Direct Observation of Toughening and *R*-Curve Behavior in Carbon Nanotube Reinforced Silicon Nitride

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The efficacy of toughening in nanoscale ceramic composites is currently controversial, in part because indentation based fracture toughness measurements are not reliable in these materials. To explore the relevant mechanisms, *in situ* mechanical testing was used to investigate carbon nanotube reinforced silicon nitride. Nanoindentation of microcantilever beams (cut with a focused ion beam) made it possible to probe fracture and notch sensitivity. Stable crack growth was directly observed with this approach. The measured *R*-curve for these composites was obtained from analysis of these data. These results provide *direct* evidence of significant toughening enhancements in a carbon nanotube reinforced ceramic composite.

Keywords: *ceramic composites, carbon nanotubes, fracture toughness, nanoindentation.*

The research community has long focused on methods for improving the fracture toughness of ceramic materials. It is well known that reinforcing ceramics with fibers to form ceramic matrix composites (CMCs) can have a marked effect on increasing the fracture resistance, rendering these materials usable in a variety of applications where low-toughness monolithic ceramics are not viable. Extending this approach to the nanoscale with carbon nanotubes (CNTs) has been widely investigated over the past decade^[1-7].

Significant toughening in fiber-reinforced composites is achieved by fiber bridging across the crack wake, with energy dissipation provided by fiber debonding and pullout from the matrix phase^[2, 8-11]. However, the degree to which these mechanisms contribute to toughening with CNTs is uncertain. A central issue here is that moving to smaller length scales in advanced ceramics typically leads to stronger but less tough materials. This has led to serious questions about the amount of toughening that CNT's can provide. One difficulty is that direct investigations of CNT toughening in nanoceramics have been severely hampered by the challenges inherent with studying fracture at small length scales. The most widely reported methods are based on indentation, however, these are not capable of providing accurate quantitative information about the toughness^[6,7]. Traditional large scale measurements, such as single edge notched beam (SENB), have only been used in several cases. These tests provide accurate fracture toughness values, and indicate that toughening by CNTs is possible^[7,12]. However, only a few measurements of this type have been reported. Furthermore, with the notch sizes used to initiate fracture in these tests only brittle fracture is observed. Here, it is important to note that the notch or flaw size where crack growth begins (a) can determine the nature of the fracture that is observed. It is convenient to evaluate this effect with the following dimensionless parameter^[13]:

$$\alpha = \frac{a \sigma_n}{\delta_o E'} \quad (1)$$

where the traction law that describes toughening is defined by the maximum local stress, σ_n and a cohesive zone length δ_o . Values of $\alpha \rightarrow 0$ lead to sub-critical crack growth that is notch insensitive, whereas large α correspond to notch sensitive, brittle fracture. In CMCs, Suo *et al* also point out that:

$$\frac{\delta_o E'}{\sigma_n} \propto \frac{r S}{\tau} \quad (2)$$

where r is the fiber radius, S is the deterministic fiber strength, and τ is the sliding friction at the fiber/matrix interface. In composites reinforced with conventional fibers ($r \sim 5 \mu\text{m}$ or larger), the quantity in Eq. (2) is typically $\sim 0.1 - 10 \text{ mm}$. In these materials, conventional fracture specimens correspond to $\alpha \sim 1$ or less and sub-critical crack growth is readily observed. However, in CNT reinforced materials the length scale in Eq. (2) is several orders of magnitude smaller. Thus, with large scale fracture measurements like SENB, α is much larger than it is with conventional CMC's, and only brittle fracture is observed.

This approximate analysis indicates that stable crack growth in CNT reinforced ceramics should be observable with small scale testing. Coatings in the form of unidirectional composites are attractive for these measurements, because the fiber orientation is amenable to comparisons with well-defined models (i.e., compared to materials with random fiber orientations). For example, in previous work we have reported high fracture toughness values for amorphous silicon nitride coatings reinforced with vertically aligned carbon nanotubes (VACNTs)^[14]. To investigate stable crack growth and ductility at small length scales, we now report measurements with micro-cantilevers that were obtained with focused ion beam (FIB) milling. This approach provides the flexibility to make micron sized specimens that can be prenotched and loaded with a nanoindenter. Researchers at Oxford were the first to use FIB machined cantilevers to study fracture toughness^[15]. They report values of $3.2 \text{ MPa m}^{0.5}$ for a WC coating after performing similar tests on reference silicon beams to quote a value of $1.1 \text{ MPa m}^{0.5}$, thus substantiating the accuracy of the toughness values reported. This method has also been employed to study the fracture toughness of individual copper grains by aligning the axis of the cantilevers to specific crystallographic directions^[16], and more recently in several ceramic materials^[17,18]. In the work reported here, we have extended this approach beyond measuring fracture toughness values, to provide *in situ* measurements of stable crack growth. This type of direct measurement of toughening behavior in a CNT reinforced ceramic nanocomposite has not been previously reported.

