Quantification and Promotion of Interfacial Interactions between Carbon Nanotubes and Polymer Derived Ceramics

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Abstract

Carbon nanotubes (CNTs) have been considered an ideal reinforcement for light-weight and high-strength ceramic matrix composites. Understanding the interfacial properties between CNTs and the matrix is crucial for engineering the desired properties in such composites. Here *in-situ* pull-out experiments with a polymer derived ceramic (PDC) matrix are carried out with both pristine CNTs and CNTs coated with Al₂O₃ (CNT/Al₂O₃) produced by Atomic Layer Deposition (ALD), using micro-fabricated devices in a scanning electron microscope. This carefully designed comparative study makes it possible to better understand the interfacial interactions between CNTs and PDC matrices. The interfacial shear strength (IFSS) of CNT-PDC is 9.99±2.84 MPa, while the IFSS of (CNT/Al₂O₃)/PDC with ~3 nm Al₂O₃ coating thickness is 14.52±2.66 MPa, demonstrating a 45.3% improvement. The non-linear failure observed with the coated CNTs is also indicative of energy dissipation mechanisms that promote toughening in ceramic matrix composites. The improved properties in (CNT/Al₂O₃)/PDC are believed to originate from increased surface roughness, which leads to mechanical interlocking at the interface during the pull-out process. The combination of special interlayer structures such as ALD Al₂O₃ and strong CNTs opens up interesting opportunities for improving the mechanical properties of ceramic nanocomposites reinforced by CNTs.

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1. Introduction

The mechanical performance of fiber reinforced composites depends not only on the intrinsic properties of the constituents but also largely on the reinforcement/matrix interface. Thus, understanding the interfacial properties between reinforcement and matrix is crucial for both fundamental research and engineering applications. The effect of microfiber/matrix interface on mechanical properties of composites has been widely explored [1-7]. Several established methods, including the push-out test [6,8], the pull-out test [9-11], the microbond test [12,13], the micro-indentation test [14,15], and the fragmentation test [7,16,17], etc, have been employed to characterize the interfacial strength. For example, Rebillat *et al.* used push-out tests to investigate the interface and interphase characteristics of strongly bonded two-dimensional (2D) SiC/C/SiC composites.[5] The main advantages of push-out tests lie on the fact that specific fibers in the composite can be probed. Miller *et al.* developed a microbond pull-out technique to study the interfacial bonding between fiber and resin.[18] Compared to the other interfacial characterization methods, the pull-out test holds several advantages: (i) There is no limitation in sample size, such that both microscale and nanoscale wires/rods can be pulled out from matrix; (ii) The pull-out tests are generally simpler than the other methods mentioned. For instance, fragmentation tests require the failure strain of the matrix to be at least three times higher than the failure strain of the fiber[17], however, no such specific requirements are needed in the pull-out test; and (iii) In pull-out tests, the sample geometry can be well defined and the experimental results usually exhibit high reproducibility. Although the current techniques can be effectively used to obtain the interfacial strength of composites reinforced by microfibers, it is extremely challenging to obtain the interfacial strength between nanoscale reinforcements and the matrix.

On the other hand, CNTs have been considered as an ideal reinforcement for light-weight, and high-strength ceramic matrix composites (CMCs) including CNT/ Al_2O_3 [19-21], CNT/SiC[22,23], and CNT/ B_4C [24,25] nanocomposites. Despite the early success of incorporating CNTs into ceramic matrices, the direct and quantitative assessment of the important CNT/ceramic interface remains elusive. Previously, atomic force microscopy (AFM) and nanoindentation techniques have been used to obtain elastic modulus and fracture strength of various nanostructures.[23,26-29] However, it is challenging to directly apply these techniques to obtain the interfacial strength of ceramic-based nanocomposites. Barber *et al.*[10] successfully attached a CNT to an AFM probe and then dipped the CNT into a liquid polymer. The subsequent pull-out test was carried out after the polymer was cured, and the interfacial strength of ~ 47 MPa between the CNT and the polymer was reported. Unfortunately, this method cannot be extended to pull out the CNTs from ceramics, which would require sintering of ceramic matrix with an embedded CNT at high temperature. Nozaka *et al.*[11] developed an inclined slit-based pullout (ISP) method, which utilized a nanomanipulator driven AFM probe inside scanning electron microscope (SEM) to pull out a protruding CNT. The interfacial strength between CNT and alumina matrix was measured to be 19.2 ± 6.6 MPa. The pull-out test is easy to carry out and there is no limitation to matrix type. However, the CNT sample alignment with the loading axis is a substantial challenge in this method. More recently, a micro-fabricated device has been developed which can perform the pull-out experiment.[30-33] The “push-pull” micro-device, actuated by an inSEM quantitative nanoindenter, measures the load and displacement independently. The corresponding stress-strain curve can be used for further analysis, such that elastic modulus, fracture strength, and interfacial strength, and even fracture toughness can be precisely measured.[30-33] This design has the advantage of minimizing the sources of errors in

