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# Oxygen Plasma Treatment and Deposition of CN<sub>x</sub> on a Fluorinated Polymer Matrix Composite for Improved Erosion Resistance

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# Oxygen plasma treatment and deposition of $CN_x$ on a fluorinated polymer matrix composite for improved erosion resistance

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The use of polymer matrix composites in aerospace propulsion applications is currently limited by insufficient resistance to erosion by abrasive media. Erosion resistant coatings may provide necessary protection; however, adhesion to many high temperature polymer matrix composite (PMC) materials is poor. A low pressure oxygen plasma treatment process was developed to improve adhesion of  $CN_x$  coatings to a carbon reinforced, fluorinated polymer matrix composite. Fullerene-like  $CN_x$  was selected as an erosion resistant coating for its high hardness-to-elastic modulus ratio and elastic resilience which were expected to reduce erosion from media incident at different angles (normal or glancing) relative to the surface. *In situ* x-ray photoelectron spectroscopy was used to evaluate the effect of the plasma treatment on surface chemistry, and electron microscopy was used to identify changes in the surface morphology of the PMC substrate after plasma exposure. The fluorine concentration at the surface was significantly reduced and the carbon fibers were exposed after plasma treatment.  $CN_x$  coatings were then deposited on oxygen treated PMC substrates. Qualitative tests demonstrated that plasma treatment improved coating adhesion resulting in an erosion resistance improvement of a factor of 2 compared to untreated coated composite substrates. The combination of PMC pretreatment and coating with  $CN_x$  reduced the erosion rate by an order of magnitude for normally incident particles. © 2007 American Vacuum Society. [DOI: 10.1116/1.2746049]

## I. INTRODUCTION

Advanced polymer matrix composites (PMCs) are light-weight and exhibit mechanical properties that meet or exceed aerospace alloys in some applications;<sup>1</sup> however, their use in propulsion applications such as air intake and compression in jet engines or leading edges of rotor blades is currently limited by susceptibility to erosive wear.<sup>2,3</sup> Coating PMC parts with a thin (5–100  $\mu\text{m}$ ) layer of protective material may allow the use of PMCs in components that are vulnerable to

high-velocity sand or other particulate media carried in the air. Such protective coatings should be hard in order to resist microcutting from media impinging at grazing angles, yet be elastically or plastically compliant to absorb impact energy to resist cracking and decohesion under direct particle impacts normal to the surface.<sup>4,5</sup>

Fullerene-like carbon nitride ( $CN_x$ ) is a material that has demonstrated high hardness (15–30 GPa) and elasticity (>80%), and therefore has potential for PMC erosion protection.<sup>6</sup> Moreover, the coefficient of thermal expansion (CTE) of fullerene-like  $CN_x$ , with its high fraction of  $sp^2$

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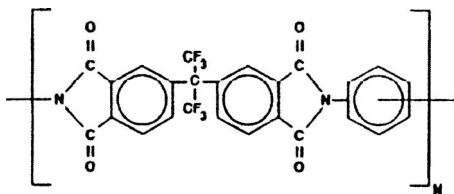


FIG. 1. Molecular structure of fluorinated polyimide matrix of the composite material.

bonding,<sup>6,7</sup> should demonstrate less CTE mismatch with a PMC substrate than other metallic erosion resistant coatings.<sup>8</sup> Matching the coating CTE to that of the substrate is desirable, as it would expand the range of potential propulsion applications of PMCs to include those that operate at both subzero and elevated temperatures.<sup>2</sup>

Erosion resistance is also dependent on adhesion of the coating to the substrate.<sup>9–11</sup> The majority of protective ceramic coatings currently in use were developed for metal alloys and utilize mechanical interlocking of the coating with the roughened workpiece surface.<sup>12</sup> The relatively low yield strength of the polymer matrix limits the utility of this approach for improving adhesion. Furthermore, many high-temperature PMC materials are comprised of stiff fibers embedded in a fluorinated polymer matrix. The fluorinated polymer chemistry, combined with the resin-rich mold release agent-coated surface, severely inhibits coating adhesion.<sup>13–17</sup>

