***In Situ* Direct Observation of Toughening in Isotropic Nanocomposites of
Alumina Ceramic and Multiwall Carbon Nanotubes**

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For: *Acta Materialia* (Manuscript No. A-16-3318 Revised)

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Abstract

Toughening of brittle ceramics by multiwall carbon nanotube (MWCNT) reinforcements is an attractive approach. However, *in situ* direct observation of crack propagation and direct toughness-curve (*T*-curve) measurements using sharp starter-cracks in well-controlled ceramic/MWCNTs nanocomposites are lacking. Here, fully-dense, isotropic Al₂O₃/10%MWCNTs nanocomposites with individually dispersed acid-treated MWCNTs are fabricated using colloidal

processing and spark plasma sintering (SPS). The MWCNTs are primarily embedded within Al_2O_3 grain boundaries, and appear to be clamped by a large compressive residual stress of the order of -3.7 GPa. *In situ*-direct and *ex situ* characterization of crack propagation is performed, observations from which provide insights into the exceptional crack-bridging toughening mechanisms in these nanocomposites. It is revealed that random MWCNTs bridge the crack by ‘unfurling’ (or disentangling), aligning normal to the crack plane, and pulling out. It is confirmed that the MWCNTs pullout occurs primarily between the weakly bonded nested layers (‘sword-sheath’), accompanied by some helical unraveling. The *T*-curve ($T(\Delta c)$) measured using four-point bending on Al_2O_3 /10%MWCNTs nanocomposite specimens containing sharp starter-cracks of various lengths (Δc) shows modest toughening, with the steady-state toughness reaching $4.6 \text{ MPa}\cdot\text{m}^{0.5}$. Crack profile of a stable equilibrium crack in the Al_2O_3 /10%MWCNTs nanocomposite is measured, and it is used to calculate the bridging-stress constitutive relation. This relation is used to calculate the *T*-curve independently, and it is found to compare favorably with the experimentally measured *T*-curve. The implications of this new understanding of toughening in isotropic ceramic/MWCNTs nanocomposites are discussed.

I. Introduction

The discovery and development of carbon nanotubes (CNTs) — dubbed as the ‘ultimate fiber’[1] — has created an opportunity to use them as reinforcements in brittle polycrystalline ceramics for obtaining tough, damage-tolerant nanocomposites. The past 15 years has seen great rise in the research on such ceramic/CNTs nanocomposites (see reviews Refs.[2-5]). Early research focused on the use of single-wall CNTs (SWCNTs),[2, 6, 7] while majority of the research remains in the use of multiwall CNTs (MWCNTs) to reinforce a wide range of polycrystalline ceramics, including alumina (Al_2O_3), zirconia (ZrO_2), silicon nitride (Si_3N_4), silicon carbide (SiC), spinel (MgAl_2O_4), *etc.*[3-5] This is primarily because of the wide commercial availability of the relatively inexpensive MWCNTs compared to SWCNTs. However, the success in enhancing the toughness of ceramic/CNTs nanocomposites in general has been mixed. A small number of studies have shown several-fold increase in the toughness over the base matrix, while majority of the studies show moderate toughening or no toughening at all, and in some cases even a reduction in the toughness.[3, 4] This can be attributed to two main reasons. First, there is tremendous variability in the final microstructures of such nanocomposites. This is

due to some of the well known issues such as agglomeration and non-uniform dispersion of CNTs, and the damage to the CNTs during sintering. In fact, in several of the studies the CNTs may be graphitized, making them ceramic/graphite, not ceramic/CNTs, nanocomposites. The quality, the amount (vol%), and the characteristics (internal/external diameters, number of walls, length, defects concentration, *etc.*) of the starting CNTs also vary greatly from one study to the other, which can result in large variations in the microstructures. Second, the testing methods employed to measure the toughness of these nanocomposites in many studies may be invalid.[7, 8] For example, the anomalous elastic/plastic behavior of some of these nanocomposites renders the use of the simple indentation-toughness method invalid, resulting in the overestimation of toughness values.[2, 7, 8] In several studies that do use direct toughness measurements (bend-testing methods), the starter-notch or -crack may not be adequately sharp, which also results in the overestimation of the toughness values. But perhaps the most significant gap in ceramic/CNTs nanocomposites research is the complete lack of *in situ* direct observations of crack propagation, which can provide deep insights into the toughening mechanisms in these interesting nanocomposites.[2]

