Direct observation of toughening mechanisms in carbon nanotube ceramic matrix composites

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Abstract

The excellent mechanical properties of carbon nanotubes (CNTs) are driving research into the creation of new strong, tough nanocomposite systems. Here, the first evidence of toughening mechanisms operating in carbon-nanotube-reinforced ceramic composites is presented. A highly ordered array of parallel multiwall CNTs in an alumina matrix was fabricated. Nanoindentation introduced controlled cracks and the damage was examined by scanning electron microscopy. These nanocomposites exhibit the three hallmarks of toughening found in micron-scale fiber composites: crack deflection at the CNT/matrix interface; crack bridging by CNTs; and CNT pullout on the fracture surfaces. Interface debonding and sliding can thus occur in materials with microstructures approaching the atomic scale. Furthermore, for certain geometries a new mechanism of nanotube collapse in “shear bands” occurs, rather than crack formation, suggesting that these materials can have multiaxial damage tolerance. The quantitative indentation data and computational models are used to determine the multiwall CNT axial Young’s modulus as 200–570 GPa, depending on the nanotube geometry and quality. Three-dimensional FEM analysis indicates that matrix residual stresses on the order of 300 MPa are sustained in these materials without spontaneous cracking, suggesting that residual stress can be used to engineer enhanced performance. These nanoscale ceramic composites thus have potential for toughening and damage tolerance at submicron scales, and so are excellent candidates for wear-resistant coatings.

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1. Introduction

The discovery of carbon nanotubes (CNTs) has sparked considerable interest in their use as reinforcements in various matrix materials to impart stiffness, strength, and toughness [1]. Novel mechanical tests on individual CNTs [2,3] in polymer matrices and atomistic calculations [4–6] suggest that CNTs have high elastic moduli, approaching 1 TPa, and exceptional tensile strengths, in the range of 20–100 GPa. The transference of these properties into correspondingly good mechanical properties in actual composites depends on many other in situ features: the CNT/matrix interfacial adhesion, the CNT/matrix interfacial sliding behavior after any decohesion [7], the interwall sliding within multiwall nanotubes, and the fracture behavior and fracture strength statistics of CNTs, among others. These features have proven difficult to assess, even qualitatively, in real systems due to the difficulty in (i) fabricating well-controlled CNT composites and (ii) testing such systems. Although some enhanced mechanical properties in polymer matrices and observations of deformation mechanisms have been reported [8–12], and properties of multiwall CNT/ceramics and toughening in a polycrystalline alumina with dispersed single-walled CNTs have very recently been reported [13–15], there has been no direct evidence regarding the deformation, damage, and toughening mechanisms at the nanoscale in CNT/
ceramic composites. Furthermore, whether composite fracture and damage mechanics at the nanoscale differs from that at the micron-scale due to the near-atomic-scale geometry of the material is simply unknown. Here, we show direct evidence that the critical deformation and damage modes associated with toughening in “standard” ceramic matrix composites do occur in a CNT-reinforced ceramic matrix material. Furthermore, the nanocomposite systems can exhibit entirely new deformation mechanisms.

There are three hallmarks of tough behavior in “standard” ceramic matrix composites, i.e. materials containing micron-scale reinforcing fibers [7]. The first key characteristic is crack deflection at the fiber/matrix interface. This is typically observed by studying cracks that grow transverse to the axial direction of the fibers, where the fibers actually weaken the material such that cracks propagate easily. The second key characteristic is fiber bridging of cracks that propagate perpendicular to the axial direction of the fibers. The bridging of the fibers restrains the crack from opening and reduces the driving force for crack propagation in the matrix. The third key characteristic is fiber pullout on the fracture surface. Fiber pullout demonstrates that the bridging fibers eventually fail away from the crack plane. The work required to pull the embedded broken fibers out against any residual frictional stresses at the fiber/matrix interface can be the major contribution to the macroscopic toughness of the composite. In this work, we fabricated and studied a CNT-alumina nanocomposite matrix in which highly ordered and densely packed arrays of uniform, parallel nanotubes are grown in an alumina matrix. We show that all three of the above phenomena occur in this carefully controlled carbon-nanotube-reinforced ceramic matrix composite.

We also observe a new deformation mechanism in the aligned nanotube composites and the associated porous alumina matrices studied here. Specifically, for larger diameter nanotubes in the composite material and in the porous system, nanotube or pore collapse/buckling in shear bands can accommodate the indentation deformation without the formation of cracks under transverse loading. Coupled with crack bridging under axial crack growth, these results suggest that materials engineering of the detailed nanocomposite structure, e.g., nanotube diameter, wall thickness, and spacing, can generate materials that exhibit multiaxial damage resistance.

Detailed analysis of the indentation results permits the determination of nanotube, matrix, and composite material properties. Of particular interest is the axial nanotube modulus, which is measured here to be in the range of 200–570 GPa. This range is somewhat lower than the typically quoted moduli of about 1 TPa for ideal CNTs, but is comparable to experimental values obtained by other methods [16–19]. Residual stresses can play an important role in composite behavior as well. Based on energetic arguments, nanocomposites are expected to be capable of withstanding large residual stresses without spontaneous cracking. Finite element calculations on the CNT/alumina system, reported below, show matrix residual stresses on the order of 300 MPa, and yet the materials studied here contain no initial cracks upon processing. These residual stresses influence the growth path for transverse cracks, drive longitudinal matrix cracking, and affect the interfacial sliding resistance of the fibers against the matrix. Also of interest are the overall composite toughness and the toughness imparted by the bridging fibers, but these quantities are more difficult to determine due to the combination of indentation loading, residual stresses, and crack bridging. Analysis is underway but will be reported in a separate publication.

