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OXYGEN PLASMA TREATMENT AND DEPOSITION OF CN_x ON A FLUORINATED POLYMER MATRIX COMPOSITE FOR IMPROVED EROSION RESISTANCE (Preprint)

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14. ABSTRACT
High-performance polymer matrix composites (PMCs) are an appealing choice for materials in aerospace applications due to their high strength-to-weight ratio and stability over a broad temperature range for thousands of service hours. The use of PMCs in propulsion applications is currently limited only by insufficient resistance to erosion by abrasive media. Erosion-resistant coatings may provide the necessary protection, however their application is not straightforward, as surface preparation is a challenge. Specifically, it is because of the resin-rich outer plies, mold release agents, and fluorinated high-temperature polymer matricies that treatment prior to deposition is required. A low pressure oxygen plasma treatment process was developed to improve adhesion of CN_x coatings to a polymer matrix composite. CN_x was selected as a protective coating for its high hardness-to-elastic ratio, coupled with elastic resilience. 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. CN_x coatings were then deposited on treated PMC substrates. The effect of the plasma predeposition treatment on coating adhesion and erosion resistance was evaluated. The combination of PMC pretreatment and coating with CN_x reduced the erosion rate by an order of magnitude.

15. SUBJECT TERMS
Polymer matrix composites (PMCs), erosion, erosion-resistant coatings, plies, CN_x

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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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Abstract

High-performance polymer matrix composites (PMCs) are an appealing choice for materials in aerospace applications due to their high strength-to-weight ratio and stability over a broad temperature range for thousands of service hours. The use of PMCs in propulsion applications is currently limited only by insufficient resistance to erosion by abrasive media. Erosion-resistant coatings may provide the necessary protection, however their application is not straightforward, as surface preparation is a challenge. Specifically, it is because of the resin-rich outer plies, mold release agents, and fluorinated high-temperature polymer matricies that treatment prior to deposition is required. A low pressure oxygen plasma treatment process was developed to improve adhesion of CN_x coatings to a polymer matrix composite. CN_x was selected as a protective coating for its high hardness-to-elastic modulus ratio, coupled with elastic resilience. *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. CN_x coatings were then deposited on treated PMC substrates. The effect of the plasma pre-deposition treatment on coating adhesion and erosion resistance was evaluated. The combination of PMC pre-treatment and coating with CN_x reduced the erosion rate by an order of magnitude.

I. Introduction

Advanced polymer matrix composites (PMCs) are lightweight and exhibit mechanical properties that meet or exceed aerospace alloys in some applications,[1] 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[2,3]. Coating the PMC parts with a thin (5-100μm) 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 complient to absorb impact energy to resist cracking and decohesion under direct particle impacts normal to the surface. [4,5]

Fullerene-like carbon nitrde (CN_x) is a material that has demonstrated high hardness (15-30 GPa) and elasticity (>80%), and therefore has potential for PMC erosion protection[6]. Moreover,the coefficient of thermal expansion of fullerene-like CN_x, with its high fraction of sp^2 bonding[6,7] should demonstrate less CTE mismatch with a PMC substrate than other metallic erosion-resistant coatings[8]. 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[2] .

Erosion resistance is also dependent on adhesion of the coating to the substrate. [9-11] 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. [12] 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 chemistry, combined with the resin-rich mold release agent-coated surface inhibits coating adhesion. [13-17]

To explore the effect of adhesion on the erosion resistance of CN_x coatings on the composite of interest (with the polymer matrix molecule shown in Figure 1), it was necessary to introduce a pre-deposition treatment method. Exposure to low-pressure plasmas is a well-documented technique for defluorinating and roughening fluorinated polymer surfaces.[14,15,17-21] Generally these treatments are performed by exposing the polymer to a remotely generated plasma,[15,18-22] produced away from the workpiece. In the current work, mid-frequency pulsed power was applied directly to the PMC workpiece to drive a pure oxygen dc glow discharge. CN_x coatings were grown on oxygen treated and untreated substrates, and 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 as well as the additional wear resistance associated with application of the CN_x coating material.