Here we have observed *in situ*, for the first time, crack propagation in a high-quality $\text{Al}_2\text{O}_3/\text{MWCNTs}$ nanocomposite inside a scanning electron microscope (SEM), where crack-wake bridging by MWCNTs is found to be the dominant toughening mechanism. Toughness as a function of crack length (*T*-curve) using sharp starter-crack and four-point bend test is measured, also for the first time. Furthermore, crack profiles as a function of crack length are measured. Crack-wake bridging parameters are calculated using the crack-profile data, and they are used to calculate the *T*-curve independently, which compares favorably with the measured *T*-curve. These results provide new, comprehensive understanding of toughening in $\text{Al}_2\text{O}_3/\text{MWCNTs}$ nanocomposites, and pave the way for similar systematic studies of ceramic/CNTs nanocomposites in general.

2. Experimental Procedure

2.1. Processing

Commercially available high-quality MWCNTs (Bussan Nanotech, Tokyo, Japan), with diameter 50-70 nm and average length $\sim 5\ \mu\text{m}$, were covalently functionalized to disperse them in water. A mixture of H_2SO_4 (98%; Fisher Scientific, Fair Lawn, NJ) and HNO_3 (68%; Macron,

Center Valley, PA) 3:1 by volume was used to acid-treat the as-received MWCNTs for 20 min at 110 °C according to a method described elsewhere.[9] The acid-treated MWCNTs with negatively charged functional groups COO^- and O^- were then washed by distilled water until the pH of the solution reached ~4, to obtain a stable colloid. As-received nanopowder (size ~100 nm) of $\gamma\text{-Al}_2\text{O}_3$ (Nanophase, Romeoville, IL) was heat-treated at 1300 °C for 10 min in air using a box furnace to convert it to $\alpha\text{-Al}_2\text{O}_3$. The $\alpha\text{-Al}_2\text{O}_3$ nanopowder was then ball-milled (in water with Al_2O_3 balls) for 24 h to breakup any agglomerates, and it was dispersed in an aqueous solution at a pH of ~4 (dilute HNO_3 was used to adjust the pH). Since the isoelectric point of Al_2O_3 is pH~8,[10] the Al_2O_3 -nanoparticle surfaces are expected to be positively charged at pH~4. The MWCNTs and the Al_2O_3 -nanopowder colloids were ultrasonically agitated (Branson, St. Louis, MO) separately for 2 h, and then the colloids were mixed to achieve an hetero-aggregation of 90 vol% Al_2O_3 and 10 vol% MWCNTs in water. The mixture was then stirred for 1.5 h, and dried on a hot-plate (while stirring) to obtain a homogenous powder mixture of Al_2O_3 and MWCNTs. The powder mixture was loaded into graphite dies (20 mm or 30 mm diameter) lined with graphite foil, and densified in a spark plasma sintering (SPS) furnace (Thermal Technologies LLC, Santa Rosa, CA) in Ar

atmosphere. The SPS conditions were relatively mild to avoid damage to the MWCNTs: 75 MPa applied pressure, 50 °C.min⁻¹ heating rate, 1300 °C hold temperature, 5 or 10 min hold time, and 100 °C.min⁻¹ cooling rate. All surfaces of the resulting Al₂O₃/10%MWCNTs nanocomposite disks were ground to remove any remnants of the graphite foil.

In related experiments aimed at making the nanocomposites electrically more conducting for improved *in situ* SEM observations of crack propagation, in some cases commercially obtained titanium nitride (TiN) powder (<3 µm size) (Sigma Aldrich, St. Louis, MO) was added to the Al₂O₃ nanopowder before the ball-milling step. The resulting nanocomposites consisted of 75 vol% Al₂O₃, 15 vol% TiN, and 10 vol% MWCNTs.

2.2. Characterization

The density of the nanocomposites was measured using the Archimedes principle with distilled water as the immersion medium. The theoretical density of the Al₂O₃/10%MWCNTs nanocomposite was assumed to be 3.765 Mg.m⁻³, which is based on rule-of-mixture using the following densities of the pure phases: Al₂O₃: 3.950 Mg.m⁻³ and MWCNTs: 2.10 Mg.m⁻³. [11]

Cross-sections of the nanocomposites were cut from the disks, and using routine metallographic procedures they were polished to an 1- μm finish. The cross-sections were observed in a SEM (LEO 1530VP, Carl Zeiss, Munich, Germany), operated at 10 KV accelerating voltage. The Al_2O_3 grain size was measured using the SEM micrographs in conjunction with a public-domain image analysis software (ImageJ). Some specimens were fractured, and the fracture surfaces were also observed in the SEM.

