

Tribocorrosion Evaluations of Carbide-derived Carbon (CDC) Surface Modification for Hip Implants

Yani Sun¹, Kyle Kinnerk², Tony Mirshed³, Michael McNallan¹, Mathew Mathew^{2,4}

¹Department of Civil, Materials and Environmental Engineering, University of Illinois at Chicago, Chicago, IL, ²Department of Biomedical Engineering, University of Illinois at Chicago, Chicago, IL, ³Department of Biological Sciences, University of Illinois at Chicago, Chicago, IL, ⁴Department of Biomedical Sciences, UIC College of Medicine at Rockford, Rockford, IL
ysun98@uic.edu, mtmathew@uic.edu

Disclosures: Yani Sun (N), Kyle Kinnerk (N), Tony Mirshed (N), Michael McNallan (N), Mathew Mathew (N)

INTRODUCTION: In the case of severe arthritis and rheumatic joint diseases, total joint replacement is a widely accepted procedure. Currently, there are 2.4 million estimated annual incidence of primary total hip replacement (THR) surgeries in the US[1]. Historically, metal-on-metal (MoM) THR was popular, however, due to many adverse clinical reports, it was totally recalled from the US market in 2009. Nonetheless, MoM THR has many promising benefits, such as a good choice for the younger population and lower rate of wear products. Hence, many researchers focused on how to solve the concerns on MoM. One of the interesting findings is on the discovery of tribolayer, in the metal-metal interface, a layer of metal-organic complexes formed dynamically due to mechanical mixing and tribochemical reactions[2]. However, such tribolayer is not very stable and homogeneous. Therefore, in our research, we focused on developing very similar types of surface modification to the tribolayer, called carbide-derived carbon (CDC). We previously fabricated CDC on Ti6Al4V, and found that CDC could provide superior protection to the substrate in a tribocorrosive environment under the open-circuit potential (OCP) condition[3]. However, to fully understand the tribocorrosion behavior of CDC, other electrochemical conditions and tribocorrosion synergism need to be studied. Therefore, the objective of this work is (i) to evaluate CDC's tribocorrosion performance under various electrochemical conditions, including OCP and potentiostatic (PS) with anodic, cathodic, and open potentials, (ii) to analyze the weight loss ratio (K_w/K_c) to determine the synergism of each group. We hypothesize that CDC will show better tribocorrosion performance than Ti6Al4V under all electrochemical conditions and will show a tribocorrosion regime of antagonism (beneficial effects).

METHODS: CDC was prepared on a Ti6Al4V substrate via the electrolysis approach we described previously[3]. Ti6Al4V was ground with sandpapers, and polished with diamond paste and silica suspension until the samples had a mirror-like finish ($R_a < 50$ nm). Alumina was used as the pin to simulate a ceramic counter body, and bovine calf serum (BCS) was selected to emulate biological fluids. Two groups of samples were tested, alumina (Al_2O_3)-Ti6Al4V (control group) and alumina-CDC, using a customized tribocorrosion system as in **Figure 1** with reciprocal sliding at 1 Hz for 3600 cycles. A standard electrochemical protocol was followed, including an initial stabilization, a testing stage, and a final stabilization. OCP and PS were applied during the testing stages, respectively. Electrochemical impedance spectroscopy (EIS) was conducted before and after the testing stage to analyze the local corrosion kinetics. SEM-EDS was used to observe the wear scar and acquire the surface composition, 3D profiler will be used to measure the wear volume.

RESULTS: **Figure 2(a)** displays the changes in the OCP of Ti6Al4V and CDC. CDC possesses a higher free potential (83 mV) than Ti6Al4V (-290 mV), suggesting that CDC has a higher resistance than Ti6Al4V. At 600 s, the pin started sliding on the disk, causing the removal of the passive layer, and contributing to the drop in OCP. While CDC shows an OCP drop of 86.15 mV, Ti6Al4V presents a more significant change of 783.99 mV, around 10-fold of the CDC. In addition, during the motion stage, CDC's potential variation (0.626 mV) is lower than Ti6Al4V (1.91 mV). As can be seen in **Figure 2(b)**, the induced current density of the cathodic group is the highest for both CDC and Ti6Al4V among all applied potentials, and Ti6Al4V displays a higher current density in general than CDC. The plots were magnified in **Figure 2(c)** for 4 cycles (2630 – 2634 s), where it is obvious that Ti6Al4V exhibits higher induced current than CDC under sliding. For Ti6Al4V, obvious fluctuations can be observed for all three groups, whereas for CDC, no obvious current change can be found in the free potential (CDC- E_{oc}) group, and the variation in current density is similar in CDC- E_{ano} and CDC- E_{cath} groups. After the testing, all samples were scanned by 3D profiler as shown in **Figure 2(d)**, where Ti6Al4V shows a wider scar than CDC.