II. Expermental Procedure

Figure 2 shows a schematic of the processing and characterization chamber. The processing chamber was pumped to a base pressure $\leq 3 \times 10^{-7}$ Torr , then 40 sccm of UHP oxygen or argon gas was admitted to the chamber. A throttle valve was used to maintain a total pressure of 30 mTorr as measured with a low pressure capacitance manometer. The power lead from an Advanced Energy Pinnacle Plus power supply was connected to a 2.54 cm diameter x 0.4 cm thick disk of carbon fiber reinforced fluorinated polymer matrix composite (PMC). Samples of PMC were biased to -600 V dc (nominally) at 150 kHz with a 1 μs reverse time for a duration of 30-240 seconds. The PMC workpiece was surrounded by a 2 cm 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 material. Based on the results from examination of treatment time on surface chemistry and morphology, oxygen plasma exposure times (prior to CN_x coating deposition) of 0, 60 and 240 seconds were selected. Substrates were treated under identical conditions for the different times prior to the coating growth.

For CN_x 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 carbon interlayer was deposited by laser ablation from a rotating graphite target for 1 minute using 840 mJ, 248 nm laser pulses (Fig. 2). The 20 ns laser pulses were directed to random positions and focused to an approximately 1.5 x 0.5 cm^2 spot on the 5 cm 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, and the system throttle valve adjusted to maintain a total chamber pressure of 10 mTorr. The laser continued to operate in the nitrogen atmosphere for 9 hours to produce a CN_x layer of approximately 5μm thickness (±150 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**.** [6]

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 [23] to qualitatively determine the effect of treatment time on adhesion. Scratch tests were conducted with a 0.2 mm radius diamond tip dragged with a constant speed of 5 mm min^{-1} on the coating surface. The applied load was increased linearly up to 100 N at a rate of 50 N min^{-1}. Daimler-Benz testing consisted of indentation at 60 and 150 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° and 90 ° 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 mid-frequency 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 (Figure 4a) after exposure to the oxygen plasma. Figure 4b 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 de-fluorination occurred after 60 seconds, with only a small decrease after longer treatments.

Figure 5a 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 seconds (Fig. 5b), 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 seconds (Fig. 5c) resulted in complete exposure of the carbon fibers. The remaining polymer matrix had no evidence of any decohesion along the matrix/fiber interface.

Figure 6 shows the contact angle of water on (a) the untreated surface and (b) the surface after 60 seconds of exposure to the oxygen plasma. A 60 second treatment resulted in a reduction in contact angle from 105° to 43°. 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 Figures 7a-c. The coating deposited on the untreated substrate demonstrated periodic delamination of the coating across the surface (Figs. 7a and b), while the substrates treated for 60 seconds or longer were uniformly coated (Figs. a and c). XPS of all coated samples showed that the coating was composed of approximately 80 atomic percent carbon and 20 atomic percent 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 GPa and an elastic modulus of approximately 120 GPa. The elasticity of the coating was measured to be approximately 75 percent for a 1000 nm displacement (Figure 8). These measurements were consistent with mechanical properties of fullerene-like CN_x coatings.[6,24]

Figure 9 shows how the pre-deposition oxygen treatment affected coating adhesion after severe substrate deformation. As seen in Fig.9a, the coating showed extensive cracking around the perimeter of the 150 g indent on the untreated sample, while the edges remained intact for the samples treated for (b) 60 and (c) 240 seconds. Examination of the scratch tracks in Fig. 10 also showed differences in adhesion resulting from plasma pre-treatment of the substrates. The inset in Fig. 10a 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 Figure 10b, 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.

Figure 11 shows sand erosion scars for the (a-b) untreated/uncoated, (c-d) untreated/coated, and (e-f) treated/coated PMC specimens, with the erodent impinging at angles of 90° and 40° relative to the surface, respectively. Table II lists the worn volume and erosion rates (in terms of mass lost per gram of erodent) for the samples. The CN_x 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 for the normal incidence test, and a factor of three 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 mid-frequency 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.[14,15,18,19] 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.

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. 9a) is related to weak interfacial bonding.[25] The crack patterns in Figures 10 a and b are consistent with those described by Burnett and Rickerby for scratch testing of slightly different coating/ substrate systems.[26] They illustrated how spallation resulting from total coating failure results in scratch tracks that look like that shown in Fig. 10a. 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. 10b, 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.[9-11]

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 to typical ceramic wear protective coatings.[7] The erosion rate of the uncoated PMC was slightly higher when the erodent media was incident on the surface at 40 degrees compared to that measured when the media was 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 not only significantly reduced but also the rates were higher at 90 degree incidence angles. Thus, deposition of the CN_x coating on the PMC resulted in a transition from the surface erosion behavior characteristic of a soft material to that of a hard material. [4,5]

Deposition of adherent CN_x coatings substantially reduced the erosion rate of the polymer, even though the 5 μm coating was very thin compared to those typically found in erosion resistant applications[2,3]. Typical thicknesses of erosion protective hard coatings used on metal alloys in jet engines are on an order of 100 to 1000 microns. 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 will be evaluated in a future work.