Raman spectra from as-received MWCNTs, acid-treated MWCNTs, and as-sintered Al_2O_3 /10%MWCNTs nanocomposite were obtained using a confocal Raman microscope (Alpha 300, WiTec, Ulm, Germany) with Nd-YAG 532 nm wavelength laser excitation.

2.3. In Situ SEM Observation of Crack Propagation

Stable propagation of the crack is of paramount importance in these experiments. To that end, Al_2O_3 /10% MWCNTs nanocomposite specimens were machined into the geometry shown in Fig. 1.[12] The compression of such a specimen results in the stable propagation of a sharp crack (Δc) at the root of the notch. This test geometry can be considered as one half of the classic double-cantilever drilled-hole (DCDC) geometry, where the Mode I K -field induced at the crack

tip due to the constrained bending of the ‘pillars’ is independent of the crack size.[12] This make crack propagation highly stable. Specimens according to Fig. 1 were precisely machined and polished, and a pre-crack was introduced by razor-blade ‘sawing’ with 1- μm diamond paste using a procedure described elsewhere.[13] These specimens were loaded using a piezo-driven micro-test device (MT10141, Deben, Woolpit, UK) mounted on to the SEM stage. One of the drawbacks of this test geometry is the high compressive force needed to propagate the crack, limiting the size of the specimen that can be tested in the micro-test device. The propagation of crack was observed *in situ* in the SEM using three different approaches. First, the SEM was focused on the tip of the crack and it was followed, at low and high magnifications, as it propagated through the nanocomposite. Second, the load was held constant, which halted the crack-tip propagation, and the entire wake of the crack tip was imaged. This was done for various total crack lengths. These results were used to measure the crack opening displacements (CODs) along the crack length, giving us the crack profiles. Third, the SEM was focused on one region just behind the crack tip in the wake, and the crack tip was propagated by increasing the applied load. This resulted in a series of images of the same region as the crack walls separated.

The freshly created new surfaces during the crack propagation were found to charge in the SEM due to the insufficient electrical conductivity in these nanocomposites. In some cases this obscured the important microstructural details inside the cracks. To address this issue, additional experiments were performed on $\text{Al}_2\text{O}_3/15\%\text{TiN}/10\%\text{MWCNTs}$ nanocomposites containing 15 vol% TiN with high electrical conductivity.

2.4. T-Curve Measurement

Single-edge ‘V’ notch beam (SEVNB) specimens (3 mm width $\times$ 4 mm thickness $\times$ 25 mm long) of $\text{Al}_2\text{O}_3/10\%\text{MWCNTs}$ nanocomposites were machined with a shallow notch introduced using a diamond-saw blade. A sharper ‘V’ notch was later introduced using the razor-blade procedure described elsewhere.[13] A sharp crack was propagated from the root of the sharp notch using the sandwich beam method.[14] Here the SEVNB sample was sandwiched between two steel beams (5 mm width $\times$ 5 mm thickness $\times$ 30 mm long) and loaded in four-point bending (10 mm inner span, 20 mm outer span) in a universal testing machine (Model 5800, Instron, Norwood, MA) until a through-thickness crack ‘popped-in.’ The crack extensions (Δc) beyond the ‘V’ notch were measured accurately using an optical microscope. While this is a well-known method for

obtaining a sharp crack,[14] the length of the crack cannot be predicted *a priori*. Also, it is intractable to obtain a very short through-thickness starter-crack using this method. Several specimens were subjected to this procedure to obtain a few acceptable SEVNB specimens with well-defined sharp cracks of different lengths. These specimens were then tested in four-point bending in the universal testing machine at a fast loading rate (0.1 mm.min⁻¹ crosshead speed) to fracture them. The breaking load, and the dimensions of the specimen and the crack (*c*), were used to calculate the Mode I toughness, *T*, using the following equations:[15]

$$T=\psi\sigma_A c^{0.5}, \quad (1a)$$

where σ_A is the breaking stress, and ψ is given by:

$$\psi = \left[\frac{\sqrt{\pi(1+2\alpha)}}{(1-\alpha)^{1.5}} \right] \times [1.12-3.68\alpha+11.95\alpha^2-25.85\alpha^3+33.10\alpha^4-22.44\alpha^5+6.18\alpha^6] \times [1-2\alpha(0.64-0.37\alpha+0.058\alpha^2)], \quad (1b)$$

as a function of α , which is the ratio of the crack length and the beam thickness, $\alpha=c/t$.