To explore the effect of adhesion on the erosion resistance of CN<sub>x</sub> coatings on the composite of interest (with the polymer matrix molecule shown in Fig. 1), it was necessary to introduce a predeposition treatment method. Exposure to low pressure plasmas, or reactive species produced in a plasma, is a well-documented technique for defluorinating and roughening fluorinated polymer surfaces.<sup>15,17–22</sup> Generally these treatments are performed by exposing the polymer to a remotely generated plasma produced away from the workpiece.<sup>15,18,19,21–23</sup> In the current work, midfrequency pulsed power was applied directly to the PMC workpiece to drive a pure oxygen dc glow discharge. CN<sub>x</sub> coatings were grown on oxygen treated and untreated substrates, which were then subjected to qualitative adhesion tests to determine the effect of the plasma treatment. Erosion testing further demonstrated the effectiveness of the substrate treatment technique for improving coating adhesion in addition to the erosive wear resistance associated with application of the CN<sub>x</sub> coating material.

## II. EXPERIMENTAL PROCEDURE

Figure 2 shows a schematic of the processing and characterization chamber. The processing chamber was pumped to a base pressure  $\leq 4 \times 10^{-5}$  Pa, then 40 SCCM of ultrahigh purity oxygen or argon gas was admitted to the chamber. A throttle valve was used to maintain a total pressure of 4 Pa as measured with a low pressure capacitance manometer. The power lead from an Advanced Energy Pinnacle Plus power supply was connected to a 25.4 mm diameter  $\times$  4.0 mm thick

TABLE I. Erosion test conditions.

Media	80 $\mu\text{m}$ Al <sub>2</sub> O <sub>3</sub> powder
Feed rate	2 g min <sup>-1</sup>
Gas pressure	80 psi
Sample position	10 mm from nozzle tip
Cycle description	50 s on/50 s off
Number of cycles	10
Total mass of erodent	16.7 g

PMC disk, which consisted of an electrically insulating fluorinated polyimide resin matrix reinforced with T650/35-3K carbon fibers. The composite substrates were fabricated into laminates with approximately 60% fiber volume using standard autoclave processing techniques and then waterjet machined into the disk geometry. Samples of PMC were biased to  $-600$  V (nominally) at 150 kHz with a 1  $\mu\text{s}$  reverse time for a duration of 30–240 s. The PMC workpiece was surrounded by a 20 mm thick PTFE holder to eliminate plasma generation from any surface other than that intended for treatment. A new polymer sample was used for each treatment time investigated. An optical emission monitor was used to measure the time-averaged spectra resulting from the pulsed oxygen plasma approximately 1 cm above the cathode surface.

After exposure to the plasma, the treated PMC was transferred to the x-ray photoelectron spectroscopy (XPS) analysis chamber under vacuum (Fig. 2). The XPS system employed a magnesium anode and was used to analyze the changes in surface chemistry of the PMC substrates after each plasma treatment. Upon completion of the surface analysis, samples were removed from the characterization chamber and examined in the scanning electron microscope. The contact angle of water was also measured on the surface of treated and untreated PMC materials. Based on the results from examination of treatment time on surface chemistry and morphology, oxygen plasma exposure times (prior to CN<sub>x</sub> coating deposition) of 0, 60, and 240 s were selected. Substrates were treated under identical conditions for the different times prior to the coating growth.

For CN<sub>x</sub> coating growth on plasma treated PMC samples, oxygen was evacuated from the chamber and the applied potential on the PMC substrate was adjusted to  $-70$  V dc. A

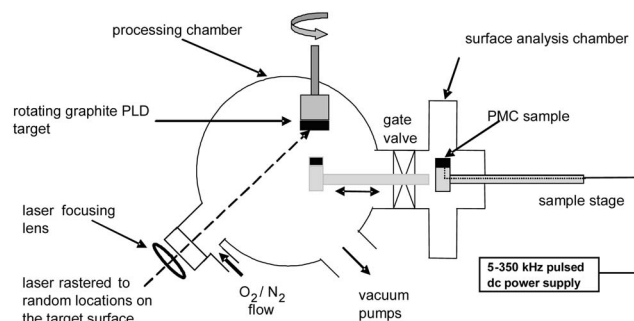


FIG. 2. Schematic of the processing and surface analysis chambers.