V. Conclusions

Erosion resistant coatings may allow increased use of polymer matrix composite components in propulsion applications. Many PMCs suitable for such high temperature performance are comprised of a fluorinated polymer matrix that requires surface treatment to promote coating adhesion. A simple process to improve coating adhesion to a fluorinated polymer matrix composite substrate was developed. The process employed a mid-frequency pulsed DC power supply to drive the polymer workpiece as a cathode in a pure oxygen environment. A thin, adherent coating of hard, elastic CN_x deposited on the PMC reduced the erosion rate of the part by about a factor of 10. Improvements in coating adhesion, realized with oxygen plasma pre-treatment, reduced the erosion rate by a factor of two.

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REFERENCES

1 National Materials Advisory Board, *Going to Extremes: Meeting the Emerging Demand for Durable Polymer Matrix Composites* (The National Academies Press, 2005), p. 10.

2 M. Ivosevic, R. Knight, S. R. Kalindindi, G. R. Palmese, and J. K. Sutter, Surf.Coat.Technol. **200**, 5145 (2006).

3 K. Miyoshi, J. K. Sutter, R. A. Horan, S. K. Naik, and R. J. Cupp, Tribol.Lett. **17**, 377 (2004).

4 Y. Gachon, P. Ienny, A. Forner, G. Farges, M. C. Sainte Catherine, and A. B. Vannes, Surf.Coat.Technol. **113**, 140 (1999).

5 D. W. Wheeler and R. J. K. Wood, Wear **258**, 526 (2005).

6 A. A. Voevodin, J. G. Jones, J. S. Zabinski, Zs. Czigany, and L. Hultman, J.Appl.Phys. **92**, 4980 (2002).

7 H. Riascos, J. Neidhardt, G. Z. Radnoczi, J. Emmerlich, G. Zambrano, L. Hultman, and P. Prieto, Thin Solid Films **497**, 1 (2006).

8 A. Champi, R. G. Lacerda, G. A. Viana, and F. C. Marques, J. of Non-Cryst. Solids **338-340**, 499 (2004).

9 D. S. Rickerby and P. J. Burnett, Surf.Coat.Technol. **33**, 191 (1987).

10 K. L. Rutherford and I. M. Hutchings, Surf.Coat.Technol. **86-87**, 542 (1996).

11 P. H. Shipway and I. M. Hutchings, Surf.Coat.Technol. **71**, 1 (1995).

12 A. Liu, M. Guo, M. Zhao, H. Ma, and S. Hu, Surf.Coat.Technol. **200**, 3073 (2006).

13 C.-A. Chang, J. E. E. Baglin, A. G. Schrott, and K. C. Llin, Appl.Phys.Lett. **51**, 103 (1987).

14 S. Han, Y. Lee, H. Kim, G. h. Kim, J. Lee, J. H. Yoon, and G. Kim, Surf. Coat. Technol. **93**, 261 (1997).

15 Y. W. Park and N. Inagaki, Polymer **44**, 1569 (2003).

16 R. R. Rye, A. J. Howard, and A. J. Ricco, Thin Solid Films **262**, 73 (1995).

17 T. G. Vargo, J. M. Calvert, K. J. Wynne, J. K. Avlyanov, A. G. MacDiarmid, and M. F. Rubner, Supramolec.Sci. **2**, 169 (1995).

18 K. De Bruyn, M. Van Stappen, H. De Deurwaerder, L. Rouxhet, and J. P. Celis, Surf.Coat.Technol. **163-164**, 710 (2003).

19 J. M. Grace and L. J. Gerenser, J.Disper.Sci.Technol. **24**, 305 (2003).

20 D. Leonhardt, C. Muratore, S. G. Walton, and R. A. Meger, Surf. Coat Technol. **188-189**, 299 (2004).

21 N. Vandencasteele, H. Fairbrother, and F. Reniers, Plasma Process.Polym. **2**, 493 (2005).

22 C. Muratore, S.G. Walton, D. Leonhardt, R.F. Fernsler, and R.A. Meger, "Materials processing in electron beam generated plasmas", 24 April, 2004, Society of Vacuum Coaters ,p. 412.

23 H. Jehn, G. Reiners, and N. E. Siegel, in *DIN Fachbericht 39, Characterisierung Dunner Schichten*, (Beuth Verlag, Berlin, 1993) p. 213.