Overall, the new observations and analysis methods reported here demonstrate the prospects for tough nanotube composites, show new nanomechanical phenomena, yield specific nanotube and composite properties, and provide a firm foundation for the future engineering of nanotube and nanofiber composites to optimize mechanical performance under various conditions such as contact and wear.

The remainder of this paper is organized as follows. In Section 2, we discuss the material fabrication and testing methods used. In Section 3, we present evidence of the three key phenomena (deflection, bridging, fiber pullout) acting in these nanocomposites and show several new deformation modes that occur in these systems. In Section 4, we describe the computational models and analyses used to obtain constituent moduli and composite residual stresses. Section 5 contains further discussion of this work and its implications for nanocomposite design.

2. Material fabrication and testing methods

Fabrication of the composites studied here follows the route first demonstrated in [20], and extends it to unprecedented coating thicknesses of 20–90 μm. Interested readers should consult [20] for processing details. Briefly, high-purity aluminum is anodized in a multistep process to generate an amorphous nanoporous alumina matrix having a hexagonal array of straight pores extending from the substrate to the matrix surface. After anodization, the alumina pore diameters are in the range of 30–40 nm; there is some modest control of this diameter over a narrow range. During subsequent processing, however, there is some further widening of the pore diameter. Co or Ni catalyst particles are deposited into the bottom of the deep, nanometer-diameter pores and a low-temperature (645 °C) CVD process is used to grow multiwall CNTs up the pore walls, creating an
ideal unidirectional CNT ceramic matrix composite in the form of a coating on the aluminum substrate. The samples studied here are 20 and 90 μm-thick coatings. The composite sample underwent a post-growth treatment, including RIE followed by wet etching, to remove chemical residuals and carbon particles and to expose the top end of the nanotubes. A scanning electron micrograph of the top surface of the resulting 90 μm-thick composite is shown in Fig. 1(a). We also prepared 20 and 90 μm-thick coatings of porous alumina with no nanotubes, and subjected one of the 90 μm-thick samples to the subsequent composite processing but without the reactant gases in the CVD step (645 °C for 12 h in flowing Ar). The behavior of the porous matrix material thus serves as a reference for the behavior of the nanocomposites, although it has not been possible to obtain porous matrix materials with exactly the same pore size as the composites.

After dissolving the alumina matrix from pieces of the nanocomposite samples, the nanotubes were examined with a JEOL2010 transmission electron microscope (TEM). Fig. 1(b)–(d) show the typical microstructures of the CNTs in the 20 and 90 μm-thick specimens, respectively. Special bamboo-like, bottleneck-like and other unclassified structures (Fig. 1(c)) are found to be common in the 20 μm-thick specimen but rare in the 90 μm-thick specimen, in which the CNTs are also more uniform and straight. Close examination of high resolution TEM images (e.g., Fig. 1(b)) indicate that the carbon structure is only partially ordered. This is attributed to the relatively low processing temperature. Annealing of the CVD grown nanotubes is effective in improving the crystallinity, and results in high quality graphic lines in high resolution TEM images, as have been confirmed in separate studies of ours and others [21]. However, the nanotubes examined in this study are in the as-grown form, partly because annealing is found to substantially alter the alumina matrix properties which (i) makes it difficult to dissolve the alumina matrix by the same wet etchants and (ii) causes a highly non-uniform distribution of residual stress in the matrix. To estimate the CNT outer diameter and thickness, about 30 fibers were measured by TEM for each specimen. The average CNT outer diameter is 51 nm for the 20 μm-thick specimen and 56 nm for the 90 μm-thick specimen. The average multiwall CNT thicknesses are about 12.3 and 4.5 nm for the 20 and 90 μm-thick specimens, respectively.

Scanning electron microscopic observations on matrix-dissolved cross-sections of the 90 μm-thick specimen

Fig. 1. (a) SEM photograph of as-fabricated CNT/ceramic composite viewed from the top, showing high degree of hexagonal order (mottled surface due to deposited conductive gold coating); (b and c) TEM photographs of CNTs showing normal and other microstructures in the 20 μm-thick samples after dissolving the alumina matrix; (d) TEM photograph of CNTs in the 90 μm-thick sample.
show a steady increase in the nanotube diameter through the thickness of the composite, as shown in Fig. 2(a), with concomitant changes in the pore diameter since the nanotubes are conformal to the porous template. The average diameter at the top surface, a micrograph of which is shown in Fig. 1(a), is 70 nm, somewhat larger than the overall average of 56 nm; the CNT wall thickness is independent of the tube diameter, however. The variation in nanotube geometry correlates with mechanical performance, as shown in Fig. 2 and discussed below. The heat-treated 90-μm-thick porous alumina samples also show some variation in diameter through the thickness, and associated mechanical property variations, but without the increase in diameter found in the composite materials just near the top surface (Fig. 2(b)). The pore diameter in the composites is 5–10 nm larger than that of the as-anodized porous material. This indicates that chemical agents react with the template matrix to widen the channels during post-anodization processing and CVD growth.

