## Spectromicroscopy studies of tribochemistry: X-PEEM characterization of self-mated fretting wear in humidity-controlled environments, and nanoscale wear against diamond for tetrahedral amorphous carbon films

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## Introduction

There is a great interest in studying tetrahedral amorphous carbon (ta-C), a new class of hydrogen-free hard amorphous carbon films with unique properties that are very close to those of diamond. ta-C films have excellent mechanical properties (Hardness: 80 GPa, Young's Modulus: 759 GPa) and macroscale tribological properties (low wear rate: 1×10<sup>-8</sup> mm<sup>3</sup>N<sup>-1</sup>m<sup>-1</sup>, friction coefficient: 0.1), and have hydrophobic and chemically inert surfaces [1]. The material is best described as an amorphous mixture of nanophases of tetrahedrallycoordinated (sp<sup>3</sup>) carbon, comprising about 75-85% of the total, with three-fold coordinated (sp<sup>2</sup>) carbon comprising the remaining 15-25%. The three-fold coordinated carbon is not randomly distributed but is instead clustered as conjugated chain-like or, perhaps, sheet-like structures that is responsible for moderate electrical conductivity. This allows for the fabrication of electrically actuated MEMS structures without doping [2][3]. The material is deposited at room temperature using an energetic pure carbon beam that contains a significant fraction of carbon ions with energies peaked near 100 eV. The ablation plume created by focusing 248 nm light from a pulsed excimer laser on to a graphite target provides a suitable pure carbon source. The resulting films are hard, optically transparent, moderately conductive, and atomically smooth (0.1 nm RMS roughness on Si, 1 nm roughness on SiO<sub>2</sub>) [1].

In order to investigate the tribo-chemistry of ta-C sliding on ta-C, small amplitude reciprocating wear and pin-on-disk experiments in dry N<sub>2</sub> with relative humidity values of 0%, 25% and 50% were conducted. Friction was measured during sliding, and the wear tracks were subsequently examined with both atomic force microscopy (AFM) and X-PEEM-XANES (X-ray photoelectron emission microscopy combined with X-ray spectroscopy) absorption near-edge structure spectromicroscopy. The primary goal was to determine if X-PEEM could discern chemical differences between the wear track and the unworn film. Not only does X-PEEM show chemical differences in the wear tracks, but the changes are distinct enough to allow quantitative interpretation of the changes in the bonding structure due to wear. Thus, these measurements give information regarding the wear mechanisms. Studies performed on ta-C at 50% humidity showed extremely low friction. According to X-PEEM, a weakly bonded carbonaceous layer that initially covers the ta-C

film is worn away inside the track. Surprisingly, this leaves high-quality ta-C inside the wear track and creates graphitized and oxygenated debris regions along the border of the wear track. As with polycrystalline diamond films, friction increases as the relative humidity decreases, and surprisingly, the degree of oxidation of the wear track and the debris increases as well. We will discuss changes observed in both friction and the chemical signature of the surface as the percentage of relative humidity in the environment is varied, and the relation between humidity in the environment and the level of graphitization that occurs in the wear track.

Part of this work was funded by Sandia. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. Part of this work was also supported by the US Department of Energy BES-Materials Sciences at Argonne National Laboratory, under Contract DE-FG02-02ER46016, and the Air Force Office of Scientific Research under Contract FA9550-05-1-0204. This work is based upon research conducted at the Synchrotron Radiation Center, University of Wisconsin-Madison, which is supported by the NSF under Award No. DMR-0084402.

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