

Corrosion Evaluation of the Titanium Diffusion Hardened (TDH) Surface Modification for Spinal Discs

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INTRODUCTION: Spinal pain is almost ubiquitous in man[1]. Total disc replacement (TDR) is a procedure to treat low back or cervical back pain related to disc disease. Alloy corrosion has been shown to have negative effects for the arthroplasty device and host[2]. Titanium diffusion hardening (TDH) is a surface treatment that involves the application of sustained heat in a controlled environment. TDH improves the mechanical properties and wear performance of titanium alloys and may also improve corrosion resistance. In the present study, we aim to investigate the corrosion resistance properties of TDH-treated cervical disc arthroplasties compared to three clinically relevant controls: Ti6Al4V (the most common metal alloy used in orthopedic implants), Ti/TiC metal matrix composite (the current material from which the marketed arthroplasty device is fabricated), and CoCrMo (the most commonly used metal alloy bearing in human arthroplasty). We hypothesize that TDH treated specimens will show better corrosion resistance.

METHODS: The current PRESTIGE LP cervical disc (size: 5 mm x 12 mm; made from Ti/TiC) and TDH treated cervical disc (5 mm x12 mm) specimens were provided by Neuro-Innovations LLC and used as received, as displayed in Figure 1(a). Four materials were tested: (i) TDH-treated Ti6Al6V, (ii) substrate material alone, Ti6Al4V, (iii) Ti/TiC metal matrix composite, and (iv) CoCrMo. Figure 1(b) shows that a customized corrosion chamber was employed, and bovine calf serum (BCS) with 30g/L protein was selected as the electrolyte to mimic the human body fluids. Furthermore, the standard corrosion testing protocol was followed (ASTM G61), consisting of open-circuit potential (OCP), potentiostatic (PS), OCP, electrochemical impedance spectroscopy (EIS), cyclic polarization (CP) and OCP. After experiments, the corroded surface was examined under scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) and white-light profilometry.

RESULTS: According to Tafel's equation, the corrosion current density (I_{corr}) and potential (E_{corr}) were derived from the CP results as in Figure 2(a). As displayed in Figure 2(b), TDH's I_{corr} ($0.070 \pm 0.034 \mu\text{A}/\text{cm}^2$) is similar to Ti6Al4V ($0.063 \pm 0.031 \mu\text{A}/\text{cm}^2$), but significantly lower ($p < 0.05$) than Ti/TiC ($0.139 \pm 0.033 \mu\text{A}/\text{cm}^2$) and CoCrMo ($2.550 \pm 1.420 \mu\text{A}/\text{cm}^2$). Also, in Figure 2(c), TDH's E_{corr} ($-0.295 \pm 0.096 \text{ V}$) is similar to Ti6Al4V ($-1.700 \pm 0.060 \text{ V}$), but significantly higher than Ti/TiC ($-0.62 \pm 0.034 \text{ V}$, $p < 0.05$) and CoCrMo ($-0.680 \pm 0.024 \text{ V}$, $p < 0.01$). Furthermore, EIS results are shown in Figure 2(d) Bode plots and Figure 2(e) Nyquist plots, to which a modified Randle circuit was applied. Then polarization resistance (R_p) and double-layer capacitance (C_{dl}) were estimated from the circuit modeling as presented in Figure 2(f) and (g), where the TDH presents the highest R_p ($9.86 \pm 2.56 \text{ M}\Omega \cdot \text{cm}^2$) and the second lowest C_{dl} ($9.24 \pm 0.12 \mu\text{F}$), which agrees with the CP results. Lastly, according to SEM images in Figure 3(a), no apparent corrosion damage was observed on the Ti6Al4V and TDH, whereas damages were observed on Ti/TiC, especially around the composite particles, and pitting was found on CoCrMo. Figure 3(b) exhibits the 3D profiles of Ti/TiC and TDH treated samples obtained from white-light profilometry after corrosion.