3. Results and Discussion

3.1. Microstructure

The relative density of Al₂O₃/10%MWCNTs nanocomposite is measured to be 3.730 Mg.m⁻³

or ~99%. Figure 2 is a SEM micrographs of the polished nanocomposite showing dense and uniform nature of the microstructure with no texture. The average grain size of the Al_2O_3 is estimated at ~360 nm. The MWCNTs appear to be random and located at alumina grain boundaries primarily.

Figure 3 shows Raman spectra of the as-received MWCNTs, acid-treated MWCNTs, and Al_2O_3 /10%MWCNTs nanocomposite. The classic D, G, and G' bands[11] are clearly visible in all three spectra, confirming that the MWCNTs are preserved during the acid-treatment and the subsequent SPS process, making these materials true Al_2O_3 /MWCNTs nanocomposites. The D/G intensities ratios are found to increase from 0.125 to 0.290 to 0.394 going from as-received MWCNTs to acid-treated MWCNTs to Al_2O_3 /10%MWCNTs nanocomposite, respectively. This suggests progressively increasing concentration of defects in the MWCNTs during processing,[11] which is not unexpected. It is interesting to note that all three bands (D, G, and G') are shifted to higher wavenumbers in the nanocomposite. This can be attributed to the residual compressive stress in the MWCNTs during cooling from the SPS temperature ($\Delta T=1275^\circ\text{C}$). Thomsen *et al.*[16] have experimentally calibrated the G-band shift in MWCNTs with applied compressive stress

(using a diamond anvil cell), and they have shown that the linear proportionality constant is 4.3 GPa.(cm⁻¹)⁻¹. Using the G-band shift of 15.9 cm⁻¹ (from 1564.7 cm⁻¹ to 1580.6 cm⁻¹) in Fig. 3 and the calibration constant, the compressive residual stress (σ_R) in the MWCNTs in the nanocomposite is estimated at -3.7 GPa. Considering that the coefficient of thermal expansion (CTE or α) of MWCNTs is near zero,[17] and that of Al₂O₃ is $\sim 9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$,[18] radial compressive σ_R in MWCNTs is estimated to be -3.47 GPa. This is using the simple relation for a cylindrical fiber (F) embedded in an infinite matrix (M):[19]

$$\sigma_R = \frac{(E_F E_M)(1+\nu_F)(\Delta\alpha\Delta T)}{(1+\nu_F)E_M(1-2\nu_F) + E_F(1+\nu_M)}, \quad (2)$$

and the higher-end elastic modulus of MWCNTs $E_F=810$ GPa[20] and that of alumina $E_M=390$ GPa[21] (Poisson's ratios $\nu_M=\nu_F=0.2$ [21]). This calculated value of σ_R and that estimated from the Raman shift measurements compare favorably despite the simplified nature of this analysis.

3.2. T-Curve and *Ex Situ* Observations

Figure 4 plots the measured T values at different crack extensions, Δc , in the Al₂O₃/10%MWCNTs nanocomposite reaching a plateau toughness of $T_\infty=4.6 \text{ MPa.m}^{0.5}$. As mentioned earlier, it is difficult to obtain short-crack toughness reliably, and, therefore, the initial

toughness ($T_0=2.75 \text{ MPa.m}^{0.5}$) is taken to be the grain-boundary toughness of Al_2O_3 , [21] which is a reasonable assumption considering the intergranular nature of fracture in this nanocomposite. Overall, the toughening in this nanocomposite is modest, and it is attributed to crack-wake bridging by the MWCNTs. The curve in Fig. 4 is a fit from a crack-wake bridging model described in section 3.4, and the square point is the toughness estimate from the crack-profile measurements (section 3.4).

