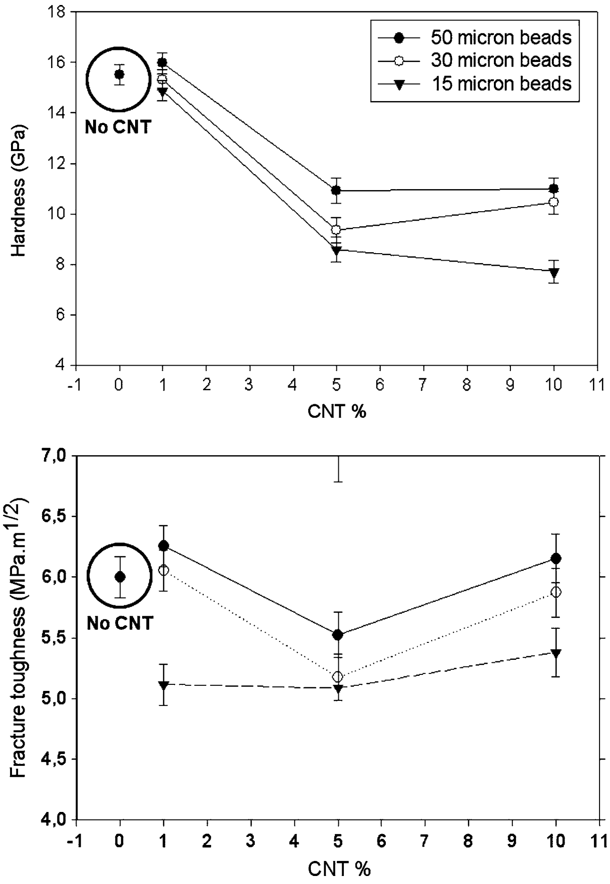

Fig. 5—Vickers hardness and fracture toughness of ZrO_2-CNT composites sintered in SPS after treatment with different bead sizes.

In the current study, the possibility to generate a high concentration of carbon fibers well dispersed in a ceramic matrix (5 or 10 wt pct of CNTs) is a new achievement in this field. In particular, 10 wt pct of fibers in a well-dispersed ceramic matrix and with homogeneous distribution have not been obtained previously.

In spite of no improvement in the mechanical properties for all CNT concentrations in the matrix, this result can lead to future improved results by preparing same processing routes with surface-treated carbon fibers or different fibers.

The fracture toughness (K_{IC}) results show that, with the addition of CNTs, the K_{IC} shows an improvement with the addition of 1 wt pct of CNTs. This improvement can be seen only for the colloidal treatment in bead milling with 50-micron beads. This means that the fiber included in the bulk material improves the fracture toughness when the CNTs are well dispersed. A larger amount of carbon fibers in the bulk material does not improve the mechanical properties, supporting the observation of a decrease in the Vickers hardness.

Figure 5 also shows important results related with processing. It is clear that the mechanical properties present different behaviors for different bead sizes. In the top, it is seen that 15-micron beads present a deficient dispersion, which was evidenced by the particle size observation and density. The mechanical properties, hardness, and fracture toughness also show a similar behavior. The low values are shown for the probes obtained from suspensions treated with smaller beads.

In spite of achieving a high concentration of CNTs in the ceramic matrix, the bonding between the nanotubes with the ceramic matrix can be considered as a very weak[35] because of the different behaviors of the materials. It is not possible to generate a strong bonding between the CNT and the zirconia surface without surface chemical treatment of the CNTs.[36,37] This is the main reason that these kinds of composites do not lead to significant improvement in the mechanical properties for a high concentration of CNTs.

The chemical treatment of carbon fibers with strong acid solutions can generate different reactions enabling a strong bonding between CNTs and ZrO_2[36,37] to generate a final zirconia ceramic that is lighter and with improved mechanical properties.

IV. CONCLUSIONS

It is difficult to achieve fully dense composite ceramics containing CNTs. Concentrations of CNTs higher than 5 wt pct generated highly agglomerated materials before the current study. Aqueous colloidal processing of composites was very difficult to achieve because of the differences in the surface and material characteristics.

In the current study, however, an efficient processing technique called bead milling is shown to be a very effective technique for dispersing CNTs in water-based suspensions and adequate to generate homogeneous composites of zirconia containing high concentrations of CNTs.

Different dispersion conditions were tested, and 50-micron beads were found to be the best-milling media for producing stable and dispersed CNT-zirconia suspensions. Slip casting is suitable for the production of green compacts with a fully dispersed and homogeneous distribution of fibers in the ceramic matrix.

SPS sintering represents a suitable technique for obtaining zirconia-CNT fully dense composites.

The mechanical properties were measured by the indentation technique, and the results showed slight improvements for optimum colloidal processing and low CNT content (1 wt pct). A higher fiber concentration showed a decrement in these properties.

In spite of the results in mechanical properties, the achievement of a colloidal processing route for preparing high-concentration (10 wt pct) CNT in a zirconia matrix with no apparent agglomeration is an important advancement in this field.

Bead milling, slip casting, and SPS sintering proved to be effective colloidal processing methods for obtaining fully dense CNT-zirconia ceramic composites.

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