the CNT/matrix interfacial study, since the CNT loaded on the device can be well aligned and the embedded length can also be precisely controlled.

It is well known that the interface dictates the load transfer from matrix to reinforcements. A weak composite interface will lead to insignificant load transfer, resulting in easy pull-out of the reinforcements. A strong interfacial bonding between reinforcement and matrix is often desirable for high strength composites. However, with a brittle matrix improved fracture toughness requires an interface that is weak enough to permit crack deflection around the reinforcement. During subsequent pull-out, energy dissipation due to frictional sliding along the fiber/matrix interface provides an additional contribution to toughening. In conventional micron-scale fiber-reinforced ceramics, these interface properties are usually controlled by depositing an intermediate layer to modify the interfacial bonding. To apply this strategy to the nanocomposites in this study, Al_2O_3 with a thickness of a few nanometers was grown on CNTs with atomic layer deposition (ALD). Alumina (Al_2O_3), a conventional ceramic material with high elastic modulus and thermal stability, is a well-studied material with valuable applications in mechanical reinforcement.[34, 35] Al_2O_3 also possesses lower density compared to most of metal materials. Without van der Waals attraction, Al_2O_3 nanostructures can be easily dispersed into matrix. For example, nanosized Al_2O_3 powders have been widely used in composites.[36, 37] CNT coated by Al_2O_3 can be well dispersed in PDC, which makes it possible to fabricate homogenous dispersed nanocomposites reinforced by CNT/ Al_2O_3 . Finally alumina can be readily produced by ALD, thus making this an appropriate system for the initial investigation that is presented here. The silicon-based ceramic derived from a polymer precursor was directly fabricated on the micro-fabricated device. CNTs with and without Al_2O_3 coatings were used to investigate interfacial properties. The *in-situ* pull-outs of individual CNT or CNT/ Al_2O_3 from the

polymer derived ceramic (PDC) were directly observed in SEM. The results show that Al_2O_3 shells with ~ 3 nm thickness can significantly increase both the interfacial strength and frictional sliding resistance between CNTs and the PDC by promoting interlocking between the Al_2O_3 and PDC.

2. Experimental

2.1 Materials

MWCNTs with diameter between 60 and 120 nm were obtained from Mitstui Corp., Japan. The PDC precursors were obtained from Extreme Environment Materials Solutions, LLC, New York, United States. The latter includes two components: a liquid polymer (CSO-230) and the crosslinking agent (CLC-PL005). The CSO-230 polymer is based on silicon alkoxide chemistry ($\text{Si}(\text{OR})_4$) with some OR sites substituted by hydride and vinyl groups. The precursor is prepared by mixing CSO-230 and CLC-PL005 platinum catalyst with a weight ratio of 50:1.