Nanocomposite fabrication: The vertically aligned CNT (VACNT) array and the amorphous silicon nitride matrix were both produced by chemical vapor deposition (CVD). The $200 \mu\text{m}$ thick coating shown in Figure 1 consists of $10 \mu\text{m}$ by $10 \mu\text{m}$ CNT reinforced columns, with $\sim 2 \mu\text{m}$ of dense matrix in between each pillar. This “dual” structure was obtained by using

photolithography to pattern catalyst islands for the CNT growth. These arrays were then infiltrated with amorphous silicon nitride in a low pressure chemical vapor deposition (LPCVD) chamber at 725 °C, with ammonia and dichlorosilane precursor gases. This results in a composite coating with ~200 µm thick columns. More detailed information on the fabrication methodology is provided elsewhere^[19,20].

Microcantilever beams: The composite microcantilevers were cut from the CNT reinforced material shown in Fig. 1. A Helios NanoLab dual beam FIB was used to mill out beams with pentagonal cross-section^[15] such that the nanotubes are oriented parallel to the beam axis. A larger beam current of 21 nA to dig trenches around the beam followed by a smaller beam current to minimize the re-deposition due to Ga ions. The cantilever was notched by using another two-step procedure, wherein a relatively larger current of 28 pA was used to create a rough rectangular section that is 300 nm deep followed by a smaller current to mill a sharp notch that was more than 800 nm deep. Transmission electron microscopy (TEM) images on select samples show that notch root radius is less than 50 nm. In porous materials such as these, residual stresses introduced by Ga ion re-deposition during the milling procedure are localized and may lead to underestimated strength values^[21].

Mechanical testing: The free end of the cantilevers was loaded with a Hysitron nanoindenter equipped with a Berkovich tip. These tests were run to various maximum displacements, at indenter displacement rates of 2.5 nm·s⁻¹. A variety of precautions were taken to ensure accurate measurements. The maximum displacement error at maximum load was estimated to be ~2 nm, and can thus be neglected.

Brittle fracture was observed in five composite cantilevers, with a nearly linear load increase followed by an instantaneous load drop (see Figure 2a). In these specimens a small decrease in stiffness occurred just before the failure point. The fracture surface from a composite beam in Fig. 2b shows clear evidence of CNT pull-out. Reference microcantilevers machined from a <110> oriented Si wafer also underwent brittle fracture wherein failure occurred at the notch.

For brittle fracture, K_{Ic} values were obtained with the following expression:

$$K_{Ic} = \sigma_c \sqrt{\pi a} F\left(\frac{a}{b}\right) Y(\rho) \quad (4)$$

$$\sigma_c = \frac{P l y}{I} \quad (5)$$

where P is the applied load, a is the notch depth, b the beam thickness, and w the beam width. These expressions were obtained by DiMaio *et al*, who used a 3D finite element model to obtain^[15]:

$$F\left(\frac{a}{b}\right) = 1.85 - 3.38\left(\frac{a}{b}\right) + 13.24\left(\frac{a}{b}\right)^2 - 23.26\left(\frac{a}{b}\right)^3 + 16.8\left(\frac{a}{b}\right)^4 \quad (6)$$

noting that this expression is valid for $0.3 < \frac{a}{b} < 0.6$. This previous approach is based on materials with isotropic elastic properties, whereas the unidirectional nanotube reinforced silicon nitride materials studied here have a strong orthotropic character. To account for these orthotropic properties a correction factor $Y(\rho)$ was also added to Eq. (4)^[22]. This factor requires accurate knowledge of the elastic constants, and for the volume fractions of the constituent materials. Nanoindentation on the top and side of the composites gave E_{11} and E_{22} values (375 ± 25 GPa and 80 ± 20 GPa, respectively). Volume fractions of nanotubes, V_f and porosity, V_p , were estimated using ImageJ analysis of SEM micrographs. Others^[23-27] have used more detailed correction factors for rotation of the crack tip, shear deformation, uneven bending moments and non-linearity arising due to changing direction of the load point for large bending displacements to account for non-linearity measured in the load displacement data obtained from special configurations of beam bending experiments. However, $Y(\rho)$ provides sufficient accuracy for our current analysis.