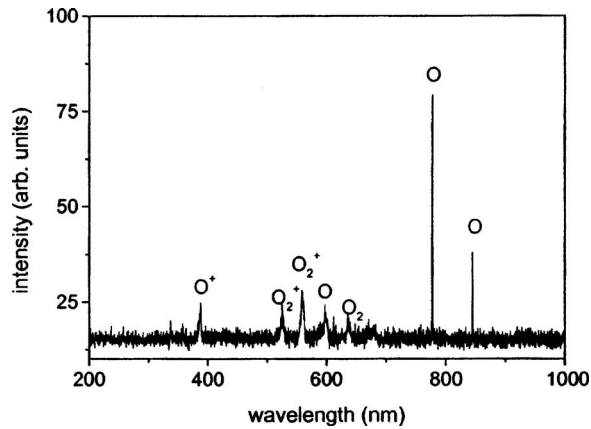


FIG. 3. Optical emission spectrum of the pulsed dc oxygen plasma used for pretreatment.

carbon interlayer was deposited by laser ablation from a rotating graphite target for 1 min using 840 mJ, 248 nm laser pulses (Fig. 2). The 20 ns laser pulses were directed to random positions and focused to an approximately 15

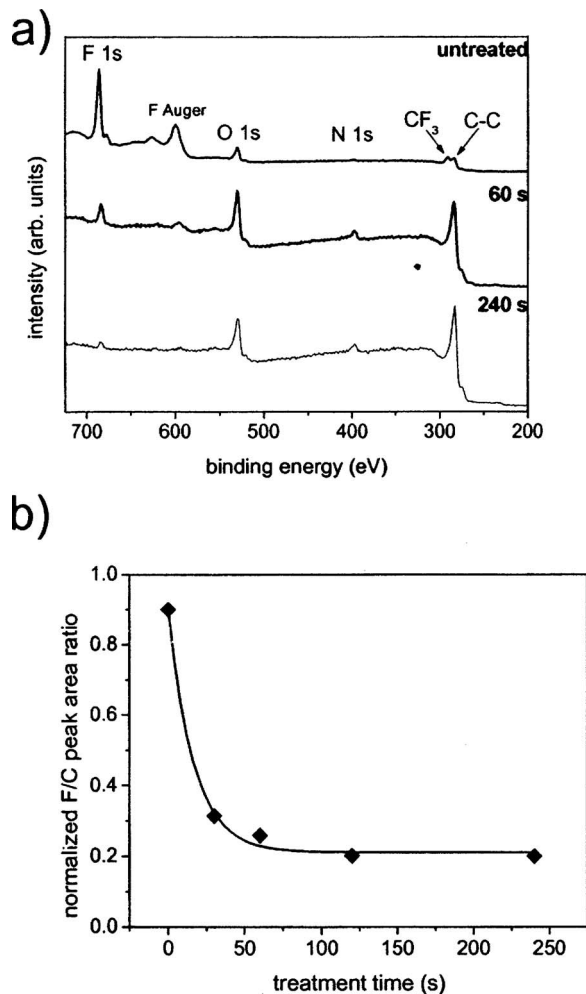


FIG. 4. (a) XPS spectra from the polymer matrix composite after exposure to the oxygen plasma and processed data (b) showing the fluorine-to-carbon peak intensity ratios from PMCs exposed to oxygen plasma.