The specimens were subjected to nanoindentation, using a Nanoindenter® Model II with a Berkovitch indenter and a cube-cornered indenter, on the top and side of the nanocomposite. The Berkovitch indenter was used primarily to measure hardness and elastic modulus. The effective Young’s modulus $E_{\text{eff}}$ calculated from the measured unloading tangent stiffness $S$ is

$$
\frac{1}{E_{\text{eff}}} = \frac{2\beta(1-\nu^2)\sqrt{A}}{\sqrt{\pi S}} + \frac{1-\nu^2}{E_i},
$$

where $\beta$ is a constant which depends on the geometry of the indenter ($\beta = 1.034$ for Berkovitch), ($E_i$, $\nu$ = 0.2) and ($E_i$ = 1100 GPa, $\nu_i$ = 0.07) are the Young’s modulus and Poisson’s ratio for the specimen and diamond indenter, respectively [22]. Implicit in the use of Eq. (1) is the assumption of material isotropy. The effective Young’s modulus and hardness of the composite and heat-treated porous alumina are also shown in Fig. 2(a) and (b), respectively. $E_{\text{eff}}$ and $H$ for the porous alumina and the composite both decrease with the distance away from the Al/Al2O3 interface, reflecting the effect of the pore size variation.

The sharper cube-corner indenter was employed so that cracks were most likely to be generated, and at the lowest possible loads. Loads between 20 and 650 mN were used. The cube-corner indenter induced cracks in the specimens at the higher loads. Indentation onto the top surface of the composite coating generates planar cracks parallel to the fiber axis. The samples were also embedded in epoxy, polished on the side surfaces, and subjected to indentation on the side surfaces away from both the composite/aluminum and composite/epoxy interfaces. Side indentation generated planar cracks oriented roughly perpendicular to the fiber axis. Thus, both dominant cracking modes are explored by these two test orientations. Additional results using a Wilson Vickers micro-indenter (model Tukon 2100) will also be presented. Indentation crack patterns and deformation were observed with a Hitachi S-4700 scanning electron microscope (SEM).

3. Results

The main purpose of this work is to demonstrate the existence of toughening mechanisms in these nanocomposites. We thus begin by reporting on our observations of damage and deformation mechanisms under the indentation loading.

3.1. Transverse cracking and crack deflection

To investigate crack deflection at the CNT/matrix interface, we study transverse cracks produced by top indentation. This mode of fracture is not expected to show crack bridging but rather is used to clearly observe the key crack deflection process. A crack induced by top indentation of the 20 μm-thick sample is shown in Fig. 3(a) and (b). The detail of Fig. 3(b)
shows that the crack intersects the successive CNT/matrix interfaces and deflects around the CNTs along the interface, demonstrating the phenomenon of crack deflection. The CNT/matrix interface has a sufficiently low toughness, relative to that of crack propagation through the CNT cross-section, for deflection to be preferable. Fig. 4 shows the surface of a sample that was completely fractured in the transverse direction; free standing CNTs are evident as well as extremely sharp circular arcs at the nanotube/matrix interface, both indicating that the cracks do deflect around the CNTs. Crack deflection between the walls of the multiwall CNTs, with the outer CNT layer(s) remaining adhered to the matrix, may occur but this cannot be resolved by SEM. We believe this is unlikely, however, since it would require fracture of the outer CNT walls. Future TEM studies of the CNT/alumina interface and the fracture path should resolve this issue.

3.2. Crack bridging

With crack deflection demonstrated, we now turn to analyze the results of side indentation, where the toughening mechanism of crack bridging by nanotubes could be observed directly. Fig. 5(a) and (b) shows the separated crack surfaces in the 90 µm-thick sample indented on the side. CNTs are observed to bridge the gap between the surfaces over a large fraction of the crack surface. The bridging is consistent with the crack deflection found in Fig. 3: perpendicular cracks reach the CNT/matrix interface and deflect longitudinally along the interface (which, being internal, cannot be observed directly) rather than propagating through the CNTs. The CNTs thus remain intact to bridge the crack, providing toughening via restraining forces acting against the desire of the crack to open and to grow further under the indentation load.

Some CNTs are broken within the 70 nm crack opening, which may be due to one of several factors. First, these multiwall CNTs do contain defects so that their tensile strengths may not be high enough to hold the imposed stresses. Second, a high residual radial compression \( r_{rr} \) at the CNT/matrix interface generates a high sliding stress \( \tau = \mu r_{rr} \), where \( \mu \) is the friction coefficient. A high sliding stress can, in turn, cause high stress concentrations in the CNTs near the matrix-crack/CNT junction that may drive premature CNT failure [15]. Third, the crack propagation is not precisely perpendicular to the fibers, and hence some kinking of the fibers may drive premature fracture. In addition, a residual longitudinal tension in the matrix (see below) increases the crack opening, as well, reducing the ability of the CNTs to bridge the crack. Future experiments and analysis will assess these possibilities.
3.3. Fiber pullout

Driving side indentation into the 20 μm-thick sample at high loads caused the formation of large subsurface cracks and chipping of the material. The resulting fracture surface geometry is not the ideal one of a surface perpendicular to the axis of the fibers, but does provide a surface across which the CNTs must fracture. Fig. 6(a) and (b) show one such surface in which the CNTs clearly project out of the fracture surface, demonstrating CNT pullout. The angle of the fracture causes some regions of longitudinal delamination exposing the nanotube surfaces, consistent with the crack deflection found in Fig. 3(b) and necessary to cause the bridging behavior of Fig. 5. Fig. 6(a) also show residual holes where CNTs have been pulled out on the mating piece of the fracture surface.