For the Si reference material, $Y(\rho) = 1$, and inserting measured values^[28] into Eq. (4) gives a K_{Ic} value of $0.9 \text{ MPa-m}^{0.5}$. This agrees well with values reported elsewhere^[29,30]. Evaluating $Y(\rho)$ for the orthotropic composite beams^[28] and applying Eq. (4) gives K_{Ic} of 5.1 to $7.1 \pm 0.3 \text{ MPa-m}^{0.5}$ for the composite beams where brittle fracture was observed (plus one unusually low value of $2.9 \pm 0.2 \text{ MPa-m}^{0.5}$). This range is consistent with values obtained previously for similar materials, using a more complex analysis of indentation measurements^[31]. The error ranges listed here are associated with the accuracy of measuring the dimensions in Eqs. (4)–(6).

In a majority of the composite beams tested the nanoindentation response showed evidence for stable crack propagation. This occurred in all of the beams milled from the central

region of the composite coatings, and from approximately half of the other specimens obtained either near the surface or near the substrate. In several cases the indentation experiments were halted before complete fracture of the beam to validate this slow crack growth (see Figure 3). In other cases complete failure occurred but a sharp load drop associated with brittle fracture was not evident. This behavior is indicative of progressive damage that is often referred to as *R*-curve behavior. In several experiments additional quantitative information was obtained with start-stop testing, where the beam was loaded to increase the displacement in successive experiments, followed by intermittent crack position monitoring (see Figure 3b).

During stable crack growth the fracture toughness is equal to the SIF in Eq. (4), which increases as the load increases. This was applied to brittle fracture (above) using the initial notch size, a_o (i.e., $K_{Ic} = K_r(a_o)$). However, for stable crack growth K_r varies with crack length. Equations (4 – 6) can still be employed, except that the factor F in Eq. (6) was originally obtained for $a/b < 0.6$. Larger values of a/b occurred in most of the specimens where stable crack growth was observed and thus an additional configurational adjustment was made by employing a finite element model (FEM) to describe stresses in the specimen^[28]. This FEM employed a contour integral method to evaluate the K field with larger a/b values, leading to the corrected values in Figure 4. The increasing K_r values shown here are a direct measure of *R*-curve behavior.

The measured *R*-curve response in Fig. 4 provides clear evidence that CNTs can toughen a ceramic composite. The stable crack growth observed here is the type of ductile fracture that Suo *et al* attribute to low values of α (see section 1). These measurements also indicate that the size of the damage zone, L_d , is a significant fraction of the crack length in these CNT-reinforced materials. Under these conditions, the *R*-curve response in Fig. 4 depends on the specimen geometry and thus is not a characteristic material property^[13,32]. With this “large scale bridging”, cohesive zone (CZ) models are typically used to provide a more accurate view of the material properties that govern fracture. A central feature of many CZ formulations is that fracture can be described with two key parameters. In our case, it is convenient to view these as the fracture energy, G_C , and the maximum normal traction across the cohesive zone, σ_n ^[32]. With these parameters set, a value for δ_o (the cohesive length scale that appears in Eq. (1)) depends on the specific CZ traction law. However, variations in δ_o with different CZ models are relatively small, since it has been shown that different traction laws lead to similar descriptions of the

fracture process for given values of G_C and σ_n ^[32,33]. Thus reasonable CZ approximations can be obtained with a simple rectilinear law (i.e., $\sigma(\delta) = \sigma_n$ for $0 < \delta < \delta_o$ and $\sigma(\delta) = 0$ for $\delta > \delta_o$).