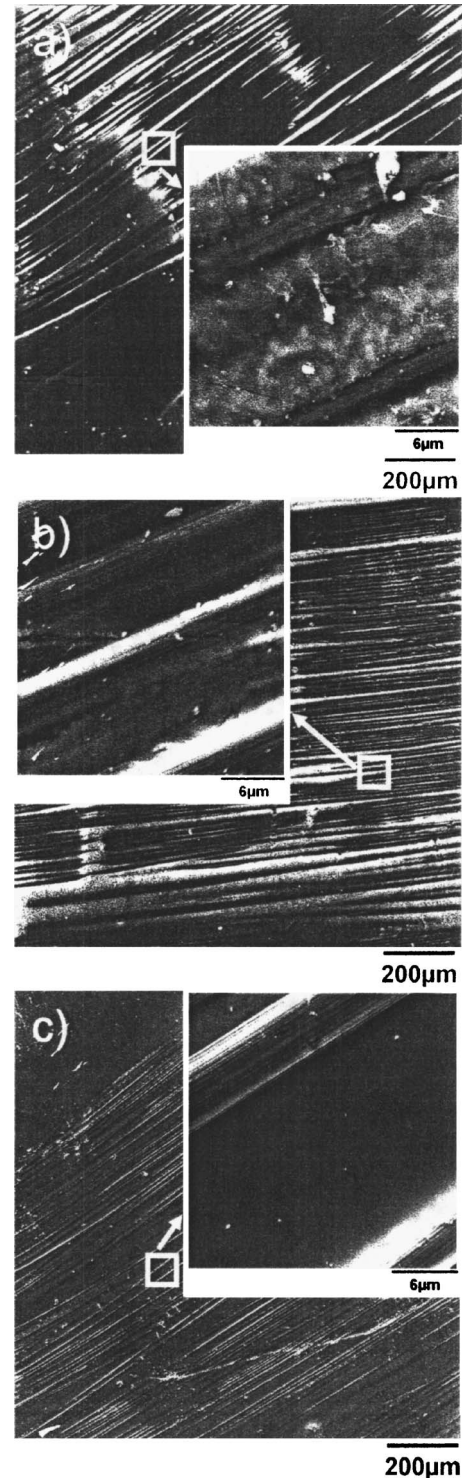


FIG. 5. Scanning electron micrographs of polymer matrix composite surfaces (a) as received, and after (b) 60 s and (c) 240 s of exposure to oxygen plasma.

$\times 5.0 \text{ mm}^2$  spot on the 50 mm diameter target surface at a repetition rate of 10 Hz. After the initial carbon layer deposition, nitrogen was introduced at a flow rate of 27.5 SCCM (SCCM denotes cubic centimeter per minute at STP), and the system throttle valve adjusted to maintain a total chamber pressure of 1.33 Pa. The laser continued to operate in the

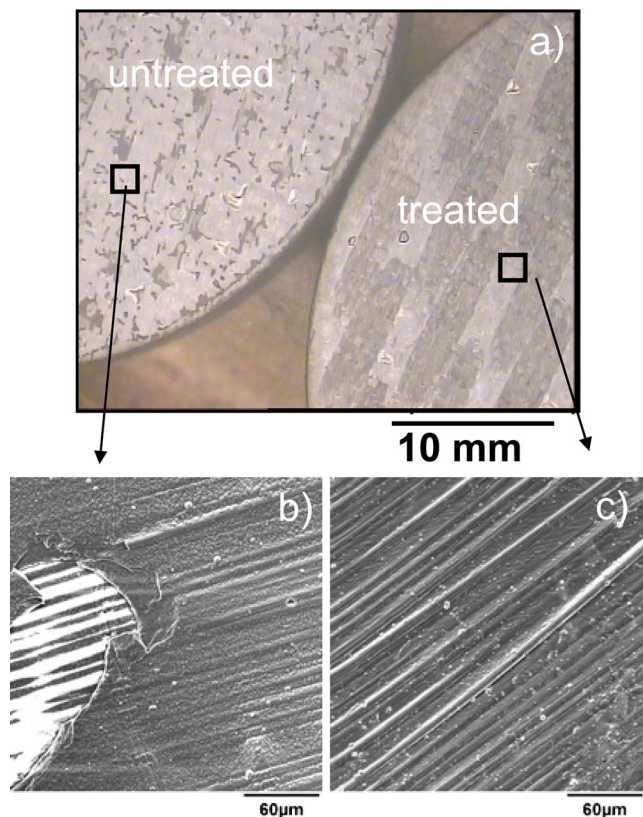


FIG. 6. (a) Micrographs of the treated and untreated polymer samples after coating with  $CN_x$ . (b) and (c) show higher magnification views of each sample.

nitrogen atmosphere for 9 h to produce a  $CN_x$  layer of approximately  $5 \mu\text{m}$  thickness ( $\pm 150 \text{ nm}$ ), as measured with a contact profilometer. These coating growth conditions were consistent with those used in a previous study for the deposition of hard and elastically resilient fullerene-like  $CN_x$ .<sup>6</sup>