Figure 5A is a SEM image of a crack in the nanocomposite before failure showing bridging by MWCNTs. There are several observations of note in these *ex situ* experiments. First, the density of bridges is very high; in a given plane the MWCNTs bridges appears to be about ~500 nm apart. Considering that the diameter and the concentration of the MWCNTs are 50-70 nm and 10 vol%, respectively, almost every MWCNT in the nanocomposite appears to take part in crack-wake bridging. Second, the MWCNTs appear tapered (arrows in Fig. 5A). The fully pulled out MWCNTs in the fractured nanocomposite confirm this tapered failure of MWCNTs (arrows in Fig. 5B). Figure 5C (arrows) shows embedded MWCNTs with missing core which appears to have been pulled out during fracture. Figure 5C further confirms the intergranular fracture in the Al_2O_3

matrix and the location of the MWCNTs at the Al_2O_3 grain boundaries primarily. This type of ‘sword-sheath’ pullout and failure of MWCNTs has been reported.[5,22] Considering the very high compressive σ_R in the MWCNTs in these nanocomposites, the clamping of the MWCNTs embedded in the Al_2O_3 matrix is expected to be very effective, precluding frictional pullout at the Al_2O_3 -MWCNT interface. Furthermore, it has been shown that occasional covalent bonding exists between adjacent ‘shells’ within a MWCNT.[23] Thus, the pullout of the MWCNTs occurs by this unique process, where inner ‘shells’ not only slide but also unravel (referred to as plastic deformation) and fail.[5] Thus, the tapered shape results from the complex geometry, where the unraveling and the failure occur within different shells and along various locations along the MWCNT length. Al signal could not be detected on the pulled-out MWCNTs, indicating that shear fracture within the Al_2O_3 matrix does not occur in the immediate vicinity surrounding the MWCNTs. This is in contrast to MWCNTs-reinforced glassy-matrix nanocomposites, where shear fracture within the brittle glassy matrix has been shown to occur, with the pulled-out MWCNTs having a coating of glass at the base of the pullout zone.[24-26]

3.3. In Situ Observation of Crack Propagation

Figures 6A-6D show a series of SEM micrographs along the wake of a static, stable crack (crack tip at the bottom) in a Al_2O_3 /10%MWCNTs nanocomposite under a fixed compressive load (Fig. 1 shows specimen geometry). Extensive crack-bridging is observed in Figs. 6C-6D closer to the crack tip, and extensive pullout is observed in Figs. 6A and 6B further away from the crack tip. Figures 7A-7C show a sequence of SEM micrographs from a fixed location in the wake of the crack tip, in a different Al_2O_3 /10%MWCNTs nanocomposite specimen, as the load is increased and the crack tip propagates stably (downwards). Extensive crack-wake bridging by MWCNTs and pullout is observed in these micrographs as well. The MWCNTs appear tapered, similar to what is seen in Fig. 5A. Unfortunately, charging of the fresh fracture surfaces in SEM due to the poor electrical conductivity of these nanocomposites obscures the details in Figs. 6 and 7. It was discovered that at slightly chipped top surface (instead of polished top surface) of the specimen, charging is less severe, allowing more details to be observed. Figures 8A-8D show a sequence of SEM micrographs from a fixed location in such a Al_2O_3 /10%MWCNTs nanocomposite specimen with increasing load, where extensive crack-bridging pullout is visible more clearly deep into the

crack. Perhaps the most surprising observation in Figs. 6-8 is the proliferation of aligned MWCNTs crack-bridges, despite the fact that these materials are random polycrystalline nanocomposites (isotropic). In orthotropic ceramic-matrix nanocomposites, reinforced by unidirectionally aligned MWCNTs, such extensive aligned MWCNTs crack-bridging is observed, which is to be expected.[17, 25, 27] Thus, the *in situ* observations in Figs. 6-8 suggest that the randomly oriented crack-bridging MWCNTs ‘unfurl’ (or disentangle) and align as the crack walls separate. Unfortunately, the view of the initial formation of the MWCNTs crack-bridges near the tip is still obscured by the charging effect in the SEM.

In order to address this charging issue, *in situ* direct SEM observation of crack propagation in better-conducting $\text{Al}_2\text{O}_3/15\%\text{TiN}/10\%\text{MWCNTs}$ nanocomposites was performed. It is assumed that the small amount of TiN does not affect the overall toughening mechanism of crack-bridging by MWCNTs. Figures 9A-9E show a sequence of SEM micrographs from a fixed location in the wake of the crack tip in a $\text{Al}_2\text{O}_3/15\%\text{TiN}/10\%\text{MWCNTs}$ nanocomposite specimen as the load is increased and the crack tip propagates stably (downwards). Overall there is less charging in this specimen, but the region at the crack tip still charges. However, just behind the