24 J. F. Palacio, S. J. Bull, J. Neidhardt, and L. Hultman, Thin Solid Films **494**, 63 (2006).

25 V. L. Rabinovich and V. K. Sarin, Mat.Sci.Engr.A **209**, 82 (1996).

26 P. J. Burnett and D. S. Rickerby, Thin Solid Films **154**, 403 (1987).

Figure captions

Figure 1: Molecular structure of polymer matrix of the composite material.

Figure 2: Schematic of the processing and surface analysis chambers.

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

Figure 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.

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

Figure 6: Photographs of water droplets on the (a) as-received PMC and (b) the PMC treated for 60 seconds in oxygen plasma.

Figure 7: (a) Micrographs of the treated and untreated polymer samples after coating with CN_x. Figures (b) and (c) show higher magnification views of each sample.

Figure 8: Load-displacement curve for the treated and coated PMC.

Figure 9: Optical micrographs of 150 kg indents on coated samples (a) with no pretreatment, (b) 60 second oxygen pretreatment and (c) 240 second oxygen pretreatment.

Figure 10: Electron micrographs of scratch tracks on the coated surfaces of the (a) untreated and (b) 60 second treated PMC substrates.

Figure 11: Images generated from a white light interferometer of the erosion scars of samples identified in each figure at normal incidence (a-c) and grazing incidence (d-f).

TABLE I: Erosion test conditions

media	80 μm Al_2O_3 powder
feed rate	2 g min^{-1}
gas pressure	80 psi
sample position	10 mm from nozzle tip
cycle description	50 sec. on/50 sec. off
number of cycles	10
total mass of erodent	16.7 grams

TABLE II: Erosion data for all samples

		40° incidence		90° incidence	
substrate pretreatment	CN_x coating	volume loss (cm^3 x 10^{-3})	erosion rate (cm^3 g^{-1})	volume loss (cm^3 x 10^{-3})	erosion rate (cm^3 g^{-1})
(none)	(none)	1.20	0.07	1.00	0.06
(none)	5 μm	0.34	0.02	0.70	0.04
oxygen plasma	5 μm	0.18	0.01	0.36	0.02