2.2 Fabrication of CNT/ Al_2O_3 by Atomic Layer Deposition (ALD)

Atomic layer deposition of MWCNTs with Al_2O_3 was performed on a CambridgeNanotech® Fiji System. The ALD process was performed in the thermal deposition mode at 250 °C. The Al_2O_3 layers were produced with the precursor Trimethyl Aluminum (TMA) and thermal co-reactant H_2O . A series of deposition cycles (10, 30 and 50) were chosen to yield different coating thickness and uniformity, considering the deposition rate of about ~ 1 Å/cycle. Correlation of ALD cycles and thickness of alumina, and surface roughness measurements are demonstrated in Supporting Information Section 1 and Section 2, respectively. No chemical bonding is found between Al_2O_3 and CNT as confirmed by XPS analysis. Details can be found in the Supporting Information Section 3.

2.3 Fabrication of CNT/PDC and (CNT/Al₂O₃)/PDC Nanocomposites

A drop of the prepared PDC precursor was first loaded onto the sample shuttle of the micromechanical device [29-32] where it formed a thin layer. Individual CNTs or CNT/Al₂O₃ were dispersed in toluene and deposited on a piece of silicon wafer. It was then picked up using a manipulator under an optical microscope, and then carefully loaded onto the sample shuttle covered by the previously deposited PDC layer. The diameter and embedded length of CNT were directly measured in the scanning electron microscope (SEM; FEI Quanta 400). Additional drops of PDC were deposited onto well-aligned individual CNT (or CNT/Al₂O₃) to fully encapsulate it enabling the desired pull-out tests. The whole device together with embedded CNT (or CNT/Al₂O₃) was put into a graphite boat using two pieces of silicon wafers as bottom and top protective covers. The PDC was first crosslinked at 100 °C for 30 minutes followed by pyrolysis. Pyrolysis was performed in a tube furnace (Lindbergh/Blue MTM, Thermo Scientific) under continuous flow of a mixture of 95% N₂ and 5% H₂ at 100 ml/min. The temperature was raised to 400 °C at a ramping rate of 5 °C/min, then further ramped at 1 °C/min to 1000 °C, held for 1 hour, cooled at 1 °C/min to 500 °C, and finally allowed to naturally cool down to room temperature over the course of 5 hours. After annealing, another drop of epoxy was loaded on the other end of CNT (or CNT/Al₂O₃) to firmly bond it to the other sample shuttle of the device before the actual tests.

2.4 CNT and CNT/Al₂O₃ Pull-out Test

The sample-loaded microdevice was subsequently glued to an SEM sample stub using crystal bond. The microdevice operates based on a spring-like “push-pull” mechanism. A quantitative Agilent inSEM nanoindenter was used to actuate the device and also to measure the load and displacement independently. The complete pull-out test was recorded by a video to

reveal the corresponding deformation and fracture processes, and to ensure the validity of such tests.

2.5 Post analysis of morphology and composition of debonded CNTs and CNTs/Al₂O₃

SEM was used to check the morphology of the pulled-out CNT (or CNT/Al₂O₃) and the resulted groove on the microdevice. After the pull-out test, the microdevice was also intentionally broken to fit the pulled-out CNT together with the sample shuttle to a Transmission Electron Microscopy (TEM) copper grid, sandwiched by another identical copper grid before loading into the TEM holder. High-resolution TEM (JEOL 2100 F) imaging and Energy Dispersive Spectroscopy (EDS) were employed to carefully re-examine the morphology and composition of the debonded CNT or CNT/Al₂O₃.

3. Results and Discussion

The pristine CNTs used in this study have diameters ranging between 60 and 120 nm. An individual CNT with diameter of 88.0 ± 8.6 nm was picked up using manipulator under an optical microscope and then carefully loaded onto the microdevice shown in Fig. 1a. Fig. 1b shows that the left end of CNT was embedded into polymer derived ceramic (PDC) precursor which was converted into ceramic matrix after the thermal treatments described earlier. The other end of CNT was anchored with epoxy after the pyrolysis of precursor. To make sure that the CNT can be pulled out from PDC side, the embedded length in PDC is controlled to be a few micrometers and is generally much shorter than that in epoxy. The pull-out experiments were actuated by an inSEM nanoindenter as described earlier in the experimental procedure section. The pulled-out CNT is shown in Fig. 1c. The video recording the entire pull-out process of the CNT can be found in the Supporting Information Video S1. After the CNT is pulled out, a groove is left in

PDC matrix, which is shown in the inset of Fig. 1c. The smooth surface of the groove implies that the bonding between CNT and PDC is relatively weak. The strong interfacial bonding should lead to severe damage of matrix. The corresponding load-displacement curve is shown in Fig. 1d. Due to the existence of slack in the CNT, the CNT is straightened first, which is reflected by the initial stage of the load-displacement curve. Once the CNT is straightened, the loading will dramatically increase. The CNT could either break or debond from the matrix. The sudden load drop observed in Fig. 1d confirms that the CNT was abruptly pulled out.