The coating surfaces were examined after deposition in optical and electron microscopes and in the XPS. The mechanical properties of the  $CN_x$  material were examined with nanoindentation. Coatings deposited on treated and untreated PMC substrates were subjected to scratch testing and Daimler-Benz tests<sup>24</sup> to qualitatively determine the effect of treatment time on adhesion. Scratch tests were conducted with a  $0.2 \text{ mm}$  radius diamond tip dragged with a constant speed of  $5 \text{ mm min}^{-1}$  on the coating surface. The applied load was increased linearly up to  $100 \text{ N}$  at a rate of  $50 \text{ N min}^{-1}$ . Daimler-Benz testing consisted of indentation at  $60$  and  $150 \text{ kg}$  with a diamond Rockwell C indenter. Both adhesion tests were followed by examination in optical and electron microscopes. Samples were also tested in a FALEX erosion test unit with the conditions listed in Table I. Erosion testing was performed at incident angles of  $40^\circ$  and  $90^\circ$  relative to the surface of the test specimens at room temperature. The wear scars on each sample were examined with a Wyco white light interferometer to measure the wear volume after erosion testing.

### III. RESULTS

Figure 3 shows the optical emission spectrum from the pure oxygen plasma generated with the midfrequency bipolar pulsed PMC cathode. A large peak corresponding to atomic oxygen was measured, as were peaks attributed to positively charged atomic and molecular oxygen ions. Examination of the surface composition by XPS immediately after processing revealed decreased concentrations of fluorine and the loss of the  $C-F_3$  peak in the spectrum [Fig. 4(a)] after exposure to the oxygen plasma. Figure 4(b) shows how the fluorine-to-carbon ratios at the surface changed with treatment time. The line shown in the figure is an exponential decay function fit to the data. Substantial defluorination occurred after  $60 \text{ s}$ , with only a small decrease after longer treatments.

Figure 5(a) is a scanning electron micrograph of as-received PMC composite surface, where the carbon fibers were coated with the fluorinated polymer matrix. The space between fibers in the as-received polymer appeared to be filled with rough, poorly adherent material exhibiting fiber/matrix decohesion at the interface. After exposure to the oxygen plasma for  $60 \text{ s}$  [Fig. 5(b)], the polymer was partially etched away, leaving some fiber surfaces exposed. The pulsed oxygen plasma treatment reduced the number of topographical features on the polymer matrix between fibers. Increasing the plasma treatment time to  $240 \text{ s}$  [Fig. 5(c)] resulted in complete exposure of the carbon fibers. The remaining polymer matrix had no evidence of any decohesion along the matrix/fiber interface.

Water contact angles on the PMC surfaces were also examined. A  $60 \text{ s}$  treatment resulted in a reduction in contact angle from  $105^\circ$  to  $43^\circ$ . This reduced contact angle was consistent with both the changes in surface chemistry and morphology, revealing a PMC surface with a higher surface energy and chemical reactivity after plasma treatment.

Micrographs of the coatings deposited on treated and untreated substrates are shown in Figs. 6(a)–6(c). The coating deposited on the untreated substrate demonstrated periodic delamination of the coating across the surface [Figs. 6(a) and 6(b)], while the substrates treated for  $60 \text{ s}$  or longer were uniformly coated [Figs. 6(a) and 6(c)]. XPS of all coated samples showed that the coating was composed of approximately  $80 \text{ at. } \%$  carbon and  $20 \text{ at. } \%$  nitrogen, independent of the processing history of the substrate.

Nanoindentation was performed on the coated samples. Results from nanoindentation tests of the coatings on untreated polymer substrates were difficult to interpret due to excessive scatter in results between measurements; however, coatings on treated substrates demonstrated repeatable measurements of hardness at  $19 \text{ GPa}$  and an elastic modulus of approximately  $120 \text{ GPa}$ . The elasticity of the coating was measured to be approximately  $75\%$  for a  $1000 \text{ nm}$  displacement (Fig. 7). These measurements were consistent with mechanical properties of fullerene-like  $CN_x$  coatings.<sup>6,25</sup>

Figure 8 shows how the predeposition oxygen treatment affected coating adhesion after severe substrate deformation. As seen in Fig. 8(a), the coating showed extensive cracking around the perimeter of the  $150 \text{ g}$  indent on the untreated