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Figure1

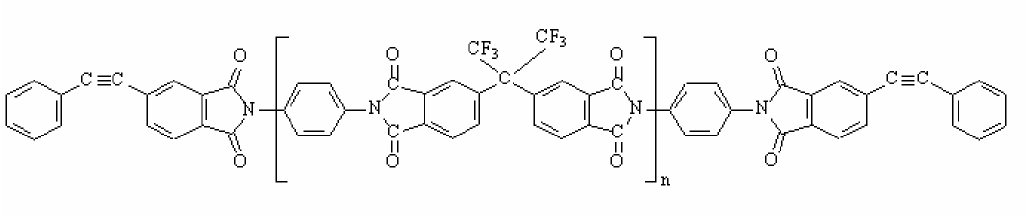

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Figure 2

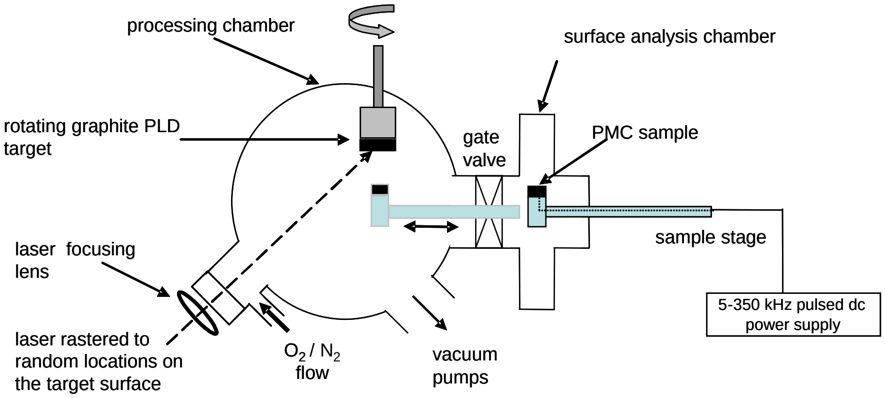

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Figure 3

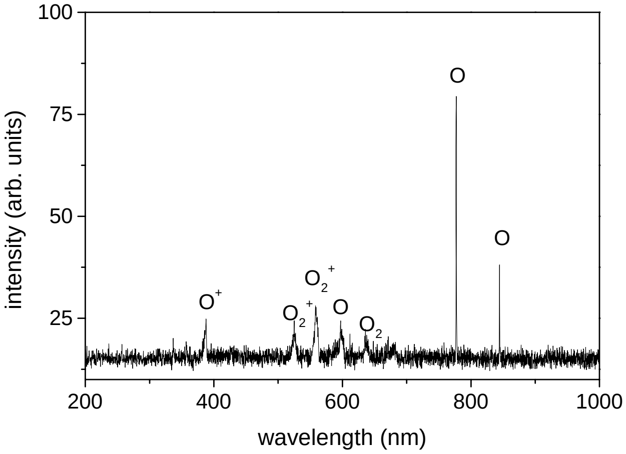

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Figure 4 (a,b)

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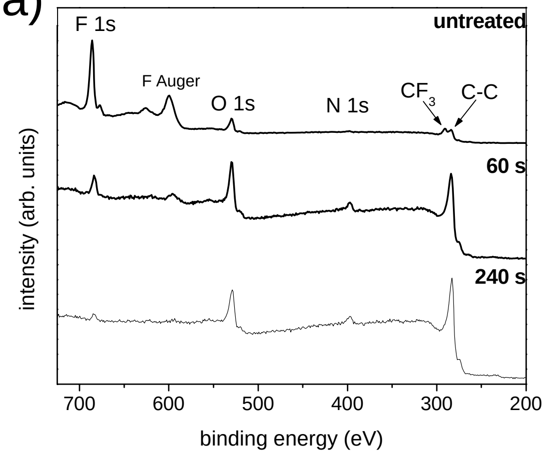

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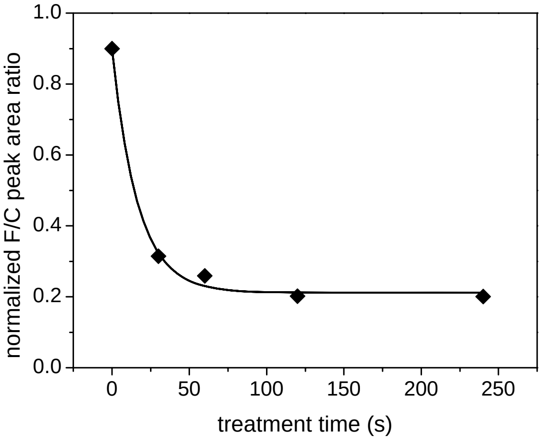

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Figure 5 (a,b, c)

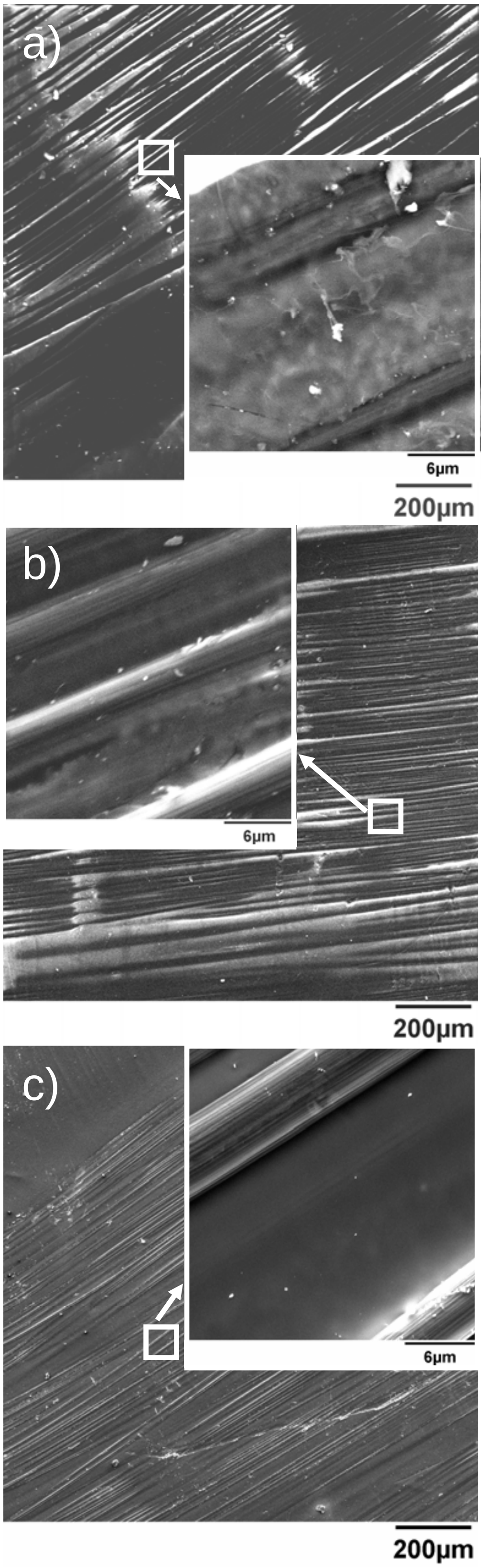

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Figure 6 (a,b)