The type of CZ modeling outlined above is largely phenomenological, however, it is important to keep in mind that it describes tractions in the crack wake. Thus, with large σ_n crack advance will be impeded until the maximum normal tractions are reached at the tip of the notch. If the value of G_C is fixed, then an increase in σ_n must correspond to smaller values of δ_o and shorter L_d (i.e., because these depend on σ_n and G_C). These relationships can be applied to our experiments, where G_C is obtained from the applied load and L_d is the measured crack extension at this load. These measured quantities then imply a value for σ_n (with δ_o then dictated by a specific CZ law, as noted above). Detailed analysis of this type requires a full numerical CZ model. However, the experimental values can be used to obtain approximate σ_n values based on previously developed analytical expressions. As noted above, the LSB in our experiments implies that the experimentally measured K_r values depend on the specimen geometry. The condition for crack extension corresponds to $K_{tip} = 0$, which can be used to obtain the following approximate relationships for the rectilinear CZ law ^[32]:

$$\sigma_n \cong \frac{K_r}{2 \sec^{-1} \eta} \sqrt{\frac{\pi}{(a_o + L_d)}} \quad (7)$$

$$\alpha_{max} = \frac{a_o \eta_{max} \sigma_n}{\delta_o E'} \cong \frac{\pi}{8 \ln \left(1 + \frac{L_{d,max}}{a_o} \right)} \quad (8)$$

where a_o is the initial notch depth and $L_{d,max}$ is the damage zone size where G_C reaches a steady-state value.

For the three successive points in Fig. 4, evaluating Eq. (7) with the experimental measurements gives σ_n values of 3.3, 3.5, and 3.9 GPa respectively. Careful analysis of the precision of these measurements indicates error ranges of approximately 10-20% ^[28]. Thus, the σ_n values obtained from these points are self-consistent. In other words, an average value of $\sigma_n = \sim 3.6$ GPa predicts the full set of experiments to within the measurement accuracy. It is important to remember that the basic CZ formulation used for this estimate is not expected to accurately describe the actual mechanisms associated with CNT pull-out, sliding, and fracture. However, the relatively high σ_n value extracted from the measurements with this approach is potentially noteworthy. For example, in fiber-reinforced composites a convenient estimate of $\sigma_n \approx \varphi_f S$ has

been suggested, where φ_f and S are the fiber volume fraction and fracture strength respectively^[13]. With an estimate of $\varphi_f \sim 0.1 - 0.2$ for these materials, the σ_n values obtained from the experiments corresponds to $S \sim 18 - 36$ GPa. This range is generally consistent with literature values for MWCNTs^[34]. Lower values are often reported for CVD grown nanotubes, although here it is important to keep in mind that S is a function of the nanotube length being sampled due to the distribution of strength limiting defects (i.e., high defect densities in CVD grown materials lead to relative low S values in nanotubes that are long enough for fracture testing). The relevant bridging lengths in the composites are significantly shorter based on the pull-out lengths observed in these composites, and thus relatively high S values are not unreasonable.

Using the data obtained from specimen AM2 to evaluate Eq. (8) gives $\alpha_{max} \cong 1.2$. This is consistent with the observation that these experiments are capable of measuring stable crack growth, but that brittle fracture also occurs in some of the specimens. In other words, an intermediate α value combined with the internal local variations in the composite structure, indicate that it is possible to move from stable to unstable fracture in a material consisting of the same matrix and CNTs. For this particular material, it appears that the change from stable to unstable crack growth is caused by only modest differences in the structure. The most apparent correlation is that specimens with higher porosity were more likely to undergo brittle fracture. However, more detailed investigations are needed to verify this effect. The apparent strain hardening observed during stable crack also requires further study, since this may be related to the different measured behaviors.

In summary, fracture processes at the nanoscale were investigated with microcantilever experiments. The notch sensitivity required to observe sub-critical fracture in nanoceramic composites is met with these FIB milled cantilevers, making it possible to monitor stable crack growth. The measured $K_I(a)$ shows an increase in fracture resistance with crack extension. To our knowledge, this is the first direct measurement of an R -curve response in a CNT toughened ceramic. This provides direct evidence of CNT toughening in ceramics, which has been elusive in much of the prior work on these materials. Evaluating the crack growth measurements with a basic cohesive zone model gives self-consistent results. More detailed analysis of these types of measurements can ultimately provide additional mechanistic insight into fracture processes at the nanoscale.

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Figure Captions

Figure 1. Cross section of CNT reinforced silicon nitride composite coating, showing some of the locations where FIB milled cantilevers were obtained.

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Graphical abstract