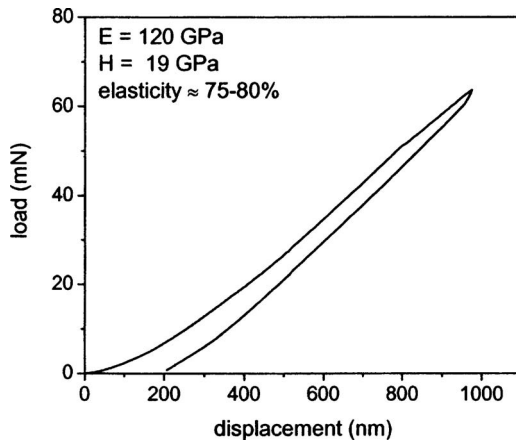


FIG. 7. Load-displacement curve for the treated and coated PMC.

sample, while the edges remained intact for the samples treated for (b) 60 and (c) 240 s. Examination of the scratch tracks in Fig. 9 also showed differences in adhesion resulting from plasma pretreatment of the substrates. The inset in Fig. 9(a) shows a low-magnification view of the scratch track in the region loaded to approximately 10 N, with alternating coated and uncoated regions at the bottom of the scratch. On the treated substrate, the coating adhered throughout the scratch. In Fig. 9(b), the scratch is shown where a 90 N load was applied. Some cracking perpendicular to the scratch directions is shown, but the coating still covers the substrate, and appears to be fully adherent.

Table II lists the worn volume and erosion rates (in terms of mass lost per gram of erodent) for the coated and uncoated samples. The CN<sub>x</sub> coating coupled with the oxygen plasma treatment yielded an erosion rate that was roughly an order of magnitude less than that measured for the PMC alone in the normal incidence test, and a factor of 3 less for the glancing angle test. Samples that were coated without oxygen pretreatment had an erosion rate that was approximately twice that of the treated and coated samples for both normal and grazing angle erosion tests.

#### IV. DISCUSSION

Driving an electrically insulating fluorinated polymer workpiece with a midfrequency pulsed dc power supply as a plasma cathode in pure oxygen was a simple and effective way to alter the structure and surface chemistry of the polymer to improve coating adhesion compared to ion beam, rf biasing, and other methods.<sup>15,18,19,26,27</sup> The reactive oxygen plasma generated with the pulsed dc PMC cathode produced reactive neutral and ionized oxygen species, which altered the surface chemistry and morphology of the PMC prior to coating deposition in a manner consistent with that reported by workers using other techniques. A frequency of 150 kHz was selected as it was the minimum frequency required to maintain a continuous glow discharge with power delivered via the insulating polymer substrate. Driving the discharge with dc power resulted in the loss of electrons at the insulating surface as the incident positive ions were neutralized by