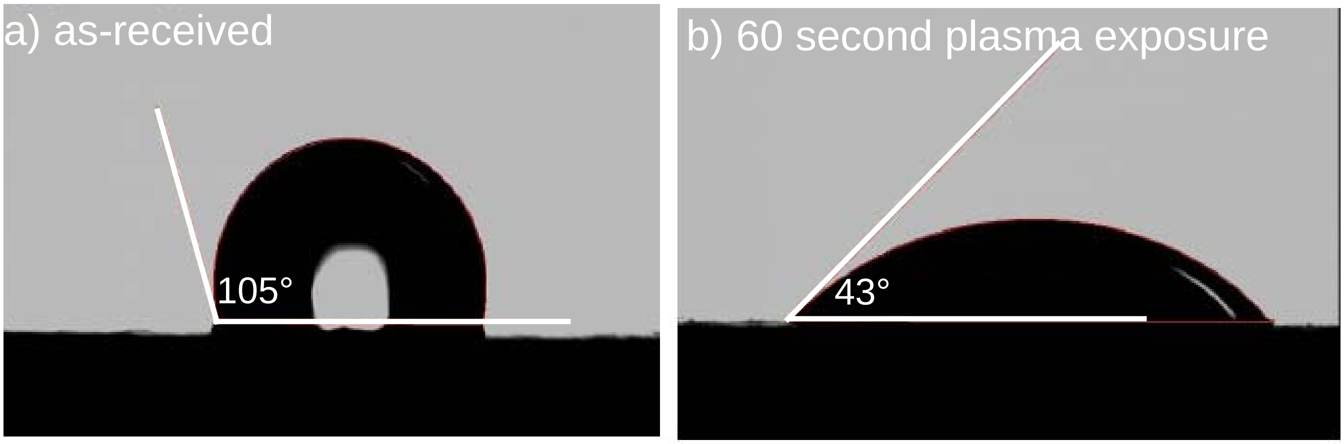

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Figure 7 (a,b,c)

