Comparison of the Electrochemical Behavior of Conventionally and Additively Manufactured Ti-6Al-4V Alloy for Orthopedic Implants

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Disclosures: Ghayoor (3A – Smith & Nephew, Inc.); Frankel, Morrison (3A, 4 – Smith & Nephew, Inc.)

INTRODUCTION: Since the 1940s, Ti-6Al-4V (Ti-64) alloys have been used for dental and orthopedic applications due to their excellent resistance to in vivo corrosion [1-3], which comes from the protective, passive oxide film that forms spontaneously to minimize corrosion. With the emergence of additive manufacturing (AM) in orthopedic applications within the last couple of decades, AM Ti-64 does not have the same extensive history of corrosion data and clinical experience as conventionally made Ti-64 medical devices. The purpose of this study was to compare the electrochemical behavior of AM Ti-64 and two conventionally processed Ti-64 materials: forged Ti-64 for cemented devices and forged Ti-64 with porous beads sintered onto the device for cementless applications.

METHODS: Six (6) AM Ti-64 coupons were printed using a laser powder bed fusion printer; the coupons underwent the standard, production-equivalent printing and post-printing processes prior to testing. For comparison to conventionally manufactured Ti-64, six (6) Ti-64 coupons were sectioned from a clinically successful, cemented tibial baseplate that was forged and machined ("Cemented Forged" samples), and an additional six (6) Ti-64 coupons were sectioned from a clinically successful, cementless tibial baseplate that was forged, sintered and machined ("Porous Forged" samples). All coupons were ground (2400-grit count) then passivated in nitric acid and cleaned in production-equivalent processes. Cyclic polarization in lactated Ringer's solution (ambient temperature and dissolved oxygen content) was conducted to evaluate the electrochemical behavior of these materials. All voltages in this study are cited in reference to the Ag/AgCl/sat KCl reference electrode. After equilibration in the corrosion cell for one hour, a cyclic polarization scan was initiated at 20 mV below the open-circuit corrosion potential (E_{oc}) up to a vertex potential (E_v) of 1.0 V. At E_v, the scan direction was reversed, and scanning in the negative direction continued until at least a voltage of 0.80 V. Throughout testing, the potential scan rate was 0.17 mV/sec with a 5 Hz conditioning filter applied during data acquisition. For each potentiodynamic polarization curve, the corrosion potential (E_{corr}) and the corrosion current (I_{corr}) were determined by Tafel extrapolation (PowerCorr). Faraday's law and the measured corrosion current density (i_{corr}) were used to calculate the corrosion-penetration rate (CPR) for each coupon according to ASTM G102-23.

$$\boldsymbol{CPR\ (mm/year) = K_1 \frac{i_{corr}}{\rho} EW}$$

where K_1 is a constant, ρ is density of Ti-64, and EW is the equivalent weight (mass of the metal that will be oxidized by the passage of one Faraday). This calculation assumes that all the measured corrosion current is associated with the flux of metal cations released into the electrolyte, but, in the case of noble alloys such as Ti-64, some portion of the current can be attributed to the passive oxide formation. As a result, the CPRs calculated in this study are likely an overestimate of the actual flux of metal cations being released into the electrolyte. One-way analysis of variance (ANOVA) with post-hoc Tukey comparison was performed (Minitab 18) to compare E_{corr}, i_{corr}, and CPR among the three groups. Test for equal variances was assessed using Levene's method. Differences were considered statistically significant for $p<0.05$.

RESULTS: The cyclic polarization curves for all three materials indicated that they were passive at E_{corr} with low open-circuit corrosion current densities. The absence of both (a) a sudden increase in current density on the up-scan and (b) a hysteresis loop upon the down-scan (i.e., after reversal of the potential scan direction) also indicated that these materials are not susceptible to localized corrosion under these conditions. Box plots for the measured E_{corr}, i_{corr}, and CPR are shown in Figure 1. No statistically significant differences in variances were detected for any of the metrics, so equal variances were assumed for ANOVA. The Tukey comparison showed no difference among groups for i_{corr} and CPR. The differences in mean i_{corr} for Cemented Forged Ti-64 and Porous Forged Ti-64 relative to AM Ti-64 were -1.6 and -4.2 µA/cm^2, respectively. E_{corr} for Cemented Forged Ti-64 was significantly lower ($p<0.001$) than those of both AM Ti-64 and Porous Forged Ti-64.

DISCUSSION: This in vitro study allowed for a direct comparison of the electrochemical behavior of Ti-64 fabricated by either conventional or additive manufacturing. Overall, no statistically significant differences were found in the electrochemical behavior of AM Ti-64 when compared with Porous Forged Ti-64. A difference in E_{corr} was observed for AM Ti-64 compared to Cemented Forged Ti-64, but this difference was also observed for porous forged Ti-64. Most importantly, the CPRs for all three materials were approximately 50 nm/year or less, which demonstrates how resistant to corrosion these materials are. Limitations of this study included a relatively small sample size and that this in vitro test does not recapitulate the various environments that these devices might be exposed to in vivo.

SIGNIFICANCE/CLINICAL RELEVANCE: Resistance to corrosion is important for minimizing ion release into the body, which could be a clinical concern. Because AM is a relatively new technology compared to traditional manufacturing methods, more information on the electrochemical behavior of AM Ti-64 could be useful when selecting a manufacturing method for implants.

REFERENCES: [1] X. Shen *et al.*, Int J Peening Sci Tech, 2020;1(4):301-332. [2] D.F. Williams, "Titanium and Titanium Alloys," in Biocompatibility of Clinical Implant Materials, FL: CRC Press, Inc., 1981. [3] C. Leyens and M. Peters, Eds, "Titanium and Titanium Alloys: Fundamentals and Applications, Germany: Wiley-VCH, 2006.

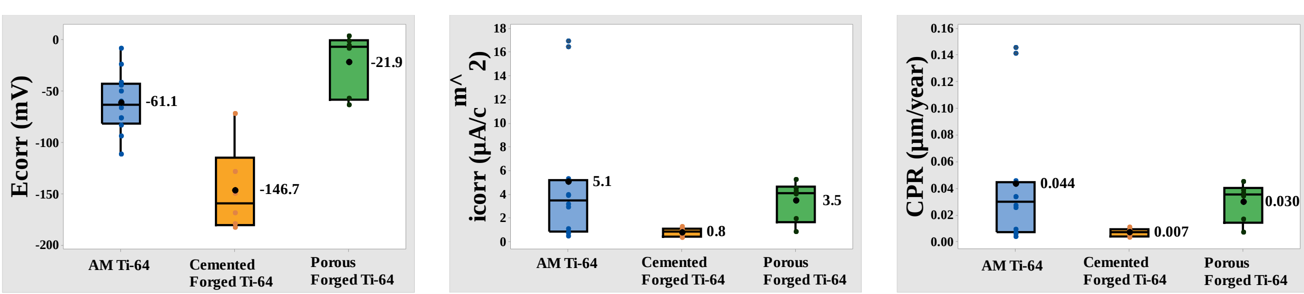

Figure 1: Box plots of the E_{corr}, i_{corr}, and CPR for AM Ti-64, Cemented Forged Ti-64, and Porous Forged Ti-64. The mean values are labeled.