The CNT pullout lengths are not long, on the order of several times the nanotube diameter. This could be caused by several factors [23]. First, a low nanotube strength can lead to fracture near the matrix crack plane because the fiber slip length is small at the relatively low applied stresses. Second, a high interfacial friction might exist, reducing the slip lengths considerably. It should be noted that short pullout lengths due to high interfacial sliding are beneficial for composite tensile strength. Third, a narrow statistical distribution of nanotube strengths (a high Weibull modulus) drives preferential failure at the highest-stress location, which is in the crack opening, and hence leads to smaller pullout. The short pullout lengths could thus be attributable to factors that are detrimental or beneficial to composite strength and toughness.

3.4. Novel nanocomposite failure modes

The results shown in Section 3.1–3.3 are consistent with the behavior of standard CMCs containing micron-scale fibers. We have also found other deformation modes in the present nanoscale materials that are not found in typical CMCs. We first consider the 20 μm-thick porous alumina matrix material without any CNTs. This material has ordered pores of about 37 nm
diameter. Top indentation onto the porous material does not cause cracking at loads up to 650 mN. Rather, in addition to the indentation mark, the deformation is accommodated by shear collapse of rows of pores. Fig. 7(a)–(c) show the deformation at various scales. At large scales, as shown in Fig. 7(a), a dark circular ring is observed around the indentation mark. Upon closer observation, this dark ring is caused by the scattering from short bands of collapsed pores, as seen in Fig. 7(b). Further inspection shows the occurrence of shear cracks between opposite sides of neighboring collapsed pores, as seen in Fig. 7(c). Similar behaviour is found for the 90 μm-thick porous alumina specimens in both as-anodized and heat-treated conditions.

The pore collapse deformation mode is similar to shear band formation and to deformation modes observed in large-scale porous metals and polymers [24]. In this case, however, the matrix material is an amorphous alumina with hardness of about 5 GPa and modulus 140 GPa (see below). The deformed shapes of the sheared pores indicate that the shear cracks have formed only after substantial pore deformation. To accommodate the shear deformation must require some flow of the alumina matrix. Although the anodized alumina is not well-characterized, such flow is not normally expected in similar materials at macroscopic scales, room temperature, and under the expected loads around the indent mark. Similar unexpectedly high apparent flow rates have been deduced in studies of relaxation of thin films with nanoscale native silica subsurface layers [25], and silica has gross mechanical properties similar to those deduced for the present amorphous alumina matrix.

Turning to the nanocomposites, Fig. 3 has already shown that, when the nanotubes are introduced into the top of the 20 μm-thick sample containing thicker-wall CNTs, the indentation drives crack formation rather than the pore collapse and the shear band formation found in the porous matrix. Such behavior can be rationalized if the comparatively stiff nanotubes provide additional resistance to shear deformation. Alternatively, the nanotubes may eliminate a free alumina matrix surface at which the possible flow behavior nucleates and is subsequently accommodated. However, top indentation onto the 90 μm-thick sample, which has a larger CNT diameter of 70 nm at the top surface and thinner CNT multiwall thickness, shows entirely different behavior from the 20 μm-thick sample. As seen in Fig. 8(a) and (b), the deformation is accommodated by lateral buckling or collapse of the nanotubes in shear bands. These shear bands form in a pattern all around the indent mark, separated by regions of undeformed nanotubes. This CNT-reinforced material behaves similarly to the porous matrix material and does not crack under indentation. The geometry and dimensions of the nanotubes thus have a marked impact on the damage modes.

Finally, top and side indentation have also been performed on the 90 μm-thick sample using a standard Vickers microindenter on a Wilson microhardness tester. The Vickers indenter has a shallower angle than that of the cube-corner indenter, and this should promote

![SEM photographs showing deformation in the porous alumina sample: (a) nanoindentation mark surrounded by dark circular regions; (b) array of "shear bands" of collapsed pores causing dark regions; (c) close-up showing small shear cracks between collapsed pores in a shear band.](image-url)
deformation mechanisms over cracking mechanisms. In fact, observations following top indentation with the Vickers indenter show few, if any, indications of crack formation up to loads of 9N, as shown in Fig. 9(a), which contrasts to the cracking observed in Fig. 3. Side indentation using the same Vickers indenter also shows no cracking perpendicular to the CNTs up to similar high loads, as seen in Fig. 9(b), which contrasts with the cracking observed in Fig. 5. For comparison, side indentation on heat-treated porous alumina generates long cracks at a load of 4.9 N, as shown in Fig. 9(c). These results show that the CNT composite system is more damage-tolerant to less-concentrated loadings. Fig. 9(b) does show axial cracking, which is presumably propagating through the matrix material only, parallel to the CNT axis and away from the CNTs, since the matrix is expected to be in radial compression near the CNTs.
The results of Figs. 8 and 9 demonstrate that the deformation behavior for loading in transverse directions normally very weak and brittle in a larger-scale composite can be controlled by the composite microstructure, i.e. the diameter and wall thickness of the CNTs, and possibly their organization. In particular, non-cracking deformation modes can be activated to accommodate aggressive contact loading. Coupled with the existence of CNT-crack-bridging toughening mechanisms for cracking perpendicular to the axial direction, these results indicate that nanotube ceramic composites can be uniquely engineered to exhibit multiaxial toughness or damage tolerance by tuning of the composite geometry and constituent properties.