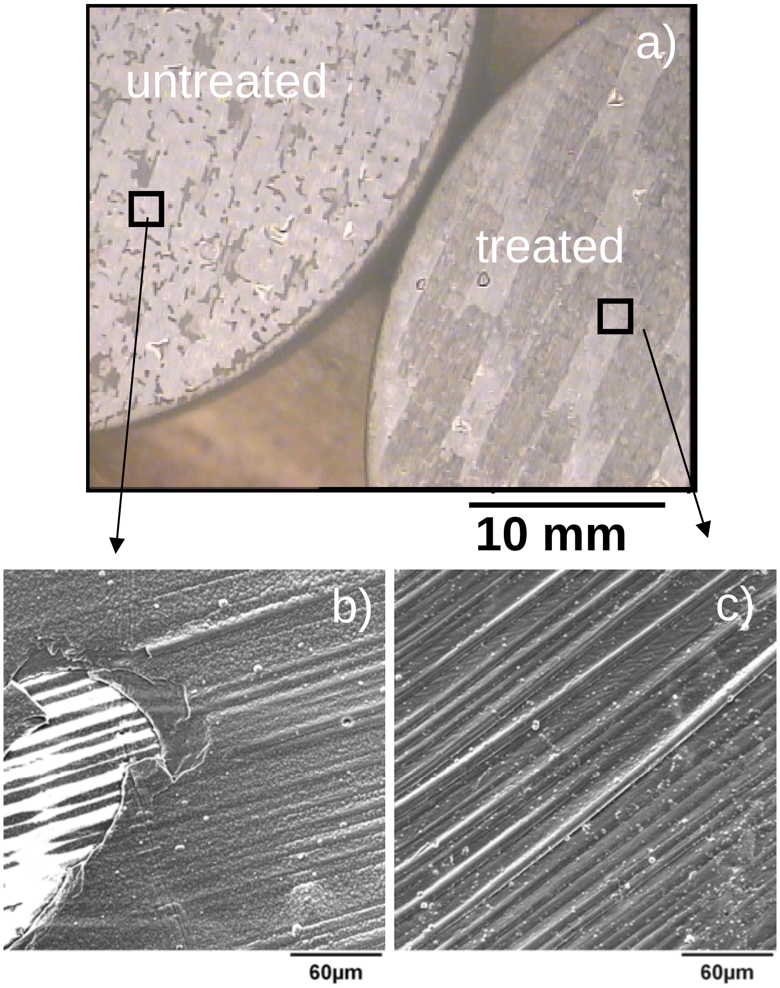

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Figure 8

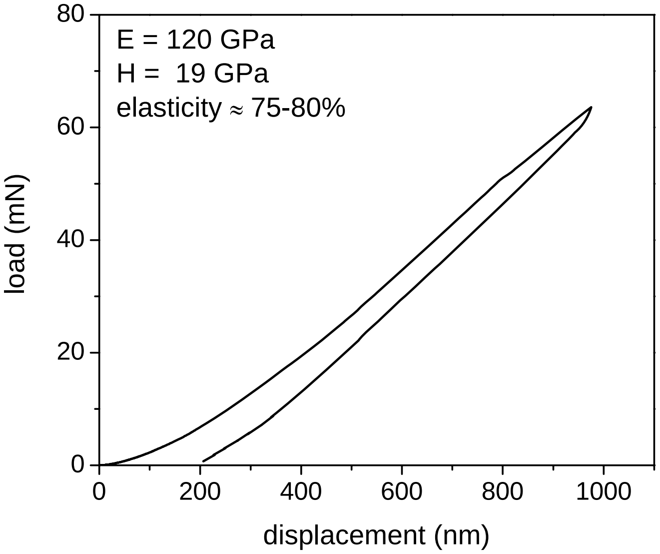

Figure 9 (a,b,c)

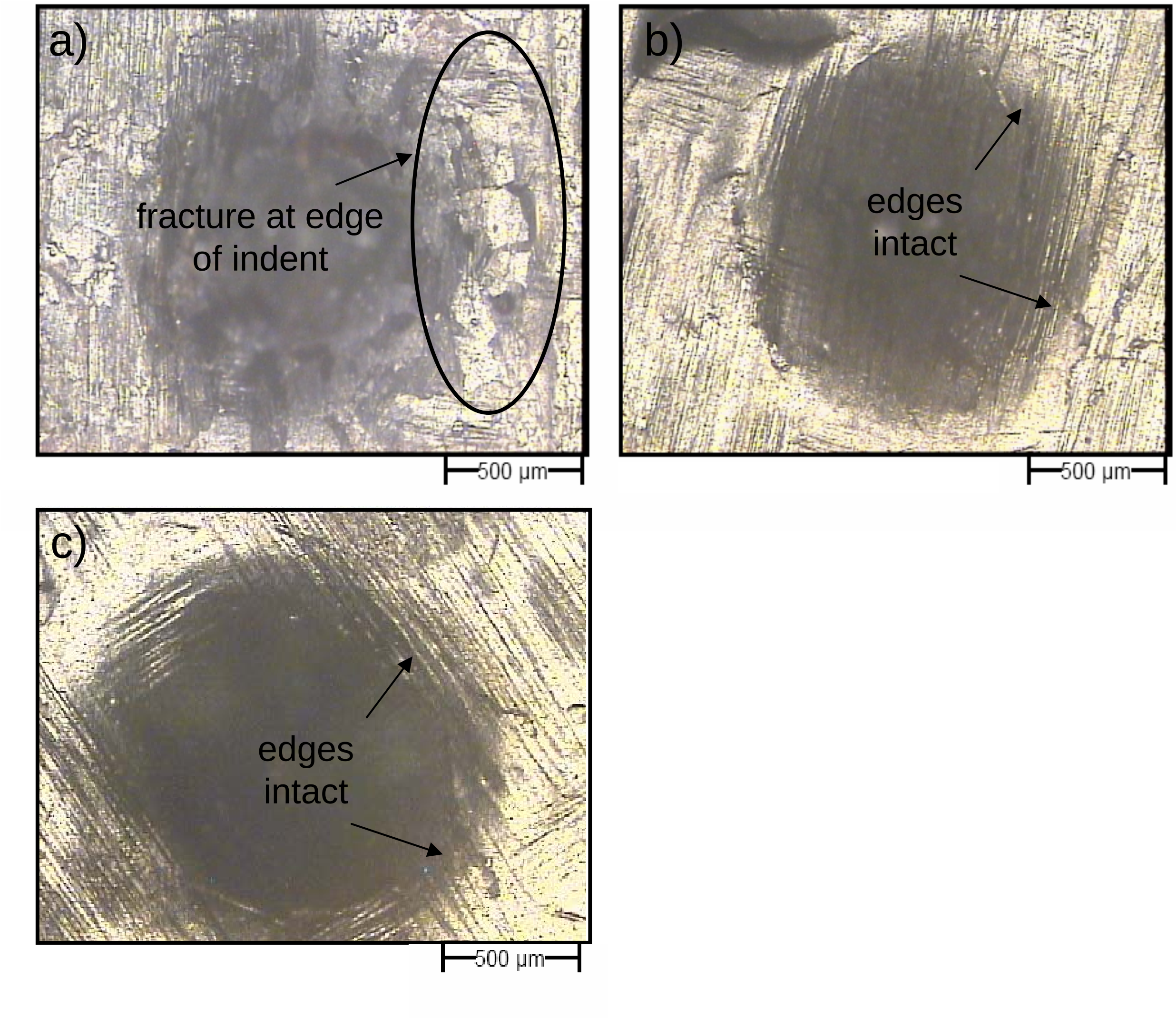
a)
fracture at edge of indent
500 µm
b)
edges intact
500 µm
c)
edges intact
500 µm

