Damping behavior of carbon nanotube reinforced aluminum oxide coatings by nanomechanical dynamic modulus mapping

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Nanomechanical dynamic analysis has been utilized to evaluate damping behavior of plasma sprayed carbon nanotube (CNT) reinforced Al2O3 ceramic coatings. Addition and dispersion of CNTs in Al2O3 matrix elicited modulus enhancement from 200 to 400 GPa. Tan delta increases from 0.26 for Al2O3 to 0.39 with 8 wt % CNT coating. CNT bending and curling, Al2O3 coating on CNT, interparticle Al2O3 friction, and CNT/splat sliding serve as strong loss mechanisms in imparting enhanced damping to Al2O3 nanocomposites reinforced with CNTs. Damping and fracture toughness of CNT-Al2O3 coating is semiempirically related to the enhancement of storage modulus and tan delta with varying CNT content and degree of dispersion. © 2008 American Institute of Physics [DOI: 10.1063/1.2978185]

I. INTRODUCTION

High surface area to weight ratio of carbon nanotubes (CNTs) and the interface friction between matrix and CNT make nanotube reinforced nanocomposites as excellent dampeners.1,2 Damping studies of CNT reinforced nanocomposite have been largely restricted to polymer matrix composites.3–4 Zhou et al.5 concluded that damping with CNT addition improved because of stick-slip frictional loss in the resin matrix. Koratkar et al.6 demonstrated strong dependence of CNT dispersion in influencing the damping of polycarbonate-CNT nanocomposite. Yap7 elicited negative stiffness associated with CNTs, where frictional energy dissipation has shown to enhance damping by up to 600%. In the present study, damping characteristics of plasma sprayed aluminum oxide ceramic coating reinforced with CNTs have been evaluated. Complexity arises in the ceramic matrix owing to the problem of CNT dispersion, and high temperature processing requirements for fabricating ceramics. Although some researchers have successfully synthesized Al2O3-CNT nanocomposites and reported fracture toughness enhancement up to three times,6–8 However damping behavior of Al2O3-CNT nanocomposite largely remains unexplored.

It is important to briefly introduce the summary of our earlier work on plasma sprayed Al2O3-CNT coatings to fully appreciate the damping behavior study described in this paper.6,9 Al2O3 (99.5% pure, 150 nm particle size) was commercially spray dried to attain spherical agglomerate of ~15–60 μm (termed A-SD powder). A-SD powder was consequently blended with 4 wt % CNT (95%+pure, 40–70 nm outside diameter, 0.5–2.0 μm long) to result A4C-B powder. CNTs were dispersed only on the surface and in the dome cavity of A4C-B powder.6 In order to improve dispersion behavior of nanotubes, Al2O3 and CNTs were spray dried together to result A4C-SD (4 wt % CNT) and A8C-SD (8 wt % CNT). These powders were plasma sprayed to result A-SD, A4C-B, A4C-SD, and A8C-SD coatings on AISI 1020 steel substrate. Typical layer by layer deposition in plasma spraying results in the improved dispersion of CNTs throughout the coating.6,10,11 Plasma spraying parameters were optimized to obtain full melting (FM) of the surface of powder particle to render melt densification and partial melting (PM) of the core to result solid state sintering densification. CNTs survived harsh environment of plasma processing and formed CNT bridges and CNT mesh in the microstructure.6 Fracture toughness improvements of up to 57% were observed with CNT reinforcement (3.22, 3.86, 4.60, and 5.04 MPa m1/2 for A-SD, A4C-B, A4C-SD, and A8C-SD, respectively).6,12 Although A4C-B and A4C-SD coatings contained same 4 wt % CNT, higher fracture toughness was displayed by A4C-SD coating due to improved CNT dispersion by using spray dried composite powder.6