Figure 1. CNT pull-out test from PDC matrix. (a) Micromechanical device with nanoindenter tip engaging on the top shuttle. (b) and (c) SEM images of a CNT with diameter of 88.0 ± 8.6 nm before and after pulled-out from PDC. (d) Load-displacement curve of the CNT debonded from PDC.

Assuming perfect interfacial bonding and uniform shear stress distribution, the corresponding maximum pullout force (F_{max}) gives:

$$\tau_b = \frac{F_{max}}{\pi D l_{emb}} \quad (1)$$

where τ_b is the shear strength of the interface (IFSS), D is the diameter of the CNT, and l_{emb} is its embedded length in the matrix. The IFSS of the CNT in Fig. 1 is calculated to be 10.43 ± 2.23 MPa. Four additional pull-out tests under the similar testing condition and with different embedded length were carried out. Details of diameter and embedded length of CNTs, critical pull-out force, maximum normal stress, and IFSS are summarized in Table 1. The average IFSS of five pristine CNTs debonded from PDC is 9.62 ± 1.85 MPa. These values are comparable to those measured by Nozaka *et al.*[11] using a nanomanipulator to pull CNTs from an alumina matrix.

Table 1. Interfacial properties between CNT and PDC.

Test #	CNT outer diameter nm	Embedded depth nm	Critical pullout force mN	Maximum normal stress GPa	IFSS τ_b MPa
1	74.9 $\pm$ 1.9	5180.6 $\pm$ 80.1	0.0106	2.40 $\pm$ 0.12	8.69 $\pm$ 0.36
2	77.2 $\pm$ 2.5	2042.1 $\pm$ 36.9	0.0061	1.31 $\pm$ 0.85	12.39 $\pm$ 0.63
3	79.1 $\pm$ 8.9	3220.3 $\pm$ 308.6	0.0083	1.70 $\pm$ 0.39	10.43 $\pm$ 2.23
4	86.3 $\pm$ 9.0	3557.9 $\pm$ 133.2	0.0087	1.48 $\pm$ 0.32	8.99 $\pm$ 1.29
5	103.9 $\pm$ 3.7	3000.4 $\pm$ 67.6	0.0075	0.88 $\pm$ 0.06	7.61 $\pm$ 0.44
Average					9.62 $\pm$ 1.85

Therefore, the interfacial properties between CNT and ceramic matrices can be measured *in-situ* by combining a simple microfabricated device with a quantitative nanoindenter inside a SEM. These IFSS values indicate that the CNT/ceramic bonding is quite weak, which is further illustrated by the smooth trace left behind the pulled-out CNT in Fig. 1c. As noted in the introduction, it is very important to engineer the interfacial properties in CNT reinforced ceramic composites to enhance their fracture toughness. Existing strategies to improve the interactions between CNTs and matrices include creating functional groups on CNT surface or increasing

surface roughness of reinforcements.[4,9,38] The conventional approaches to functionalize CNTs have mainly focused on treating the CNTs via strong acid followed by grafting active functional groups such as carboxyl, hydroxyl groups onto the CNTs surface.[39-42] However, it is challenging to control the surface treatment depth. The chemical functionalization process is also inevitably detrimental to intrinsic strength of the CNTs due to disruptions of the perfect sp^2 bonding of carbon lattices in order to attach the functional groups, resulting in a much weaker reinforcements and sub-optimal composite performance. Even though these strategies are effective for polymeric systems [42-44], their effectiveness for ceramic systems remains to be further demonstrated. In particular, increasing surface roughness by depositing an intermediate layer on CNTs provide a better option for increasing sliding resistance while maintaining high CNT strength and sufficiently weak interfacial bonding. This approach is pursued in the current study.