crack tip in Fig. 9B (inset) one can observe MWCNTs that are not aligned, supporting the above hypothesis. As discussed above, with increasing crack-wall separation, the random MWCNTs become more aligned. The extreme flexibility of the MWCNTs by virtue of their size, relative to conventional whiskers or short-fibers, allows this unique behavior. The subsequent pullout of MWCNTs can be seen more clearly in Figs. 9D and 9E. Once again, the pullout is primarily in the form of ‘sword-sheath,’ with helical unraveling of the MWCNTs. Thus, the ‘unfurling,’ alignment, and non-frictional pullout of the MWCNT reinforcements is unique to these nanocomposites, and fundamentally different relative to conventional whisker- or short-fiber-reinforced isotropic ceramic-matrix composites, where frictional pullout at the matrix-reinforcement interface is more prevalent.[28, 29]

3.4. Crack Opening Displacement Measurements and T -Curve Modeling

Figure 10 is a plot of measured COD ($2u$) as a function of distance behind the crack tip, X , for a stable, equilibrium crack ($\Delta c=865\text{ }\mu\text{m}$) in a $\text{Al}_2\text{O}_3/10\%\text{MWCNTs}$ nanocomposite specimen under a fixed compressive load in the SEM (Fig. 1 shows the specimen geometry). The calculated Irwin parabola crack profile for traction-free Al_2O_3 matrix (toughness $T_0=2.75$

MPa.m^{0.5} or crack-resistance $R_O=19.4 \text{ J.m}^{-2}$) is included in Fig. 10:[21, 30]

$$u(X) = \left(\frac{T_0}{E}\right) \left(\frac{8X}{\pi}\right)^{0.5}, \quad (3)$$

where E is the Young's modulus (390 GPa for Al₂O₃). The effect of crack-bridging in sustaining a wider COD for a given X in the nanocomposite is clearly evident in Fig. 10. To quantify this effect, the bridged crack profile is fitted using the following:[21, 30]

$$u(X) = \left\{\left(\frac{8X}{\pi}\right)^{0.5} \left(\frac{T_0}{E}\right)\right\} + \left\{\left(\frac{4}{\pi E}\right) \int_0^{\Delta c} P(X') \left(\frac{X}{X'}\right)^{0.5} - \frac{1}{2} \ln \frac{(X'^{0.5} + X^{0.5})}{(X'^{0.5} - X^{0.5})} dX'\right\}, \quad (4)$$

where X is the field point where the COD is evaluated and X' is the source point for the crack-bridging traction stress function $P(X')$. The best fit to the bridged-crack profile in Fig. 10 results in the bridging-stress function:[21, 30]

$$P(X') = P_M \left(1 - \frac{X'}{\Delta c_\infty}\right)^n, \quad (5)$$

where P_M is the maximum bridging stress (=54 MPa), Δc_∞ is the length of steady-state bridging zone (=1.1 mm), and n is the exponent (=2). Using the crack profile in Eqn. 4, the function in Eqn. 5 can be used to plot the constitutive $P(u)$ function (Fig. 11). Since this $P(u)$ function is near-linear, it can be approximated by a best fit straight line as shown in Fig. 11 and below:[21, 30]

$$P(u) = P_M \left(1 - \frac{u}{u_\infty}\right), \quad (6)$$

where P_M is found to be 56 MPa, and $2u_\infty$ is found to be 0.98 μm — the COD at the mouth of the crack when crack-bridging zone length (Δc_∞) reaches steady-state. It is interesting that the near-linear constitutive $P(u)$ function for the $\text{Al}_2\text{O}_3/10\%\text{MWCNTs}$ nanocomposite is not different from what has been observed in other crack-bridging toughened ceramics and composites where frictional grain-pullout is the dominant energy-dissipation mechanism.[21] This $P(u)$ function can now be used to calculate the T -curve independently. The steady-state crack-resistance is given by: [21]

$$R_\infty = R_0 + 2 \int_0^{u_\infty} P(u) du = R_0 + \frac{1}{2} P_M (2u_\infty), \quad (7)$$

which is 46.8 J.m^{-2} (with $R_0=19.4 \text{ J.m}^{-2}$), and the steady-state toughness is given by: [21]

