AFM Diamond Tip-Based Nanoscale Tribocorrosion of CoCrMo Alloy in Air and Physiological Solution

Hwaran Lee[1, 2], Jeremy. L Gilbert[1, 2]
[1]Department of Bioengineering, Clemson University, Clemson, SC, US
[2]The Clemson University-Medical University of South Carolina Bioengineering Program, Charleston, SC, US
hwaranl@clemson.edu

DISCLOSURES: Hwaran Lee (N), Jeremy L. Gilbert (3B-Syracuse Bio-Materials Company, Zimmer Biomet, Smith and Nephew, Stryker Orthopedics, Omnilife Sciences, Naples Community Hospital; 5-Depuy Synthes, Bayer, Inc.; 7B-J Wiley and Sons; 8-Journal of Biomedical Materials Research-Part B; 9-Council of the Society For Biomaterials)

INTRODUCTION: Cobalt-Chrome-Molybdenum (CoCrMo) alloys are excellent orthopedic biomaterials due to their biocompatibility, corrosion resistance, and wear resistance. High wear resistance is contributed to by a 1-3 nm thick passive oxide film. However, tribocorrosion, also known as mechanically assisted corrosion (MAC), and the release of metal ions (cobalt, chromium, or molybdenum ions) from head-neck tapers of total hip replacements have been of concern. The released debris and metal ions may lead to adverse local tissue reaction (ALTR) at modular taper junctions. The mechanisms of nanoscale tribocorrosion have not been fully understood. To date, there has been no atomic force microscopy (AFM) based study of multiple repetitive nanowear scratches at the near oxide to sub-oxide thickness in a single region to investigate the nanoscale tribocorrosion in physiological environments. This study used AFM diamond probe tips to simulate the cyclic micromotion within modular taper junctions of a single asperity contacting the CoCrMo surface. The progression of wear penetration and debris pile up in a single line nanoscratch as a function of the number of cycles imparted to the surface in air and physiological solution, under constant load and sliding distance. A single line scratch with multiple scratches at or less than the oxide film thickness (40, 200, and 400 cycles) were generated using an AFM diamond tip for each condition. This project hypothesizes that the wear behavior will be affected by dry or wet physiological solution. Furthermore, we hypothesize that the volume of the wear track and pile up will be approximately equal and follow a linear function of scratch cycles.

METHODS: Wrought CoCrMo alloy (ASTM F1537, low carbon) disks were polished on 240, 320, 400, and 600 grit emery paper under flowing water. Alumina powder (1 µm) contained in deionized water was used to make mirror-finished surfaces. Each sample was cleaned with deionized water and 70 % ethanol to remove any remaining particles on the surface. A diamond AFM probe tip (NM-TC, Bruker) (radius ~ 0.5 µm) was used for single line scratching (8 µm × 8 µm, disabled slow scan axis, 0.1 Hz) and imaging (12 µm × 12 µm, abled slow scan axis, 2 Hz) with 512 × 512 lines. The scratches were generated in air (in air mode) and Phosphate-Buffered Saline (PBS) (in fluid mode) under contact mode and imaged afterward. The number of scratches were 40, 200, and 400, performed in a single track on CoCrMo surface with a consistent force, applied deflection setpoint, and deflection sensitivity, respectively (164 µN, 4 V, 116.93 nm/V in air and 137 µN, 4 V, 97.60 nm/V in PBS). The Hertzian contact model was used to evaluate the AFM probe – CoCrMo surface contact mechanics. The wear track volume, pile up volume, and wear track depth were analyzed using bearing analysis of NanoScope software (version 9.4, Bruker). At least three trials of scratches ($n = 3$) were run for each test. Statistical analysis of the results was conducted using a one-way ANOVA statistic ($p = 0.0001$).

RESULTS: The AFM images demonstrated a single straight scratch wear line (darker) and pile up debris (brighter) accumulated around the wear track (Fig. 1A-1F). It was obvious that the width of wear track increased with cycles in both air and PBS. The volume of the wear track and pile up rose with increasing number of scratches. It was clear to observe the shape of pile up from deflection error images. However, there was a difference on wear track width and volume of the pile up between in air and PBS. The width and pile up volume in air according to AFM images were greater than in PBS ($p < 0.0001$). Moreover, the ratio between pile up and wear track volume in air (average: 2.39) was higher than PBS (average: 1.50) as shown in Fig. 2. The volume of wear track and pile up increased with more scratches applied both in air and PBS (Fig. 3A and 3B). However, the volume of wear and pile up in air did not rise linearly with an increasing number of scratches, but rose rapidly within the first 40 scratches. On the contrary, the wear and pile up volume in PBS grew relatively linearly. Furthermore, the wear and pile up volume in air were significantly greater than PBS condition ($p < 0.0001$). The wear volume in air was significantly greater (22, 13, and 7 times for 40, 200, 400 scratches respectively) compared to PBS condition. Similarly, pile up volume after 40, 200, and 400 scratches in air was 34, 17, and 15 time greater than in PBS. It is interesting that the wear depth after 40 to 400 scratches in air was plateaued (no significant difference) (Fig. 3C). On the other hand, the depth in PBS increased with increasing of number of cycles.