4. Quantitative results and analysis

Section 3 has presented new observations of toughening mechanisms and deformation behavior for this class of novel CNT-based ceramic composites. We now examine the quantitative data emerging from indentation testing to extract elastic constitutive properties and use the finite element method to estimate the residual stress state in the composite. Information on the constitutive properties of the matrix and CNTs and residual stresses is needed as input into future work on the modeling of the damage and toughening processes.

4.1. Hardness and elasticity

Fig. 2 has shown the Young’s modulus and hardness over the thickness of the porous alumina and composites, measured using a standard Berkovitch indenter. Table 1 presents the Young’s modulus and hardness values for the heat-treated porous alumina template materials and for the CNT composites, for indentation parallel and perpendicular to the nanotube orientations, near the middle of the specimen. The Young’s modulus and hardness for 90-μm thick porous Al2O3 are nearly the same as those of the CNT/Al2O3 composites. The effective Young’s moduli and hardness of porous alumina are close to the results reported by Alcala et al. [26] but much lower than the values of a high-quality polycrystalline alumina. Combining Fig. 2 with Table 1, one can conclude that the pore and nanotube diameter variations must contribute to the variations of the Young’s moduli and hardness of the porous alumina and nanocomposites. Although it is tempting to use the effective modulus along with a simple rule-of-mixtures approach to extract the matrix and CNT elastic moduli, such a strategy is not accurate since Eq. (1) assumes material isotropy while both porous alumina and nanocomposites are anisotropic. Proper extraction of the composite moduli and the moduli of the constituent alumina and CNTs requires careful attention to the details of the material system.

To accurately account for the anisotropy and the complexity of the indentation loading, we have developed a self-consistent numerical method based on a sequence of finite element calculations at different scales, as follows and as indicated schematically in Fig. 10. We start with the porous matrix material. We assume the matrix material itself is isotropic, and thus characterized by a Young’s modulus $E_m$ and Poisson’s ratio $\nu_m$. We then construct a fully-3d finite element model of an isotropic material containing aligned longitudinal pores in a hexagonal array. This model is subjected to both axial and transverse loadings to extract the elastic constants of the porous material in terms of the matrix material values. These values could also be obtained from homogenization methods, but the finite element model (FEM) model is ultimately needed for similar calculations on the three-phase (matrix/CNT/pore) material. A second larger-scale fully-3d FEM model is then used to represent the indentation geometry. A coating of the appropriate anisotropic homogenized porous material is placed on a thick pure aluminum substrate ($E = 70$ GPa and $\nu = 0.3$). An indentation mark is carved out, and symmetry permits the use of a reduced geometry, as shown in Fig. 10. Note that the plastic deformation associated with the indentation is ignored; elasticity upon initial unloading should be independent of the prior plastic or permanent deformation. Very fine

Table 1
<table>
<thead>
<tr>
<th>Material</th>
<th>Orientation</th>
<th>Pore or tube diameter (nm)</th>
<th>$V_m$</th>
<th>$V_i$</th>
<th>Hardness $H$ (GPa)</th>
<th>Effective $E$ (GPa)</th>
<th>FEM $E_{m}$ or $E_{m}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat-treated porous Al2O3 (90)</td>
<td>Side*</td>
<td>45.5</td>
<td>0.805</td>
<td>–</td>
<td>6.8</td>
<td>107</td>
<td>82 ($E_{m}$)</td>
</tr>
<tr>
<td></td>
<td>Top</td>
<td>60.5</td>
<td>0.654</td>
<td>–</td>
<td>4.1</td>
<td>86</td>
<td>93 ($E_{m}$)</td>
</tr>
<tr>
<td>CNT/Al2O3 (20)</td>
<td>Side*</td>
<td>51.1</td>
<td>0.754</td>
<td>0.178</td>
<td>5.6</td>
<td>96$^b$</td>
<td>91 ($E_{m}$)</td>
</tr>
<tr>
<td></td>
<td>Top</td>
<td>53.2</td>
<td>0.754</td>
<td>0.178</td>
<td>6.9</td>
<td>134</td>
<td>141 ($E_{m}$)</td>
</tr>
<tr>
<td>CNT/Al2O3 (90)</td>
<td>Side*</td>
<td>53.3</td>
<td>0.735</td>
<td>0.082</td>
<td>7.0</td>
<td>107</td>
<td>86 ($E_{m}$)</td>
</tr>
<tr>
<td></td>
<td>Top</td>
<td>70.3</td>
<td>0.534</td>
<td>0.112</td>
<td>4.0</td>
<td>87</td>
<td>106 ($E_{m}$)</td>
</tr>
</tbody>
</table>