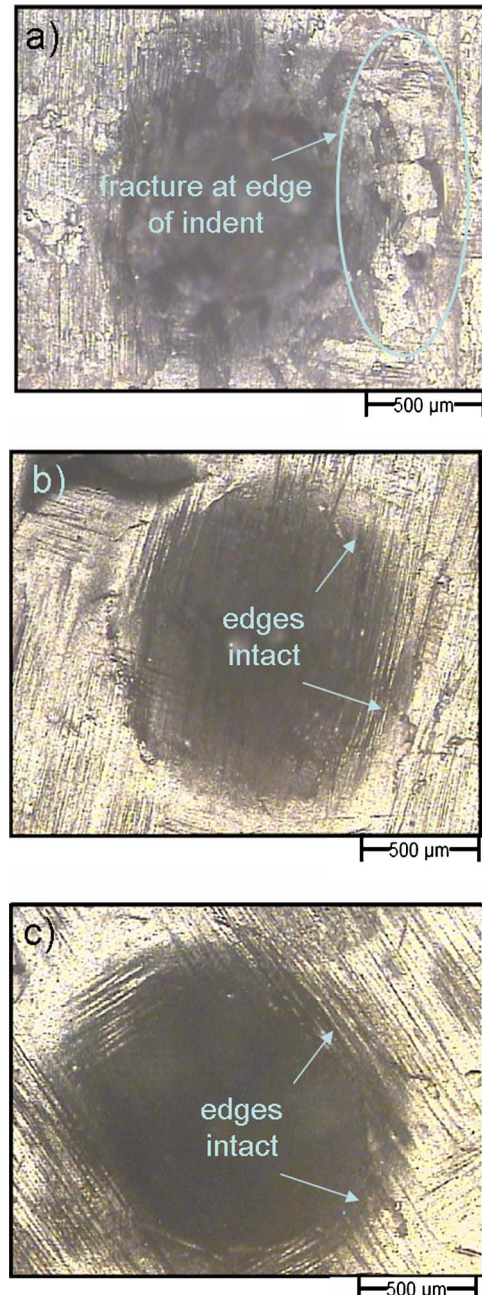


FIG. 8. Optical micrographs of 150 kg indents on coated samples (a) with no pretreatment, (b) 60 s oxygen pretreatment and (c) 240 s oxygen pretreatment.

electrons at the surface, thus reducing the voltage below that required to sustain the discharge. As argued by Chapman,<sup>28</sup> an overestimate of the time required to charge up the surface can be compared to the time to charge up a capacitor, where

$$C = Q/V = it/V,$$

thus  $t = CV/i$ .

For the expected values of capacitance ( $\approx 1$  pF/cm<sup>2</sup>), discharge voltage ( $\approx 500$ – $1000$  V), and current ( $\approx 1$  mA/cm<sup>2</sup>), the required frequency should be roughly 1 MHz. Lower frequencies (5–500 kHz) are generally sufficient as the current delivered to the insulator decreases as it charges up, unlike

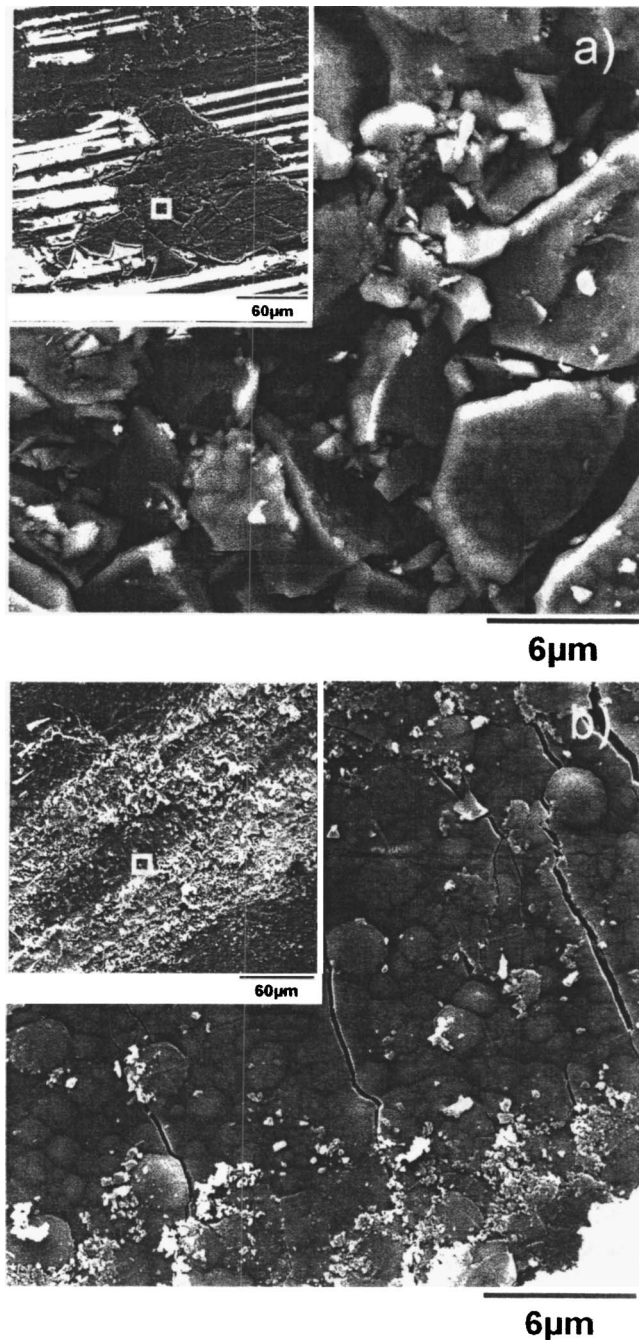


FIG. 9. Electron micrographs of scratch tracks on the coated surfaces of the (a) untreated and (b) 60 s treated PMC substrates.

the constant current model above. The PTFE holder was much thicker and had different dielectric properties than the PMC material and therefore did not produce a discharge at 150 kHz.

