Electron Beam Surface Carbon Interaction Generates Wear Resistant Coating: Growth Mechanism and Nanotribological Processes

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Disclosures: JLG: Research grants from Bayer, the FDA, DePuy Synthes, consultant for: Exactech, DePuy Synthes, Stryker, Smith and Nephew, Owner: Syracuse Bio-Materials Company, LLC, Editor, J Biomed Mat Res- Part B: Applied Biomat, member: Board of Society For Biomaterials

Introduction: Carbon surface contamination artifacts have been viewed as an imaging side effect of electron beam microscopy. While such adventitious surface carbon is inherently present it has not been seen as potentially useful surface modification method. The potential for this electron-beam induced carbon layer to protect the surface of metallic biomaterials and enhance the wear and tribocorrosion resistance has not been previously investigated. Previous studies have shown that when layered at a certain thickness, such coatings act as a corrosion resistant coating [1]. The electron-beam modified carbon is thought to be amorphous carbon with both SP2 and SP3 bonding (i.e., graphitic and diamond-like carbon [2]), of which the mechanical properties are not well understood. The goal of this study is to conduct nanowear resistance testing of the carbon layer and determine its viability as a potential wear resistant coating. It is hypothesized that the carbon layer will show increased wear resistance compared to the underlying metallic biomaterial.

Methods: Disks of high carbon Cobalt Chrome Molybdenum (CoCrMo), Titanium (Ti-6Al-4V) and Stainless Steel (316 L SS) were polished to 600 grit and had a final mirror polish applied with 0.3 µm alumina. The samples underwent carbon e-beam modification in the scanning electron microscope (SEM, Hitachi S-3700N). A magnification of 21,000x was used to create a carbon deposition of approximately 5x5 µm. The beam voltage was set to 15 kV. A spot size of 50 and working distance of 10 mm was used. Emission currents were approximately 200 µA. The vacuum pressure was 10^{-6} Torr. A scan rate of 0.05 frames per second was used. Each sample sat for 60 minutes in these conditions. The samples were then placed in an atomic force microscope (AFM, Dimension ICON AFM) and the height of middle and edge of the carbon deposition was measured. Scratches 3 µm long were made in the carbon deposition and the underlying surface material using a diamond tip (NM-TC, R=0.8 um). A sample size of 3 was used (n=3). This was repeated at increasing forces until the carbon layer delaminated from the underlying metal. The depth and width of the scratches were measured with AFM section and bearing analysis software. Two-way ANOVA was run to determine if there were significant differences between materials, force, and their interaction between the modified and unmodified surface of each metal (0.05>P). Using Hertzian analysis, a nominal stress was calculated for both the underlying metal and the carbon deposition.

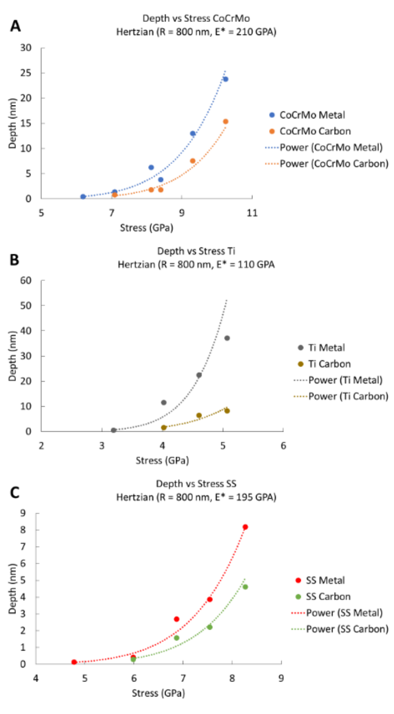
Results: Figures 1A-1C show the penetration depth versus nominal Hertzian contact stress for bare metal and e-beam modified carbon layers on CoCrMo, Ti-6Al-4V and 316L SS, respectively. For all three metals, there was a significant difference due to material type, force, and the interaction of those two factors (0.0001>P). The effect appears to be more pronounced for the Ti-6Al-4V alloy. AFM height images for coated and non-coated surfaces after scratch testing are summarized in Fig. 2. Figures 2A and 2B are coated and non-coated CoCrMo, Figures 2C and 2D are coated and non-coated Ti-6Al-4V and Figures 2E and 2F are coated and non-coated 316L SS. One can see that the width of the scratches and the extent of pileup on the coated surfaces are much less than that seen on bare alloy surfaces. Figure 3 show SEM images of the diamond tip used in the scratch tests after testing. Note the debris pile up and the nominal radius of the tip.