* Average value in the middle of the sample.
$^b$ Cube-corner data adjusted to give Berkovitch value.
meshes are used around the indent area to limit inaccuracy. The indent holes are constructed to correspond to the experimental projected area $A$ and vertical indent distance $h$, and a diamond indenter having the same size as the indent hole is also constructed. The indenter and the material are connected with gap elements that allow the indenter to slide along the interface. The coefficient of friction is arbitrarily chosen as 0.2 since it has little effect on the results. A small load $P$ is applied on the top of the indenter and the displacement $u$ of the indenter is then calculated using the finite element model. The unloading stiffness $S' = P/u$ is then calculated and compared to the measured stiffness $S$, for both top and side indentation. Based on the differences between $S$ and $S'$, the elastic properties of the alumina matrix are modified and the procedure is iterated to self-consistency. The numerical models have been verified by using isotropic material properties and comparing the FEM modulus values to those of Eq. (1).

The Young’s moduli of the porous alumina calculated using the above finite element models are shown in Table 1, and are close to the effective porous alumina moduli calculated by Eq. (1). The difference is due to anisotropy. The alumina matrix modulus as calculated using the finite element method and both side and top indentation data yield 140 GPa, shown in Table 2. This value is consistent with that of low-density irradiated alumina [27] and is much lower than the typical values of 350–390 GPa for dense polycrystalline alumina. We have also calculated the Young’s modulus of the alumina from the side indentation data at various positions along the 90-μm thick sample, accounting for the pore diameter variations. We find that the underlying alumina modulus is nearly the same with position.

Table 2
Elastic moduli of $\text{Al}_2\text{O}_3$ matrix and CNT reinforcements as calculated using the finite element model

<table>
<thead>
<tr>
<th>Materials</th>
<th>Tube diameter (nm)</th>
<th>Tube thickness (nm)</th>
<th>Average $E$ (Gpa)</th>
<th>Range of $E$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$ (heat-treated)</td>
<td>–</td>
<td>–</td>
<td>140</td>
<td>131–147</td>
</tr>
<tr>
<td>Nanotube (20) (top)</td>
<td>51.1</td>
<td>12.1</td>
<td>200 ($E_{zz}$)</td>
<td>135–281 ($E_{zz}$)</td>
</tr>
<tr>
<td>Nanotube (90) (top)</td>
<td>70.3</td>
<td>4.5</td>
<td>570 ($E_{zz}$)</td>
<td>511–620 ($E_{zz}$)</td>
</tr>
</tbody>
</table>
indicating that the variations of the $E$ and $H$ shown in Fig. 2(b) are mainly due to the pore size variation, and is the same (140 GPa) as in the unheat-treated 20-µm thick sample.

For the nanotube composite, we proceed similarly. Having derived the alumina matrix modulus, only the nanotube moduli remain to be determined. The microstructural scale FEM model is constructed using a transversely isotropic continuum tube having the five independent elastic constants $E_{zz}$, $E_{rr} = E_{tt}$, $G_{zz}$, $v_{rr}$, and $v_{tt}$, as shown in Fig. 10. Based on a molecular dynamics model of CNTs and literature data, the transverse Young’s modulus $E_{tt}$ is usually taken to be 1/2 the axial Young’s modulus $E_{zz}$. It is also assumed that $v_{zz} = v_{tt} = 0.2$ and $G_{tt} = E_{zz}/[2(1 + v_{tt})]$. The final results for unloading stiffness are not highly sensitive to these latter approximations. The elastic moduli of the nanocomposite under various axes of applied uniform loadings are then determined using the FEM model. The resulting anisotropic composite moduli are used in the larger-scale FEM model of the indentation test to calculate the unloading stiffness $S^*$, which is then compared to the experimental stiffness $S$, for both top and side loadings. The nanotube moduli are updated iteratively, holding the alumina matrix properties fixed at the values determined previously, until the calculated unloading stiffness $S^*$ matches the experimental values.

The Young’s moduli CNT/alumina composites calculated with the finite element model are shown in Table 1, and are close to the effective composite modulus calculated with Eq. (1). The CNT moduli as calculated using the finite element method are also shown in Table 2. The axial multiwall CNT modulus is calculated to be in the range of 135–281 GPa, with a mean value of 200 GPa, for the 20-µm-thick sample, using the top indentation data only because side indentation with the Berkovich indenter was not performed on these samples. The range of values corresponds to results from analyses using the maximum and minimum measured unloading stiffness $S$. Since the nanotube volume fraction is fairly large, small variations in $S$ cause rather larger variations in the estimated nanotube modulus.