$$T_\infty = (R_\infty E)^{0.5}, \quad (8)$$

which is $4.49 \text{ MPa.m}^{0.5}$, using $E=430 \text{ GPa}$ for the nanocomposite as the upper-end rule-of-mixtures estimate. This compares with the steady-state toughness $4.6 \text{ MPa.m}^{0.5}$ measured in Fig. 4. In order to calculate the rising part of the T -curve from T_0 to T_∞ , a procedure described in Ref. [21] is used. Thus, T as a function of the COD ($2u$) at the mouth of the crack-bridging zone as it expands is given by:[21]

$$T(u) = [ER_B(u) + T_0^2]^{0.5}, \quad (9)$$

where $R_B(u)$ is the bridging contribution to the crack-resistance, and it is given by: [21]

$$R_B(u) = 2P_M u \left(1 - \frac{u}{2u_\infty}\right). \quad (10)$$

To translate $T(u)$ to $T(\Delta c)$, Eqns. 9 and 10 are solved iteratively using the following crack-profile approximation: [21]

$$u(\Delta c) = \left(\frac{T(\Delta c)}{E}\right) \left(\frac{8\Delta c}{\pi}\right)^{0.5}. \quad (11)$$

The resulting T as a function of Δc is plotted in Fig. 4. While toughness at shorter Δc could not be measured experimentally, this analysis predicts a reasonable rising T -curve in the $\text{Al}_2\text{O}_3/10\%\text{MWCNTs}$ nanocomposite.

The *in situ* direct and the *ex situ* observations of crack propagation presented here have advanced our understanding of toughening mechanism in $\text{Al}_2\text{O}_3/\text{MWCNTs}$ nanocomposites. Although the toughening effect is modest, the toughening mechanism in these nanocomposites is confirmed to be exceptional, relative to conventional whisker- and short-fiber-reinforced isotropic ceramic-matrix composites. In particular, the flexible nature of individual MWCNTs results in their ‘unfurling,’ which in turn results in high density of crack-bridges even when these

$\text{Al}_2\text{O}_3/\text{MWCNTs}$ nanocomposites are isotropic. The modest toughening can be attributed to the pullout of the individual crack-bridging MWCNTs that occurs primarily at the weakly bonded (van der Waals) nested CNT layers, and not at the Al_2O_3 -MWCNT frictional interfaces which can be more effective. This is possibly due to the fact that the MWCNTs are clamped within the Al_2O_3 matrix by very high compressive residual stress ($\sigma_R \sim 3.7$ GPa) as shown in section 3.1., and also due to mechanical interlocking at the Al_2O_3 -MWCNTs interfaces.[5, 22] Thus, the use of ceramic matrices with CTEs much lower than that of Al_2O_3 , and closer to that of MWCNTs, may promote more frictional pullout at the ceramic-MWCNT interfaces for more effective toughening. Alternatively, more covalent bonds between the nested CNT layers will certainly improve the efficacy of the MWCNTs in crack-bridging. Approaches such as electron beam irradiation (EBI)[31] and carbon ion beam irradiation (CIBI)[32] have been shown to be effective in achieving stronger bonding between the nested layers in MWCNTs. However, the EBI and the CIBI approaches may have practical limitations in terms of scalability and damage to the outer layers, respectively.[33] The CIBI approach can also be used to cross-link individual MWCNTs to form strongly bonded MWCNTs bundles.[33] This could possibly result in frictional pullout at

the interfaces between the MWCNTs bundles and the ceramic matrix.[34] However, these large-diameter MWCNTs bundles are likely to be significantly less flexible compared to individual MWCNTs, which will lead them to behave more like conventional whiskers or short-fibers. In that case, only the favorably oriented bundles (normal and near-normal to crack plane) in an isotropic nanocomposite will form effective crack-bridges, while those at an angle would fracture prematurely in bending, similar to what happens in conventional whiskers or short-fibers reinforced isotropic ceramic composites.[35] Thus, navigating these trade-offs will be key to the design and creation of high-toughness isotropic ceramic/MWCNTs nanocomposites of the future.