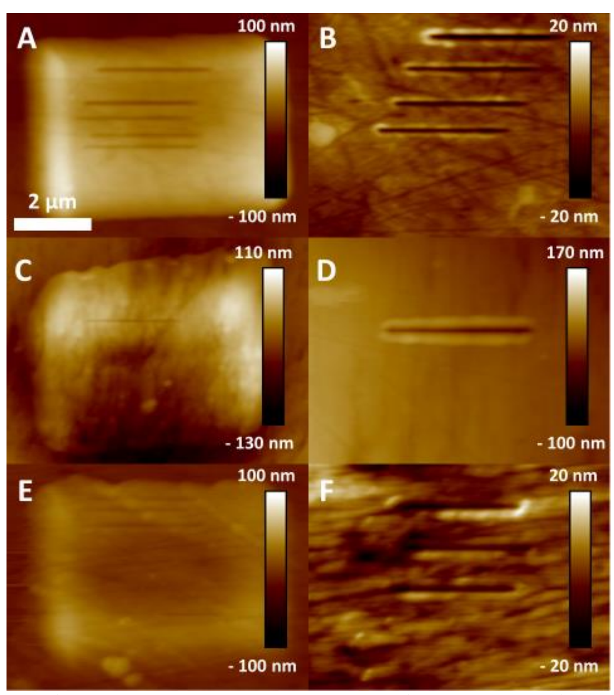
Discussion: For all three metals, the scratch depth was lower at the same force for the carbon coating than the underlying metal surface. This is reflected when looking at the nominal stress of the carbon deposition versus the underlying metal. From this it can be understood that the carbon deposition is more wear resistant than the underlying substrate metal, supporting the hypothesis. As both a corrosion resistant and wear resistant surface modification, e-beam modified carbon coatings have potential as a protective coating on orthopedic metallic surfaces.

Significance/Clinical Relevance: Wear of metallic biomaterials is a leading cause of revision surgery in both total knee and hip arthroplasty. Investigating possible surface modification to these metals in pursuit of better clinical outcomes gives this study clinical significance.

References [1] Sieber et al 2003 Electrochem. Solid-State Lett. (6) [2] Lau et al 2010 Microsc. Microanal. (16)

Figures:





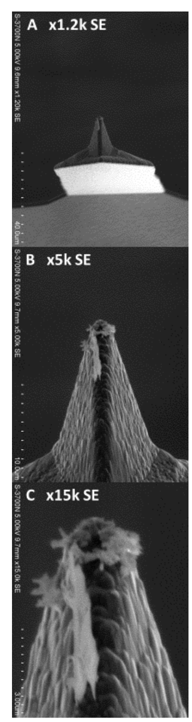


Fig 1. The calculated Hertzian stress for the metal and carbon coating for CoCrMo (A) Ti (B) and SS (C) **Fig 2** Modified (A) and unmodified (B) CoCrMo surface with 272 and 204 µN scratches, modified (C) and unmodified (D) Ti-6Al-4V surface with 120 µN scratches and modified (E) and unmodified (F) 316L SS with 166 µN scratches show that the same force creates a larger scratch on the bare metal surface then the carbon layer. **Fig 3.** The diamond tip can be seen at x1.2k (A), x5k (B) and x15k magnification (C)