For the 90-µm-thick composite specimen, the side indentation modulus varies along the CNT direction. This is attributed to variations in the CNT diameter and/or the matrix modulus. To examine if the variation of CNT diameter is the main factor causing the decrease in the composite modulus, we performed finite element calculations using the CNT diameters as shown in Fig. 2(a) with a fixed matrix ($E_m = 140$ GPa), fixed CNT modulus $E_{rr}$, and fixed CNT wall thickness. The CNT modulus was determined by fitting the FEM calculations to the side indentation data at the position of 20 µm, yielding $E_{tt} = 265$ GPa with minimal sensitivity of the results to the CNT modulus $E_{zz}$. With the CNT modulus $E_{rr} = 265$ GPa, and two values for the anisotropy ratio $E_{zz} = 2E_{tt}$ and $E_{zz} = E_{tt}$, the side unloading modulus at different positions was then calculated, taking into account the pore/nanotube diameter variation, and converted into an effective composite modulus $E_{eff}$ using Eq. (1) to yield the results shown in Fig. 11. The predicted effective moduli do not match the experimental data as a function of position, suggesting that the matrix modulus $E_m$ also varies with position, perhaps due to physical aging or chemical reaction during the CNT growth process with reactant gases. The results do show the insensitivity of the side indentation behavior to the anisotropy ratio, however. To match the experimental modulus data and rectify the differences between experiments and calculations shown in Fig. 11, the matrix modulus was adjusted as a function of position, for both $E_{zz} = 2E_{tt}$ and $E_{zz} = E_{tt}$, yielding two slightly different predictions for the matrix modulus versus position. The results indicate that, very near the top surface of the thick sample, the matrix modulus is only on the order of 80–90 GPa for $E_{tt} = 265$ GPa. Use of these reduced values for the matrix modulus in the FEM analysis of the top indentation data on the 90-µm-thick specimen then yields an axial CNT modulus of $E_{zz} = 570$ GPa for $E_{tt} = E_{zz}/2$, as shown in Table 2. The assumption of $E_{tt} = E_{zz}$ does not give reasonable results for axial CNT modulus, consistent with indications that an anisotropy ratio around 1/2 is appropriate for the CNTs. Thus, we deduce that the CNT modulus for the
70 nm diameter, 4.5 nm wall thickness nanotubes (near the top surface of the 90 µm-thick specimen) is significantly higher than for the 51 nm diameter, 12 nm wall thickness nanotubes of the 20 µm-thick specimen. The substantial increase in modulus is consistent with the notably better CNT molecular structure in the 90 µm-thick specimens, as shown in Fig. 1(d).

The Young’s moduli of the nanotubes reported in Table 2 are consistent with results from other researchers using different measurement technique, although there is a large variation in the reported values. The Young’s modulus of multiwall nanotubes prepared by arc discharge is measured as 690–1870 GPa by bending single nanotubes in an AFM [16]. Arc-grown MWCNTs yield 270–950 GPa as measured by pulling the outermost layer of a single nanotube in SEM [17]. MWCNTs prepared by pyrolysis of acetylene over film-like iron/silica substrates give values of 220–680 GPa [18] and CVD SWNT bundles give values of ~100–150 GPa, both as measured by tensile tests of very long and aligned CNTs [19]. Overall, the Young’s modulus of CVD MWCNTs measured by us and other researchers is much lower than the predictions obtained by atomistic simulation such as molecular dynamics and ab initio that yield values around 1 TPa. The low moduli found here may be due to the range of imperfections in the multiwall nanotubes, as evidenced in Fig. 1(b)–(d). The prevalence of defects in 20 µm-thick sample as compared to the more-uniform 90 µm-thick samples is consistent with the lower elastic modulus obtained for the CNTs in the 20 µm-thick sample. In spite of the existence of defects that may influence the elastic behavior, our results show that composites fabricated from these MWCNTs do exhibit the desirable toughening behavior and hence ideal CNTs (single or multiwall) are not necessary for activating toughening mechanisms in nanocomposites.

4.2. Residual stresses

It is well-established that residual stresses influence the deformation and cracking behavior in composites. Most notably, high residual matrix tension induces early matrix cracking in CMCs, and residual stresses in woven and cross-ply systems drive transverse cracking in the appropriate regions. Furthermore, the residual stress at the fiber/matrix interface is coupled to the interfacial sliding resistance, and hence to the strength and toughness of the composite.

We have used a 3d finite element model of a rectangular unit cell of the periodic hexagonal array to calculate the expected residual stresses in the 20-µm thick sample nanocomposite. The thermal expansion coefficient for CNTs has been reported in the literature to be nearly zero, and essentially isotropic (in contrast to commercial carbon fibers, which are highly anisotropic) [28]. The thermal expansion coefficient for the alumina matrix is taken as $10^{-5}$/K. Since the thermal residual stresses are calculated by linear elasticity, the results reported here are directly proportional to the difference in thermal expansion coefficient. Thus, correcting the present results using more-accurate values for the CNT or matrix c.t.e. values is trivial.

![Fig. 12. Residual stresses (in MPa) in the 20 µm-thick composite as predicted by the finite element model: (a) hoop stress; (b) radial stress; (c) axial stress. All fields are with reference to an origin at the lower left corner of the figure.](image-url)
Fig. 12(a)–(c) show the calculated residual stress fields in the 20-µm-thick sample composite, not including the additional in-plane biaxial compressive stresses expected due to thermal mismatch with the aluminum substrate. As noted earlier, the matrix is in hoop tension, radial compression, and axial tension. The magnitudes of hoop, radial, and axial stresses are approximately 540, ~300 and 275 MPa, respectively. The nanotubes are in overall compression, with an axial compression of about ~1100 MPa, and about ~590 and ~300 MPa at the nanotube/matrix interface in the hoop and radial direction, respectively. As an aside, these values agree fairly well with standard concentric-cylinders models for isotropic constituents.