DISCUSSION: The study reporting the synergistic analysis of wear and corrosion behavior of CDC for the hip implant application. According to Stack and Abdulrahman[4], and the total weight loss (K_{wc}), weight loss due to corrosion (K_c) and wear (K_w) were estimated based on the wear volume and densities, displayed in **Figure 2(e)**. According to the synergistic regime, Ti- E_{ano} was identified as wear-corrosion, while other groups belong to wear dominant regime. It is evident that the weight loss of Ti6Al4V in each aspect (K_{wc} , K_w , and K_c) is remarkably higher than CDC. It is also worth noting that the total loss K_{wc} values of Ti6Al4V under potentiostatic groups are statistically significantly higher than Ti-OCP; however, no significance was found between potentiostatic groups and OCP condition for CDC. This is potentially because the growth of the oxide layer requires electrochemical reactions, whose rate can be affected by applied potentials. Therefore, with a lower growth rate of the passive film, the wear debris accumulated in the wear tracks can cause the transition from two-body wear to three-body wear mode faster, which may lead to more adverse degradation, as illustrated in **Figure 3(a)**. Nevertheless, the electrochemical conditions did not influence CDC's performance significantly as in **Figure 3(b)**, implying that the formation of the passive layer may not be the main protection mechanism for CDC. Also, due to the porous structure and carbonaceous nature of CDC, proteins might be easier to attach on the CDC to form tribolayer, which still needs to be verified. The study has several limitations, future studies will be focused on evaluating synergistic interaction in a hip simulator and mimic more adverse conditions in in-vivo joint environment.

SIGNIFICANCE: Carbide-derived carbon (CDC) might be much better for the protein absorption and the growth of tribolayer due to its porous graphitic structure, and it may provide a similar function of tribolayer considering its superior tribocorrosion performance and low friction coefficient. These findings will also be helpful to researchers and physicians in terms of implant selection and development.

REFERENCES: [1] A Siddiqi et al., 2022, [2] M. A. Wimmer et al., 2009, [3] Y. Sun et al., 2021, [4] M. M. Stack and G. H. Abdulrahman, 2010

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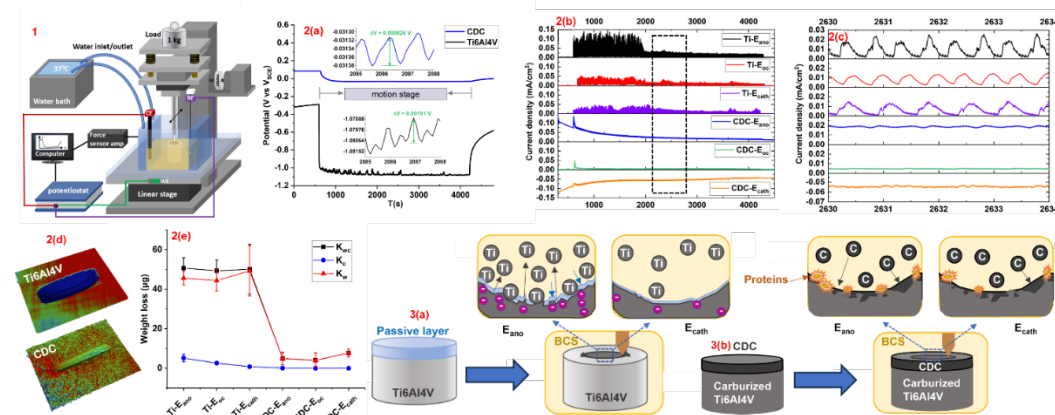


Figure 1 Customized tribocorrosion system. **Figure 2:** (a) Evolution of OCP, where CDC shows higher potential and smaller potential variance, (b) Evolution of potentiostatic curves under three potentials, (c) Magnified sections of PS curves, (d) 3D profiles of Ti6Al4V and CDC after tribocorrosion, and (e) Weight loss estimation of all groups. **Figure 3:** Possible degradation mechanisms of (a) Ti6Al4V and (b) CDC.