II. EXPERIMENTAL DETAILS

Nanomechanical dynamic modulus mapping traces the storage modulus (elastic part), and loss modulus (viscous/plastic part) of Al2O3-CNT nanocomposite coating. Hence, damping force can be quantitatively represented by the loss ratio or tan delta (td), which is a ratio of loss modulus to storage modulus. Dynamic modulus mapping was performed using Hysitron's TribolIndenter® (Minneapolis, MN) at a static force of 2.0 μN and dynamic force of 0.5 μN with lock-in frequency of 200 Hz. Time constant and sensitivity gain were optimized for good image resolution and data collection. Pyramidal Berkovich indenter tip (100 nm) rasters across the material surface and provide its topographic image via scanning probe microscopy (SPM) imaging. Modulus mapping performs 65,536 tests i.e., dynamic testing is done at each of those points providing a 256×256 pixel resolution image. Single scan provides topographic information, storage and loss stiffness, storage and loss modulus, and td maps. Contact stiffness of the indenter specimen is calculated via the Kelvin model, Fig. 1(a), from which stiffness of specimen can be calculated by directly subtracting the stiff-
ness of the indenter from the stiffness measurement in air.\textsuperscript{13,14} Herein, phase and displacement shift of material is captured, Fig. 1(b), from the quasistatic load and much smaller dynamic load of the probe tip.\textsuperscript{13} From the dynamic load, the equation of motion balances as $F_0 \sin(\omega t) = mx + Cx + kx$ where the displacement response at the same frequency oscillation is $x = X \sin(\omega t - \varphi)$. Where, $F_0$ is the maximum force, $m$ is the mass of center plate, $C$ and $k$ are combined damping and stiffness, respectively, $X$ is the amplitude of displacement oscillation, $\omega$ is angular frequency, and $\varphi$ is phase shift of displacement.

Dynamic modulus is a complex comprising real part of storage modulus and an imaginary part as loss modulus. Correspondingly, storage modulus ($E'\) and loss modulus ($E''\) and $\tan\delta$ can be calculated as $E' = k_x \sqrt{\pi/2 \Delta_c}$, $E'' = \omega C_x \sqrt{\pi/2 \Delta_c}$, and $\tan\delta = C_x \omega / k_x$, where $k_x$ and $C_x$ are the stiffness and compliance of sample deduced by subtracting the instruments stiffness and compliance, respectively, $A_c$ is the contact area, which is dependent on the contact depth. Contact depth of the indenter is described through tip area function during instrument calibration. Storage modulus relates to stiffness of ceramics, since it is in direct phase with material response to loading. This analysis assumes elastic recovery during unloading, which is indeed true for ceramics.

III. RESULTS AND DISCUSSION

Surface profile of A-SD coating, Fig. 2(a), and corresponding modulus map, Fig. 2(b), shows storage modulus as a color spread over an area of $4 \times 4$ $\mu m^2$. Red areas and black streaks in Fig. 2(b) correspond to the edge effects of the SPIM arising from the porous regions and sharp corners, respectively. The storage modulus histogram from an average of more than 2500 tests is shown in Fig. 2(c), which exhibited an average value of 200 GPa for A-SD coating. Topography, corresponding storage modulus map, and modulus histogram for A4C-B coating, A4C-SD coating, and A8C-SD coating are shown in Figs. 2(d)–2(f), respectively. When compared to A-SD coating, the average modulus in A4C-B shifted to a higher value [\textasciitilde 220 GPa, Fig. 2(f)] with a shoulder hump of \textasciitilde 250 GPa. Modulus values of A4C-SD coating show bimodal peaks at 260 and 350 GPa [Fig. 2(f)]. Distribution of modulus for A8C-SD coating [Fig. 2(f)] revealed trimodal peaks with main peak at 230 GPa, and prominent shoulder peaks at \textasciitilde 310 and \textasciitilde 400 GPa.\textsuperscript{12}

