Sub-Nano to Nanoscale Wear of Titanium Oxide-Metal Surfaces Using Atomic Force Microscopy

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INTRODUCTION: Titanium and its alloys have been widely used as biomaterials for orthopedic, dental and cardiovascular implants. A spontaneously formed passive oxide film, with thickness of 2-10 nm, protects titanium from corrosion and influences its tribological properties (wear resistance, hardness, et al.) and biocompatibility. The asperity-based tribology and tribocorrosion behavior of titanium may result in full removal/disruption or partial removal of oxide films. The near atomic-scale tribological behavior of titanium surfaces in air are reported on in this study from the atomic scale (0.2 nm) to beyond its full thickness (~10 nm) using a novel atomic force microscopy (AFM) based tribology method. Partial removal of titanium oxide was achieved and quantified by scanning AFM diamond probe on titanium surface at low load (from 70 mN). Depth of oxide removed due to multi scratch scaning started at 200 pm and increased in a load-dependent way to 10 nm and well beyond. A novel image-wear-image method, using image subtraction, was able to remove virtually all non-tribological surface topographic information leaving only the wear-based difference image from which highly precise vertical wear topography information could be obtained. Therefore, the goal of this work is to present this sub-nanoscale tribological method and relate the single asperity nature of this test to understanding wear and tribocorrosion of titanium in physiological solutions.

EXPERIMENTAL METHODS: Grade 4, commercially pure (CP) titanium discs were minor polished. Contact mode Atomic Force Microscope (Dimension ICON AFM, Brukers, US) and wear-resistant diamond-coated AFM probe (NMTC, Bruker, US) were used for scratching and imaging the surface. For the depth-load relationship study, nanotribology tests include multi-scan lines and single asperity scratch tests. In both tests, a 10 x10 µm Ti surface was imaged at a low force setpoint (no wear) at 3 Hz, 512 scan lines before and after scratching. The after-scratch image was then subtracted digitally from the original image. This has the effect of removing all surface features that are not affected by scratching and leaving a raised region where the wear occurred. These subtracted images were used for average depth analysis. During scratching, the load was controlled by setting the deflection setpoint to a specific voltage causing a higher contact load (from 0.2 V to 1.2 V (nominally 12 to 70 mN), in 0.05 V increments, n=4 repeats). In multi-scan-line wear tests, the scan frequency was set to 5 Hz and a 2 x 2 µm image was scanned at a specific wear load to induce wear damage. For single asperity scratch testing, the scan frequency was changed to 0.1 Hz and only a 3 s scan was conducted to induce a scratch and three loads (0.4 V, 0.5 V, 0.8 V) were used to determine depth versus load. The effect of the number of scan lines on wear depth was performed at 0.5 V while 4 different scan line numbers were chosen (64, 128, 256, 512) during scratching. This was done to assess how the number of scans per wear region affected depth. The AFM tip was imaged in the SEM to determine radius of curvature and calculate Hertzian contact stress.

RESULTS and DISCUSSION: Fig.1 shows a representative height difference image of a scratched area tested at a force setpoint of 0.3 V. Depth due to wear was clearly revealed by this subtraction method and the average depth removal in this case was about 0.4~0.5 nm (about 2 atom thickness). Thus, quantitative measurement of the average depth change and the materials removal at the nearatomic scale was achieved using this method. Fig.2 (a) (and inset) shows nominal contact stress-dependent nanoscale wear behavior of Ti oxide and surface. Partial removal of Ti oxide film was observed between nominal Hertzian stresses of 2.6 GPa to 4.6 GPa, with wear depth increasing from 0.2 nm to 10 nm. Deviation from Hertzian contact was observed at a larger depths/nominal contact stresses. This change may due to the penetration through the oxide and into the metal substrate. Fig. 2 (b) show the variation in wear depth with number of scan lines. A non-linear increase in average depth was observed, where depth increased from 0.96 nm at 64 scan lines to 2.1 nm at 512 scan lines. This behavior can be explained by a decrease in the inter-scratch distance with increasing scan lines thereby increasing the number of passes over the surface by the tip. Fig. 3 shows height difference image after three single asperity scratches were imparted at different setpoint loads. Depth change due to single asperity wear increased from 1.75 nm at 0.4 V to 2.75 nm at 0.8 V. Compared to the single asperity tests, multi-scan-line wear leads to larger average depth changes, which is expected based on stress field distribution in contact mechanics.

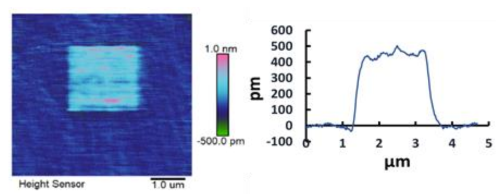

Fig.1. AFM height image shows depth variation with 0.5 nm due to scratch at 0.3 V.

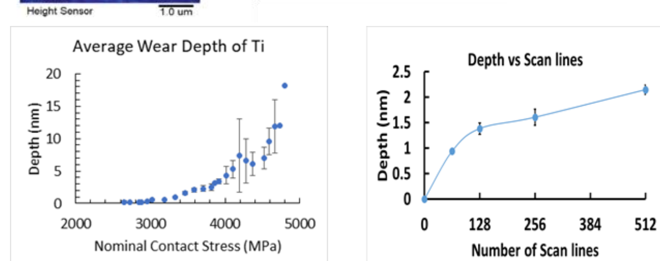

Fig.2. a) Nomical Contact Stress-dependent and b) scan lines-dependent wear depth of Ti in AFM multi-scan wear test.

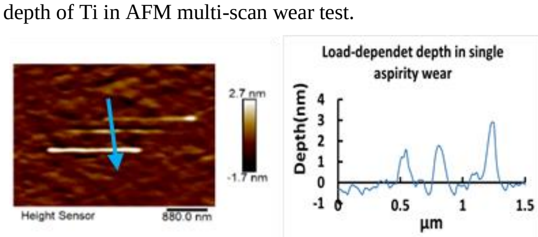

Fig.3. Wear depth variation with load in single asperity test.