4. Summary

Fully dense, isotropic Al_2O_3 /10%MWCNTs nanocomposites with individually dispersed acid-treated MWCNTs are fabricated using colloidal processing and SPS. The MWCNTs are primarily embedded within Al_2O_3 grain boundaries, and are clamped by very high compressive residual stress of the order of -3.7 GPa. The *in situ* direct and the *ex situ* observations of crack propagation in SEM provide deep insights into the exceptional crack-bridging toughening

mechanisms in these nanocomposites. It is revealed that randomly-oriented MWCNTs bridge the crack by ‘unfurling,’ aligning normal to the crack plane, and pulling out. It is confirmed that the MWCNTs pullout occurs primarily between the weakly bonded nested layers (‘sword-sheath’), accompanied by some helical unraveling. The T -curve ($T(\Delta c)$) measured using four-point bending with $\text{Al}_2\text{O}_3/10\%\text{MWCNTs}$ nanocomposite specimens containing sharp starter-cracks of various lengths shows modest toughening, with T_∞ reaching $4.6 \text{ MPa.m}^{0.5}$, from baseline Al_2O_3 grain-boundary toughness T_0 of $2.75 \text{ MPa.m}^{0.5}$. Crack profile of a stable equilibrium crack in the $\text{Al}_2\text{O}_3/10\%\text{MWCNTs}$ nanocomposite is measured, and it is used to calculate the crack-bridging-stress/COD ($P(u)$) constitutive relation. This relation is used to calculate the T -curve independently, and it is found to compare favorably with the experimentally measured T -curve.

Acknowledgements

We thank Dr. M. Estili (NIMS, Japan), Prof. V. Jayaram (IISc, India), Dr. Y. Sakka (NIMS, Japan), and Prof. B.W. Sheldon (Brown University) for fruitful discussions. The financial

support for this research from the II-VI Foundation and the US Department of Energy, Basic Energy Sciences (grant # DE-FG02-10ER4677) is gratefully acknowledged.

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Figure Captions

1. Schematic illustration of the specimen geometry allowing stable crack propagation used for the *in situ* direct observations in the SEM, with $h=0.6$ mm, $d=1.9$ mm, $w=1.2$ mm, and $b=1.1$ mm.[12]
2. SEM micrograph of polished cross-section of as-sintered $\text{Al}_2\text{O}_3/10\%\text{MWCNTs}$ nanocomposite.
3. Raman spectra of as-received MWCNTs, acid-treated MWCNTs, and as-sintered $\text{Al}_2\text{O}_3/10\%\text{MWCNTs}$ nanocomposite (532 nm laser excitation). The D, G, and G' bands are marked by dashed lines, indicating the positions for as-received MWCNTs.
4. The measured toughness of the $\text{Al}_2\text{O}_3/10\%\text{MWCNTs}$ nanocomposite at various sharp-crack extensions Δc (solid circles) using the 4-point bend test. The open circle represents grain boundary toughness (T_0) of Al_2O_3 . [21] The open square is the toughness estimated from the crack-profile measurements. The solid curve is the calculated T -curve using crack-bridging parameters determined independently from the crack-profile measurements and fitting.
5. *Ex situ* SEM micrographs of fracture in the $\text{Al}_2\text{O}_3/10\%\text{MWCNTs}$ nanocomposite: (A) bridged crack showing tapered MWCNTs pullout (arrows) in a still intact specimen, (B) half of the fractured specimen showing 'sword-sheath' MWCNTs pullout (arrows), and (C) fracture surface

showing embedded MWCNT shells (arrows) and intergranular fracture.

6. *In situ* SEM micrographs of a stable equilibrium crack in a Al_2O_3 /10%MWCNTs nanocomposite specimen showing crack-bridging by MWCNTs different locations along the crack (crack tip at the bottom).

7. *In situ* SEM micrographs of a fixed location in a Al_2O_3 /10%MWCNTs nanocomposite specimen as the crack propagates stably downwards.

8. *In situ* SEM micrographs of a fixed location in a Al_2O_3 /10%MWCNTs nanocomposite specimen, where the surface is chipped, as the crack propagates stably downwards.

9. *In situ* SEM micrographs of a fixed location in a Al_2O_3 /15%TiN/10%MWCNTs nanocomposite specimen as the crack propagates stably downwards. Inset in (B) shows a higher magnification view just behind the crack tip.

10. Profile of a stable equilibrium crack ($\Delta c=865 \mu\text{m}$) in a Al_2O_3 /10%MWCNTs nanocomposite specimen. The dashed curve is the Irwin parabola crack profile for Al_2O_3 matrix (Eqn. 3). The solid curve is a fit to Eqn. 4, profile of a bridged crack.

11. Dashed curve is the constitutive crack-bridging stress function $P(u)$ calculated from the crack

profile measurements. Solid line is the linear fit with $P_M=56$ MPa and $2u_\infty=0.98$ μm .

Figure 4