Modulus depends on (i) porosity, (ii) CNT content, (iii) CNT dispersion, (iv) microstructure (PM/FM), and (v) CNT/Al$_2$O$_3$ interface. Lower modulus value of \textasciitilde 200 GPa for A-SD coating (when compared to that of 390 GPa for monolithic Al$_2$O$_3$), is attributed to the layered structure and porosity inherent in the plasma sprayed coatings.\textsuperscript{15} Density of the A-SD, A4C-B, A4C-SD, and A8C-SD coatings is measured to be 3.47, 3.40, 3.52, and 3.53 g/cm$^3$, respectively, corresponding to the theoretical density of 87\%, 87.2\%, 90.2\%, and 94\%, respectively. Presence of porosity in the plasma sprayed coatings, thereby, has rendered lower modulus values when compared to that of its theoretical value. Modulus values obtained for A-SD have been assumed as a base for comparing with CNT-reinforced Al$_2$O$_3$ coatings. A4C-B coating has shown meager 10\% increase in the storage modulus (from 200 to 220 GPa) with 4 wt % CNT addition, which is attributed to poor CNT dispersion. Marginal CNT dispersion in A4C-B coating has resulted its shoulder peak at 250 GPa. Dominating regions of modulus (bimodally at 260 and 350 GPa) observed in A4C-SD coating are attributed to improved CNT dispersion and bimodal microstructure.\textsuperscript{6,12,16–24} It is emphasized that although CNT content of A4C-B and A4C-SD is same (4 wt \%), higher modulus values are observed for A4C-SD coating. Overall lower modulus (\textasciitilde 220 GPa) of A4C-B coating arises because of relatively poor dispersion of CNTs that causes unavailability of CNTs to anchor with Al$_2$O$_3$ matrix. Modulus ranging \textasciitilde 260 GPa in A4C-SD coating is reasoned to the presence of CNTs in PM region where particles are consolidated by solid state sintering. Increased modulus of \textasciitilde 350 GPa (\textasciitilde 75.0% improvement) is attributed to the presence of dispersed CNTs in fully melted and resolidified (FM) matrix region. When compared to A-SD coating, increase in the modulus of A8C-SD coating by two times (from 200 to 400 GPa) arises because of enhanced content of dispersed CNTs in the matrix. Hence, a high modulus (\textasciitilde 400 GPa) of dense FM region is matched by the presence of CNTs. Bi-furcating peaks at 230 and 310 GPa arise because of PM region, where CNT agglomerated regions give modulus peak \textasciitilde 230 GPa near to that of A4C-B, and CNT dispersed regions give modulus peak of \textasciitilde 310 GPa (higher than that of A4C-SD) because of enhanced CNT content in A8C-SD, as observed in Fig. 2(f).

Figure 3(a) shows CNTs interfacing with Al$_2$O$_3$ splats in PM and FM regions. CNTs embedded in the PM and FM regions reinforce the matrix and render enhanced energy loss because of increased available CNT surfaces. This bimodal microstructure (PM and FM regions) has also shown beneficial effects on entrapping crack propagation, with CNTs rendering enhanced mechanical properties (e.g., strength, hardness, and fracture toughness).\textsuperscript{6,19–24} Role of bimodal microstructure in imparting toughness to plasma sprayed coatings, and energy dissipation because of nanoparticle addition has also been validated by Kreiweis.\textsuperscript{2} Interfacial wetting of Al$_2$O$_3$ with CNT reinforcement also induce energy loss (toughening) of Al$_2$O$_3$-CNT nanocomposite via interface shearing and CNT pull out from the matrix.\textsuperscript{9,25,26} Figure 3(b) shows merging of CNT with Al$_2$O$_3$ matrix, forming an interface \textasciitilde 2 nm thick. Creation of Y junctions between CNT and Al$_2$O$_3$ induces additional toughening via formation of two-dimensional anchors.\textsuperscript{25}
Since storage modulus falls in phase with the materials response, it is a direct measure of relating the resilience. \(^{27}\) Ratio of loss modulus to storage modulus (\(t_d\)) for the plasma sprayed A-SD, A4C-B, A4C-SD, and A8C-SD coatings is presented in Fig. 4. Cumulative \(t_d\) at 50% (\(t_d_{50}\)) is taken as a reference to compare the loss ratio revealed by the plasma sprayed coatings. \(t_d\) value (\(t_d_{50}\)) of 0.26, 0.27, 0.30, and 0.39 is observed for A-SD, A4C-B, A4C-SD, and A8C-SD coatings, respectively.