Coating adhesion was qualitatively shown to improve after exposure to the oxygen plasma via indentation, scratch testing, and erosion testing. Rabinovich *et al.* describe how cracking due to indentation [as shown in Fig. 8(a)] is related to weak interfacial bonding.<sup>29</sup> The crack patterns in Figs. 9(a) and 9(b) are consistent with those described by Burnett and Rickerby for scratch testing of slightly different coating/

substrate systems.<sup>30</sup> They illustrated how spallation resulting from total coating failure results in scratch tracks that look like that shown in Fig. 9(a). Tensile cracking, which is characterized by cracks that are normal and concave with respect to the scratch direction rather than normal and convex as in Fig. 9(b), results from tensile bending moments within the coating as it is pushed down underneath the indenter, and occurs only when the coating is fully adherent. Last, the erosion rate of the coated PMC decreased when the sample was treated, consistent with reports found in the literature relating coating adhesion to erosion resistance.<sup>9–11</sup>

$CN_x$  coatings deposited on oxygen plasma treated polymer matrix composite substrates were hard, with a low modulus, resulting in  $H/E$  ratio of 0.16, which is quite high in comparison with typical ceramic wear protective coatings.<sup>7</sup> The erosion rate of the uncoated PMC was slightly higher when the erodent media was incident on the surface at  $40^\circ$  compared to that measured when the media were directed normal to the surface. Such dependence on the angle of incidence is expected for a softer, polymer-based material. For the coated PMC material, the erosion rates were significantly reduced. Erosive wear from media directed at  $90^\circ$  relative to the coated surface was suppressed more than that directed at  $40^\circ$ , suggesting that the elastic properties of the  $CN_x$  coating made a stronger contribution to the protective nature of the coating than the hardness. Deposition of adherent  $CN_x$  coatings substantially reduced the erosion rate of the polymer, even though the  $5 \mu\text{m}$  coating was very thin compared to those typically found in erosion resistant applications.<sup>2,3</sup> Typical thicknesses of erosion protective hard coatings used on metal alloys in jet engines are on the order of  $100\text{--}1000 \mu\text{m}$ . A thicker  $CN_x$  coating should provide an increased capability for elastic damping of normal incidence sand impacts and a longer scratch endurance of sand impacts at oblique angles. The production of such thick coatings requires modifications to the deposition process to increase the  $CN_x$  coating growth rates, which are currently in development. The erosion performance of thicker  $CN_x$  coatings and coatings with different hardness-to-modulus ratios will be evaluated in a future work.

## V. CONCLUSIONS

Midfrequency pulsed power was applied directly to a fluorinated polymer matrix composite workpiece in an oxygen atmosphere to generate a reactive plasma and reduce the surface fluorine concentration and remove loosely adhered surface material. A  $CN_x$  coating with a very high hardness-to-modulus ratio of 0.16 with  $>75\%$  elasticity was produced by laser ablation of carbon in a nitrogen atmosphere. Indentation, scratch, and erosion testing all showed that the adhesion of  $CN_x$  coatings deposited after oxygen plasma treatment of the PMC substrate was improved when compared to the same coatings deposited on the untreated PMC material. Improvements in coating adhesion reduced the erosion rate by a factor of 2 when compared to untreated,  $CN_x$  coated



TABLE II. Erosion data for all samples.

Substrate pretreatment	CN <sub>x</sub> coating (μm)	40° incidence		90° incidence	
		Volume loss (cm <sup>3</sup> × 10 <sup>-3</sup> )	Erosion rate (cm <sup>3</sup> g <sup>-1</sup> )	Volume loss (cm <sup>3</sup> × 10 <sup>-3</sup> )	Erosion rate (cm <sup>3</sup> g <sup>-1</sup> )
(None)	(None)	1.20	0.07	1.00	0.06
(None)	5	0.34	0.02	0.70	0.04
oxygen plasma	5	0.18	0.01	0.36	0.02

PMC samples. Uncoated substrates wore approximately ten times faster for normally incident abrasive particles compared to the treated and coated samples.

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