Figure 2 shows schematic illustrations of composites reinforced by smooth and rough fibers, respectively. The surface of the rough fibers resulting from coated layers gives rise to the “enlarged ends” or “dumbbell-shape” geometries as shown. These surface features not only provide larger interaction area with the matrix, but also could allow a more efficient load transfer between reinforcements and matrices due to a mechanical interlocking mechanism as proposed previously[45,46], enabling both higher strength and toughness of composites to be readily achieved.

Figure 2. Schematic illustrations of composites reinforced by smooth and rough fibers.

In order to promote the proposed mechanical interlocking mechanism, a rough intermediate layer needs to be deposited on the CNT surfaces. In this study, we employed Atomic Layer Deposition (ALD) form such intermediate layers made of Al_2O_3 with a nominal thickness of ~ 3 nm. Figure 3 shows TEM images of pristine CNTs and CNTs/ Al_2O_3 nanostructures. The surface of pristine CNTs in Figs. 3a and 3b is quite smooth. The outer and inner diameters of CNT are 75.9 ± 6.7 nm and 3.0 ± 1.6 nm, respectively. The graphitic walls of these CNTs are quite thick, which ensures the strength of the CNTs. Five tested CNTs successfully debonded either from PDC (i.e. a success rate of 71%), with no CNT fractures observed during the pull-out tests. The CNTs coated with Al_2O_3 are shown in Figs 3c and 3d. The Al_2O_3 islands can be clearly seen and are highlighted by arrows. The average thickness of the Al_2O_3 in Fig. 3d is 2.4 ± 1.2 nm. No lattice structures were found in the Al_2O_3 islands, which is indicative of the expected amorphous structure obtained by ALD. The Al_2O_3 islands are well attached to the CNT surface with no apparent interfacial cracks or delaminations found. Additionally, the discontinuous Al_2O_3 islands nicely resemble the schematic features of “enlarged ends” or “dumbbell-shape” as discussed earlier. This provides an opportunity for the Al_2O_3 islands and PDC matrix to form strong interlocking during the pull-out test illustrated in Fig. 2b, which allows effective load transfer from the matrix to the CNT/ Al_2O_3 . This has the

potential to enhance both the interfacial strength and the sliding resistance between the CNT/Al₂O₃ and the PDC matrix.

To characterize the effect of the Al₂O₃ layer on the interfacial bonding between CNT and PDC, an individual CNT/Al₂O₃ was pulled out using the micromechanical device shown in Figure 4 (The video recording of the pull-out test of CNT/Al₂O₃ can be found in the Supporting Information Video S2). The diameter of the CNT/Al₂O₃ in Figs. 4a and 4b is 84.9±12.8 nm. After the CNT/Al₂O₃ is pulled out from PDC, a SEM image of the resulted groove in PDC is taken and shown in Fig. 4c. It is clear that the edge of the groove is quite rough, indicating that the PDC matrix is damaged during the pull-out process. This is in sharp contrast to the smooth groove observed earlier for pristine CNT pull-out experiment, further suggesting the existence of a strong bonding between the CNT/Al₂O₃ and PDC. Unlike the load-displacement curve of pristine CNT debonded from PDC, obvious step-wise features in the curve are observed. This suggests that the interfacial bonding between CNT/Al₂O₃ and PDC fractures step by step due to the mechanical interlocking mechanism. The nonlinear behavior before failure is believed to be associated with additional energy dissipation during debonding and/or pull-out, due to the interlocked surface features. These phenomena strongly suggest that interfacial interactions between Al₂O₃, coated CNT and the PDC matrix are promoted by the rough oxide layer. Indeed, the IFSS of the CNT/Al₂O₃ that debonded from PDC in Fig. 4 is 14.40±2.46 MPa, which is much higher than the average IFSS of CNT debonded from PDC. As before, four additional pull-out tests were carried out. Details of diameter and embedded length of CNTs/Al₂O₃, critical pull-out force, maximum normal stress, and IFSS are found in Table 2. The average of IFSS between CNT/Al₂O₃ and PDC for all five tests is 14.52±2.66 MPa, demonstrating a substantial 50.9% increase over the average IFSS between pristine CNT and PDC.