It is interesting to observe that increase in the fracture toughness (3.22, 3.86, 4.60, and 5.04 MPa m\(^{1/2}\) for A-SD, A4C-B, A4C-SD, and A8C-SD coatings, respectively) with
the increasing CNT content and dispersion directly correlates with the increasing storage modulus (Fig. 2) and the increasing td (Fig. 4). Herein, we propose a model to delineate the role of CNT content and dispersion in understanding the damping behavior. This analysis is based on the Antis equation that correlates fracture toughness (K) of ceramic with the modulus (E, taken as 390 GPa) and hardness (H) as

\[ K = \frac{1}{H} \left( \frac{P}{c} \right)^{1/2} \left( \frac{E}{H} \right)^{3/2}, \]

where \( c = 0.016 \) is material independent constant, \( P \) is the applied load, and \( c \) is the crack length. Since hardness of these coatings do not vary significantly (714.2 \( \pm \) 14.9, 709.6 \( \pm \) 8.4, 738.7 \( \pm \) 12.9, 712.7 \( \pm \) 2.3 VHN, respectively, for A-SD, A4C-B, A4C-SD, and A8C-SD coatings), the role of hardness in changing the fracture toughness can be assumed as a constant.\(^6\) Thereby, rate of change in the fracture toughness (\( \delta K \)) can be related to the sum of change of square roots of storage modulus (\( \delta E' \)) and change of td \( [\delta (td_{50})] \), \( k_1 \) and \( k_2 \) being constants.

\[ \delta K = k_1 \delta E'^{1/2} + k_2 \delta (td_{50})^{1/2}. \]  

The increase in the fracture toughness is largely contributed by (i) CNT content and (ii) CNT dispersion. Table I lists the calculated values to elucidate the role of CNT content and CNT dispersion in measuring \( \delta K \) for different coatings. A-SD coating has been taken as a reference to compute the variables listed in Eq. (2). Assuming degree of dispersion as constant for A4C-SD and A8C-SD coatings, the change in property arises because of different CNT content (4 and 8 wt %). Nearly zero value of \( k_1 \) (0.025) indicates that CNT content does not play a strong role in increasing the storage modulus. In other words, increase in storage modulus cannot be expected until CNTs are comparatively more dispersed.\(^{2,4-6,8,23,25}\) (Authors would like to emphasize that research community has only stated good or bad dispersion of CNTs, but the quantification of CNT dispersion is completely missing in literature). On the other hand, high \( k_2 \) value (1.040) indicates that there is strong contribution of td in enhancing the fracture toughness since both the matrices contain similar degree of CNT dispersion. Comparative fracture toughness difference between the A4C-SD and A8C-SD coatings arises because of strong loss mechanisms (td) expected with high content of CNT dampeners (8 wt %) present in A8C-SD coating.\(^5\)