The high axial tension in the matrix drives cracking perpendicular to the nanotubes, so that the indentation cracks observed in Fig. 5 are longer than in the absence of the residual stress. However, it is important to recognize that matrix cracks do not form spontaneously in the as-fabricated material in spite of the large tensile residual stress.

The high relative hoop tension in the matrix drives radial transverse cracking as observed in Fig. 3(b). The matrix cracks in Fig. 3(b) tend to grow in toward the CNTs along radial lines and then out away from the CNTs along radial lines. Thus, the residual stresses draw the transverse cracks into the compressed CNT/matrix interface, at which point the crack must either deflect or penetrate the CNT. In the absence of this residual stress state, it would be possible for the transverse cracks to avoid the CNTs altogether and follow a low-toughness path through the brittle matrix alone. The high radial compression puts the interface in compression and makes any interfacial sliding more difficult, which could lead to property enhancement or degradation depending on the details of the interface sliding and stress concentrations.

There may be other residual stresses associated with the matrix growth process. In future work, we will measure these stresses using the wafer curvature technique. However, these stresses are superimposed upon the internal residual stresses of the composite, and so do not qualitatively influence the points discussed above.

5. Discussion and summary

Our results demonstrate, for the first time, that CNT-reinforced ceramic matrix composites exhibit all of the features associated with toughening behavior in fiber-reinforced composites: crack deflection, crack bridging, and fiber pullout. No prior work on ceramic matrix nanocomposites has demonstrated such features, in part because prior materials have typically contained low volume fractions of highly disordered CNTs. Here, the ability to clearly observe damage mechanisms stems from the exceptional order of these unidirectional composites, and the ability to introduce controlled cracks in various orientations using indentation.

An important issue for toughening in fiber-reinforced composites is the nature of the interface between the fiber and the matrix. The interface must be of sufficiently low toughness to debond upon impingement of the matrix crack and must subsequently not slide too easily or with too much difficulty. The present results show that debonding occurs at the atomic scale in these nanoscale composites, and that the residual sliding behaviour is not too low. The lack of molecular-scale perfection in the present nanotubes may provide some benefit in this regard. Ideal multiwall CNTs may exhibit extremely easy inter-wall sliding that prevents toughening behaviour, as inner walls easily telescope out from outer walls that might otherwise be held in place by higher sliding resistances. Imperfect nanotubes may provide more-effective load transfer from outer to inner walls, permitting enhanced strength and toughening. Thus, engineering of the internal nanotube structure appears feasible to optimize or control composite toughness and damage behaviour.

The nanotube-reinforced composites also show a new crack-resisting mechanism of CNT collapse in “shear bands” not seen in large-scale composites. A major problem in traditional ceramic composites is the highly anisotropic nature of the strengthening and toughening, which is enhanced only for axial loading, and thus requires the fabrication of woven and cross-ply structures to impart improved multiaxial damage tolerance. The new mechanism found here for damage tolerance under transverse loading suggests that energy can be absorbed by the shear banding in a manner qualitatively similar to mechanisms in ductile metals, leading to multiaxial damage tolerance. This deformation mechanism is presumably driven by the underlying pore-collapse mechanism found in the porous matrix material, and does not occur in all composite systems; only the system with thinner CNT wall thickness and larger (top surface) diameter exhibits this mechanism. Hence, the composite structure (nanotube diameter, wall thickness, spacing, etc.) must be engineered to optimize both longitudinal toughness and transverse damage tolerance. Furthermore, this new deformation mechanism found in both CNT composites and ordered porous ceramics may provide new insight into nanoscale toughening of structural ceramics.

Residual stresses can be used to advantage more readily in nanoscale materials than in typical micron-scale materials, because nanoscale materials can tolerate larger residual stresses without spontaneous disintegration. The residual stresses estimated here are well beyond the range tolerated in standard micron-scale composites and yet no spontaneous cracking is evident. We believe that the anisotropic fracture and toughening
behavior in these materials can further be optimized for high specific fracture performance by appropriate engineering of these residual stresses. Residual stress is thus an available “knob” that can be adjusted to aid in obtaining desired performance.

The presence of residual stresses and CNT crack bridging complicates the determination of the nano-composite toughness. Standard indentation crack formulae do not apply. To determine the actual toughness imparted by the bridging fibers in an indentation crack geometry including residual stresses requires detailed numerical analysis that is underway. Such analyses require, as basic input, the thermomechanical information that we have extracted here from indentation tests and analysis.

In summary, we have fabricated and tested highly ordered CNT-reinforced alumina composites. These CNT-based composites show behavior typical of microscale composites (crack deflection, fiber bridging and pullout) and entirely new behavior (CNT collapse and shear-banding), with the interplay of the various damage modes depending on the composite geometry, length scales, and loading conditions. Our results demonstrate a rich range of deformation phenomena in these nano-composites associated with the interplay of geometry (CNT or pore diameter and spacing, CNT wall thickness) and material properties (matrix stiffness, toughness, and yield strength; CNT stiffness and fracture toughness; thermal mismatch), a range that can now be systematically explored via experiments on these well-controlled materials.

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