DISCUSSION: This study investigated single track nanoscale wear processes on passive oxide film of CoCrMo alloys, which can vary with the environment and cycles. The number of scratches is important because the wear volume grew as the number of scratches increased in both air and PBS. The wear track was significantly wider and deeper in air than PBS, indicating that the AFM probe tip may penetrate more across the oxide film in air. As the probe tip continues to penetrate, the wear track width increases, which distributes the load over a larger area. In addition, the nominal Hertzian contact stress was 11.65 GPa in air and 10.97 GPa in PBS, so the difference on contact stress may lead to greater wear effect in air. Less debris pile up was found in PBS after the same number of scratches than air. This might be because metal ions or debris might spread over or dissolve in PBS. However, the wear and pile up volume were not equal, but almost 2-fold different. The software might overmeasure the pile up volume because there might be some gaps between debris. Also, tip-surface convolution may affect these measurements. PBS might change the properties of oxide film including coefficient of friction or topography by exposure to the solution. Thus, the depth, wear and pile volume in PBS were significantly lower than the air condition. This is in contradistinction to so-called synergistic effects. This study corresponds to our previous study, revealing that wear depth was deeper in air than PBS post single scratching on CoCrMo alloy and Ti-6Al-4V alloy using an AFM diamond tip [1][2]. In conclusion, CoCrMo alloy is more wear resistant in physiological solution than in air under these nanowear conditions.

SIGNIFICANCE/CLINICAL RELEVANCE: Nanoscale tribocorrosion in *in vivo* fluid between the crevice of modular taper junctions of orthopedic implants may occur less severely than in dry condition.

REFERENCES: [1] Y. Liu, A. Mace, H. Lee, M. Camargo, and J. L. Gilbert, "Single asperity sub-nano to nanoscale wear and tribocorrosion of wrought CoCrMo and additively manufactured CoCrMoW alloys," *Tribol. Int.*, vol. 174, Oct. 2022, doi: 10.1016/j.triboint.2022.107770. [2] Y. Liu, D. Zhu, and J. L. Gilbert, "Sub-nano to nanometer wear and tribocorrosion of titanium oxide-metal surfaces by in situ atomic force microscopy," Acta Biomater., vol. 126, pp. 477–484, 2021, doi: 10.1016/j.actbio.2021.03.049.

IMAGES AND TABLES:

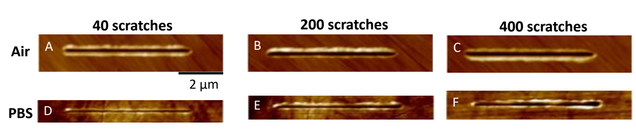

Fig 1. (A-F) AFM images showing greater pile up volume and greater scratch width in air than PBS.

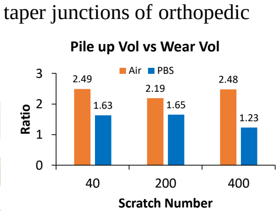

Fig 2. Higher ratio in air between pile up and wear volume than PBS

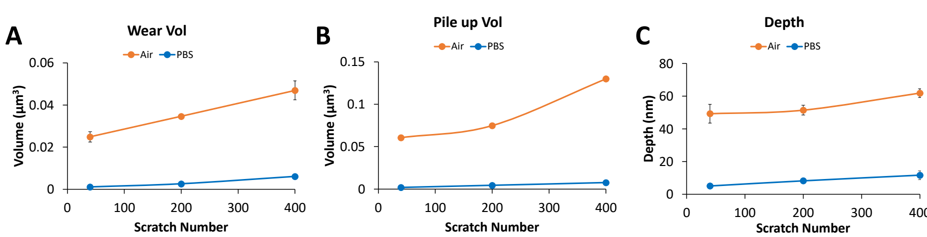

Fig 3. Greater (A) wear track volume, (B) pile up volume, and (C) wear track depth in air than PBS condition ($p < 0.0001$). Some error bars were hidden due to bigger data dots.