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Figure 10 (a,b)

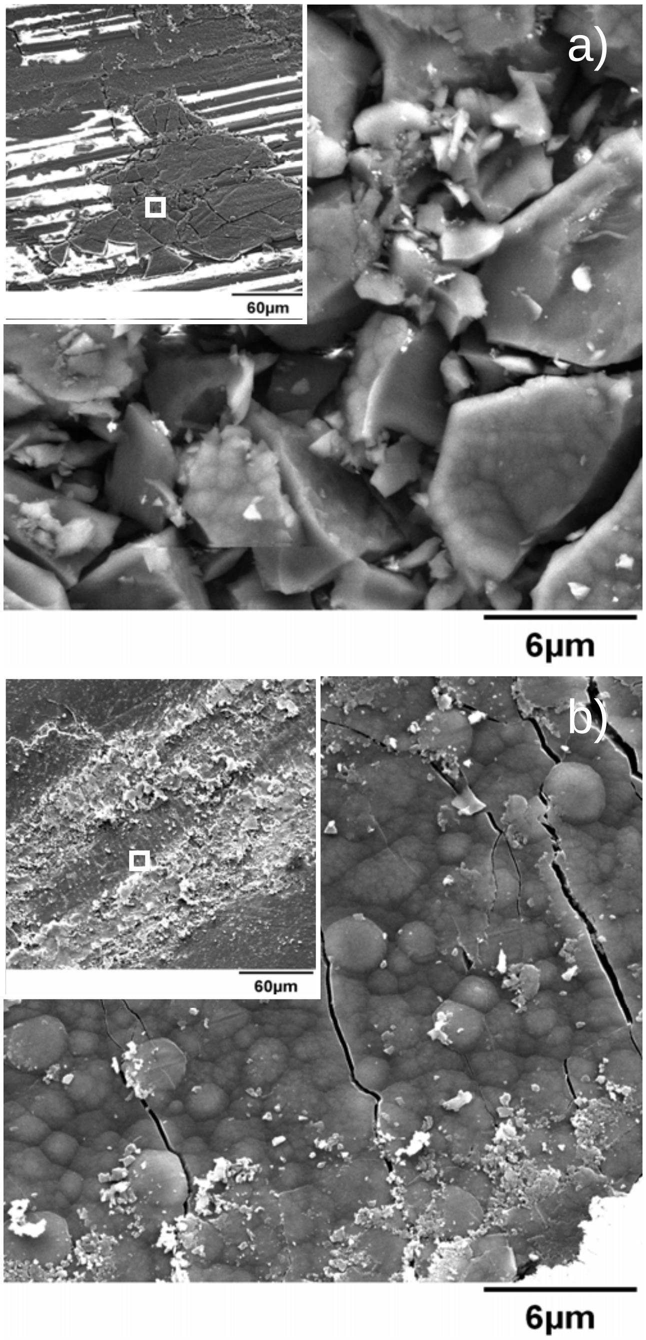

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Figure 11 (a-f)