Assuming CNT content as constant for A4C-B and A4C-SD coatings, the change in property arises because of different degrees of CNT dispersion (blended versus spray dried powder). The values for \( k_1 \) and \( k_2 \) are computed as 0.244 and 0.560, respectively, for comparing A4C-SD and A4C-B coatings (with A-SD as a reference). An increase in \( k_1 \) by more than nine times from 0.025 (CNT content) to 0.244 (CNT dispersion) confirms strong dependence of fracture toughness on the storage modulus arising because of CNT dispersion. Isolation of CNT as separate entities entraps their excellent mechanical properties (high Young’s modulus) to provide reinforcements in the Al₂O₃ matrix. Lowering of \( k_2 \) from 1.040 to 0.560 reinstates the comparatively reduced contribution of td (when compared to that of increase in storage modulus) in enhancing fracture toughness. It is expected since the increase of td strongly depends on the CNT content as a whole, but CNT anchoring to render stiffness is strongly dependent on CNT dispersion. Reduction in CNT agglomeration in A4C-SD coating, as compared to A4C-B coating, introduces new surfaces both for frictional losses (increased td) and for reinforcements (increased modulus).

To confirm the combined role of CNT addition and dispersion, comparison of A4C-B and A8C-SD coatings restitutes the ratio of \( k_1/k_2 \) as 0.734 (much higher than for CNT content, 0.024, or CNT dispersion alone, 0.436, Table I).

**FIG. 3.** (Color online) (a) Fractured surface of A8C-SD coating showing dispersed CNTs entrapped in PM and FM regions, and (b) transmission electron spectroscopy image of Al₂O₃-CNT nanocomposite eliciting CNT anchoring.

**FIG. 4.** (Color online) Variation of td (ratio of loss modulus to storage modulus) for (a) A-SD, (b) A4C-B, (c) A4C-SD, and (d) A8C-SD coating. An increase in td is observed with CNT addition and dispersion.

| TABLE I. Change in fracture toughness with change in the modulus and td. (Calculations have been made with A-SD coating as reference sample). |
|----------------------------------|----------------|----------------|----------------|----------------|----------------|
| Factor                          | \( \delta K \) | \( \delta E' \) | \( \delta (td_{50}) \) | \( k_1 \) | \( k_2 \) | \( k_1/k_2 \) |
|----------------------------------|----------------|----------------|----------------|----------------|----------------|
| Effect of CNT content            |                |                |                |                |
| (i) A4C-SD                       | 0.429          | 0.750          | 0.152          | 0.025          | 1.040          | 0.024          |
| (ii) A8C-SD                      | 0.565          | 1.00           | 0.489          |                |
| Effect of CNT dispersion         |                |                |                |                |
| (i) A4C-B                        | 0.199          | 0.25           | 0.019          | 0.244          | 0.560          | 0.436          |
| (ii) A4C-SD                      | 0.429          | 0.750          | 0.152          |                |
| Effect of CNT content and dispersion |        |                |                |                |
| (i) A4C-B                        | 0.199          | 0.25           | 0.019          | 0.289          | 0.394          | 0.734          |
| (ii) A8C-SD                      | 0.565          | 1.00           | 0.489          |                |
Hence, synergistic effect of CNT addition and dispersion is evinced because of uniform availability of CNTs both as strong reinforcements and shock absorbers.

Loss mechanisms can be explained in terms of (i) microstructural frictional loss, and (ii) CNT interfacial friction as shown schematically in Figs. 5(a)–5(h). td value of (td50) of 0.26 in A-SD coating is attributed to the energy dissipation via intersplat sliding [Fig. 5(a)] and presence of nano-Al2O3 particles in PM region that facilitates interfacial friction [Fig. 5(e)]. Addition of 4 wt % CNTs in A4C-B coating has shown insignificant increase in td50 (0.27). A4C-SD coating with similar 4 wt % CNT content (as that of A4C-B coating) has shown increased td50 of 0.30, which arises because of improved dispersion of CNTs that create large CNT/Al2O3 frictional surfaces [Fig. 5(h)]. Koratkar et al.4 observed td value of 0.35 in epoxy/CNT nanocomposites. It was attributed that improved damping is largely contributed by CNT/matrix surfaces and not CNT/CNT interfaces. Spectrum of increased loss ratio is much pronounced in A8C-SD coating matrix surfaces and not CNT/CNT interfaces. Spectrum of increased loss ratio is much pronounced in A8C-SD coating matrix surfaces and not CNT/CNT interfaces. Spectrum of increased loss ratio is much pronounced in A8C-SD coating matrix surfaces and not CNT/CNT interfaces. Spectrum of increased loss ratio is much pronounced in A8C-SD coating matrix surfaces and not CNT/CNT interfaces.