Figure 3. TEM images of CNTs and CNT/ Al_2O_3 . (a) and (b) low- and high-magnification TEM images of CNTs. (c) and (d) low- and high-magnification TEM images of CNTs with Al_2O_3 layer.

Figure 4. CNT/Al₂O₃ debonding from PDC. (a) and (b) SEM images of a CNT/Al₂O₃ with diameter of 84.9 ± 12.8 nm before and after debonding from PDC. (c) The left groove in PDC. (d) Load-displacement curve of the CNT/Al₂O₃ debonding from PDC.

Table 2. Interfacial properties between CNT/Al₂O₃ and PDC.

Test #	CNT outer diameter nm	Embedded depth nm	Critical pullout force mN	Maximum normal stress GPa	IFSS τ_b MPa
1	73.5 ± 4.0	4860.4 ± 128.6	0.0117	2.76 ± 0.30	10.44 ± 0.84
2	77.0 ± 8.8	2356.6 ± 35.2	0.0125	2.70 ± 0.63	13.98 ± 1.64
3	84.9 ± 12.8	1365.9 ± 21.8	0.0052	0.93 ± 0.29	14.40 ± 2.46
4	85.5 ± 6.6	2255.5 ± 10.7	0.0101	1.76 ± 0.28	16.72 ± 1.38
5	96.6 ± 5.4	2297.6 ± 32.5	0.0119	1.62 ± 0.18	17.07 ± 1.20
Average					14.52 ± 2.66

To further understand whether the debonding occurs between the CNT and Al₂O₃, or between the Al₂O₃ and PDC, EDS analysis on CNT surfaces was carried out. Figures 5a and 5b

show TEM images of debonded pristine CNT and CNT/Al₂O₃. It is quite difficult to identify the residues on CNT and CNT/Al₂O₃ after the pull-out tests from TEM images only, however, the EDS results in Figs. 5c and 5d clearly show the difference between the pristine CNT and CNT/Al₂O₃. Only a carbon peak is found on the debonded CNT in Fig. 5c, which indicates that the CNT is easily pulled out from PDC during these pull-out tests. The interaction between CNT and PDC is weak, so no residue from the matrix material is found on the CNT. However, the aluminum and silicon peaks are clearly shown in the EDS of CNT/Al₂O₃ debonded from PDC in Fig. 5d. The aluminum is from the residual alumina on CNT. Since silicon is the main constituent of the PDC, this silicon peak demonstrates the strong interaction between Al₂O₃ and PDC. The EDS result is also in good agreement with the rough fracture surface of the matrix observed in Fig. 4c. In fact, it seems that the rough surface of the CNT/Al₂O₃ allows the Al₂O₃ islands and matrix to embed into each other and form strong interlocks during the pull-out test, resulting in effective load transfer from the matrix to the CNT/Al₂O₃ and a higher IFSS value.

Figure 5. TEM images and EDS analysis of the debonded pristine CNT and CNT/Al₂O₃. (a) TEM image of debonded pristine CNT. (b) STEM image of debonded CNT/Al₂O₃. (c) and (d) are EDS analysis of debonded pristine CNT and CNT/Al₂O₃, respectively.

In summary, we have demonstrated that the interfacial properties between carbon nanotubes and ceramic can be quantified by pull-out tests using a microdevice. Due to the mechanical interlocking between CNTs/Al₂O₃ and PDC, the interfacial bonding and sliding resistance can be significantly increased. The average IFSS between CNT/Al₂O₃ and PDC is 14.52 ± 2.66 MPa, demonstrating 50.9% increase than that between CNT and PDC. This type of modification is expected to have significant implications in the design and optimization of CNT reinforced ceramic nanocomposites with superior mechanical properties.

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