DISCUSSION: Since I_{corr} is proportional to corrosion rate and E_{corr} refers to a potential threshold for corrosion to occur, the results indicate that TDH-treated disks show a significantly lower corrosion rate and a lower corrosion tendency compared to Ti/TiC and CoCrMo. The Ti/TiC composite material shows distinct TiC particles in the structure, potentially rendering the material more susceptible to corroding, whereas the TDH treatment provides a uniform layer on the surface, preventing corrosive damage. Also, pitting happens on CoCrMo when the passive layer is removed by corrosion, leading to further corrosion damage without the presence of repassivation process, which may be the dominant reason for the high corrosion rate[3]. Ti6Al4V's excellent corrosion behavior is also attributed to the oxide film, which can be naturally formed in a tens of nanometers. During the corrosion process, the protective oxide film can be formed by the repassivation process, resulting in the protection to the substrate and a low corrosion rate. However, this oxide film is likely to be worn off when the cervical disk is subjected to mechanical motions, causing further serious complications in clinical applications[4]. Although TDH's corrosion performance was similar to Ti6Al4V, the TDH technique is designed to improve the wear resistance to abrasion and friction to a degree that is significantly better than untreated Ti6Al4V; therefore, it might be a potential method to improve corrosion resistance of cervical disks while concomitantly providing excellent tribological performance. Nonetheless, this is an ongoing study; and additional testing is needed to validate these early promising results.

SIGNIFICANCE: Corrosion that occurs on the surface of a disk arthroplasty device can cause premature failure of the implant and adverse local tissue reaction. Titanium diffusion hardening (TDH) treated disks show enhanced corrosion resistance compared to the current composite material (Ti/TiC) and CoCrMo. Also, TDH may provide better tribocorrosion properties than Ti6Al4V, which still needs to be investigated. Therefore, TDH is a promising surface modification technique to improve tribocorrosion properties of spinal disk arthroplasty devices.

REFERENCES: [1] B. A. Casazza, 2012. [2] N. Hallab et al., *J. Bone Jt. Surg.-Am.*, 2001, [3] P. Panigrahi et al., *J. Biomed. Mater. Res. B Appl. Biomater.*, 2014, [4] D. Royhman et al., *J. Phys. Appl. Phys.*, 2013

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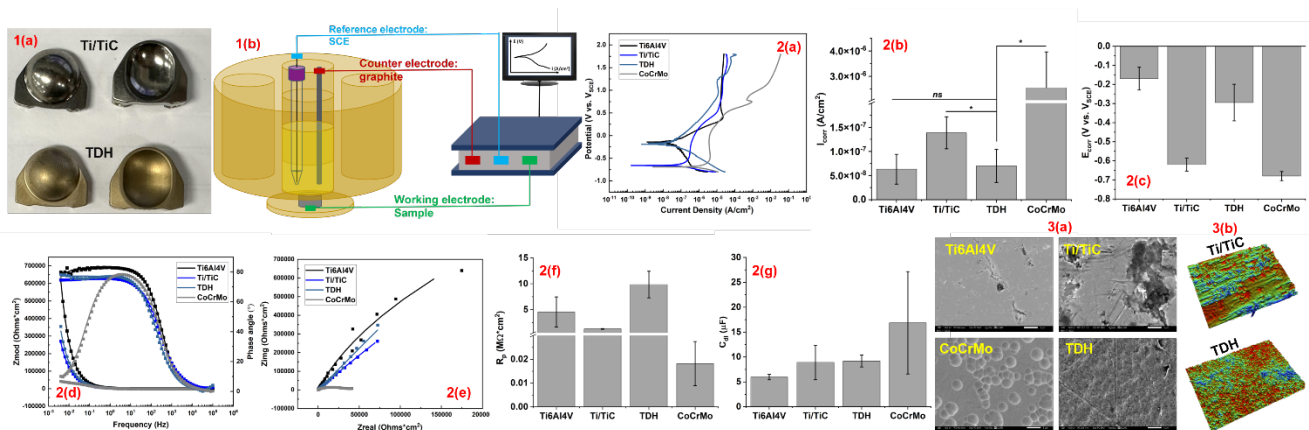


Figure 1: (a) Pictures of Ti/TiC and TDH treated cervical disks. (b) Customized 3-electrode corrosion chamber. **Figure 2:** (a) Evolution of potentiodynamic curves. (b) Bar diagram of I_{corr} . (c) Bar diagrams of E_{corr} . (d) Bode plots of EIS. (e) Nyquist plots of EIS. (f) Polarization resistance (R_p) of all groups. (g) Capacitance of all groups. **Figure 3:** (a) SEM of Ti6Al4V, Ti/TiC, TDH treated disk, and CoCrMo after corrosion. (b) 3D profiles of Ti/TiC and TDH after corrosion.