It must be noted that if surface CNTs can render frictional losses efficiently on applying load then underlying CNTs do not really contribute in enhancing the dampening. A multiplication factor (Ω) can be associated with the isolated microstructural features (PM, FM) and CNTs contributing to increase in the surface area. Correspondingly, increase in the nondimensional surface area (Ωf) can be related to the constituting microstructure of CNT reinforced coatings as

$$\Omega_f = \frac{\rho_{PM} f_{PM} + \Pi_{FM} f_{FM} + \Pi_{CNT} f_{CNT}}{\rho_{th}}$$

where $\rho$ is the density and $f$ is the fraction of features in the corresponding coating. Role of FM, PM and CNTs in contributing the multiplication factor is presented in Table II. A representative average FM splat size of 3 µm (range of 1–5 µm) with a disk geometry, PM particle size of 300 nm (range of 240–320 nm) with a spherical geometry, and CNT diameter of 55 nm (range of 40–70 nm) are taken for the calculation purpose. It can be observed that PM region tends to enhance the multiplication factor by approximately 1500 times, which arises because of higher surface area associated with submicron Al2O3 particles when compared to that of 1–5 µm melted and resolidified FM disk shaped splats. Surface area increase arising because of CNT presence cannot be understated, as it is improving the multiplication factor by

Table II. Calculation of multiplication factor for isolated FM, PM, and CNTs.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Surface area (S)</th>
<th>Projected area (P)</th>
<th>S/P ratio</th>
<th>Multiplication factor for same coverage volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>FM (disk) r=1.5 µm, t=3 µm</td>
<td>$2\pi r^2 + 2\pi rt$</td>
<td>$\pi r^2$</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>PM (sphere) r=150 nm</td>
<td>$4\pi r^2$</td>
<td>$\pi r^2$</td>
<td>4</td>
<td>($\pi r^2 t / 4 / 3 \pi r^2 = 1500$)</td>
</tr>
<tr>
<td>CNT (diameter of 40–70 nm)</td>
<td>$2\pi r^2 + 2\pi r_{c} l$</td>
<td>$\pi r^2$</td>
<td>6.37</td>
<td>($\pi r^2 t / \pi r^2 l = 4463$)</td>
</tr>
<tr>
<td>l=2 µm, r=27.5 nm</td>
<td></td>
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<td></td>
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</table>

FIG. 5. (Color online) Loss mechanisms of plasma sprayed coatings with and without CNT reinforcement. The inset table and electron microscopy images show the dominant loss mechanisms of the coatings.
4500 times. However, CNTs tend to agglomerate and fuse in A4C-B coating and only a limited area (≈30% as determined by image analysis) is exposed to the surrounding matrix. Therefore, a 30% multiplication factor is used to account for marginal dispersion of CNTs toward calculating surface area increase in A4C-B coating. Consequently, Table III depicts the net surface area increase, $\Omega$, for the plasma sprayed coatings. As evinced from Table III, only a meager increase in surface area of A4C-B coating (≈1.1 times) is observed, which is similar to almost no increase in $t_{d50}$ in comparison to A-SD coating. However with similar CNT content, surface area of A4C-SD coating increases by up to three times when compared to that of A-SD coating. Further, increase in surface area by more than five times is observed in A8C-SD coating. Hence, CNT dispersion opens up new CNT surfaces to undertake shock, allow frictional losses, and enhance $t_d$. It is emphasized that five times increase in the surface area does not imply five times improvement in the $t_d$.

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