

Comparison of the Electrochemical Behavior of Conventionally and Additively Manufactured CoCrMo Alloy for Orthopedic Implants

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INTRODUCTION: For more than five decades, CoCrMo alloys have been used in the cast or wrought form as prosthetic [1] or dental implant materials due to their favorable mechanical properties, low wear, good biocompatibility, and high corrosion resistance. The latter is based on a passive oxide (Cr_2O_3) film that forms on the metal surface within the human body environment [2,3]. An exposure to corrosive biological fluids unavoidably causes corrosion of an implant to some level. Casting, forging, and machining processes are well-established techniques to produce CoCrMo alloys, and there is an extensive history of corrosion data and clinical experience with these conventionally manufactured CoCrMo devices. With the emergence of additive manufacturing (AM) technologies within the last couple of decades in orthopedic applications, the AM CoCrMo alloy does not have the same extensive corrosion data and clinical experience as conventionally manufactured CoCrMo medical devices. The purpose of this study was to compare the electrochemical behavior of AM CoCrMo and two conventionally processed CoCrMo samples: Cast+HIP for cemented devices and Cast+Sintering+HIP for cementless devices.

METHODS: Six (6) AM CoCrMo samples were printed using a laser powder bed fusion printer; the samples underwent the standard, production-equivalent printing and post-printing processes before testing. For comparison to conventionally manufactured CoCrMo, six (6) samples were sectioned from a clinically successful, cemented femoral that was cast, HIPed and machined (conventional non-porous (CNP) samples), and an additional six (6) samples were sectioned from a clinically successful, cementless femoral that was cast, had porous beads sintered onto the femoral and then HIPed and machined (conventional porous (CP) samples). All samples were ground (2400-grit size) to uniform surface finishes, then passivated in nitric acid and cleaned in production-equivalent processes.

Electrochemical cyclic-anodic-polarization tests were conducted in lactated Ringer's solution (ambient temperature and dissolved oxygen content) using a potentiostat and an electrochemical cell that consisted of the corrosion sample, a Ag/AgCl [sat KCl] reference electrode, and a platinum mesh counter electrode. Thus, all potentials cited in this study will henceforth be in reference to that Ag/AgCl electrode. Approximately 1 cm^2 of surface area of each sample was exposed to the electrolyte and allowed to stabilize until the open-circuit potential (E_{oc}) changed by no more than 2 mV over a 5 min time period. This equilibration period and the E_{oc} were recorded. The scan was started at an initial potential (E_i) of 20 mV below E_{oc} and continued in the positive (or noble) direction at a scan rate of 0.17 mV/s. A vertex potential (E_v) of 1 V was defined as the point at which the scan direction was reversed, and scanning in the negative direction continued until a voltage of 0.50 V. 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 sample according to ASTM G102-23.

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

where K_1 is a constant, ρ is the density of CoCrMo alloy, 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 CoCrMo, 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) was performed (Minitab 21) to compare E_{corr} and CPR among the three groups. 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} and CPR are shown in Figure 1. The mean E_{corr} for AM, CNP, and CP materials were -41.3, -72.9, and -84.0 mV, respectively ($p=0.175$). Furthermore, the CPRs for AM, CNP, and CP samples were 56, 58, and 52 nm/year, respectively ($p=0.921$).

DISCUSSION: This in-vitro study allowed for a direct comparison of the electrochemical behavior of CoCrMo fabricated by either conventional or additive manufacturing. Overall, no statistically significant differences were found in the electrochemical behavior of CoCrMo when produced with the additive manufacturing process compared with Cast+HIP and Cast+Sintering+HIP. It should be noted that the CPRs for all three samples were approximately 60 nm/year or less, which demonstrates how resistant to corrosion these samples 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: 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, information on the electrochemical behavior of AM CoCrMo could be useful when selecting a manufacturing method for implants.

REFERENCES: [1] H.C. Amstutz *et al.*, Clinical Orthopaedics and Related Research, 329 (1996): S11-S34. [2] C.V. Vidal *et al.*, Electrochimica Acta 55, no. 28 (2010): 8445-8452. [3] M. Metikoš-Huković *et al.*, Corrosion Science 49, no. 9 (2007): 3570-3579.

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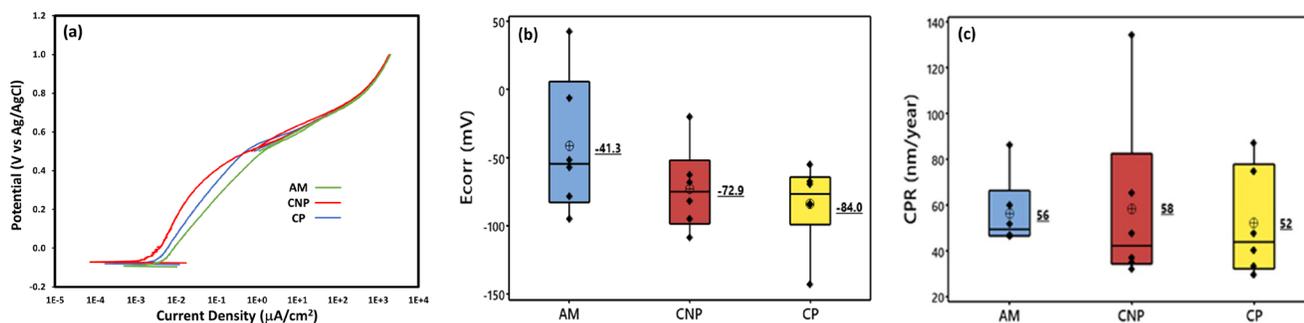


Figure 1: (a) Representative cyclic polarization plots of additively manufactured (AM), conventional non-porous (CNP), and conventional porous (CP) CoCrMo samples, (b) Box plots of the corrosion potential (E_{corr}), and (c) corrosion penetration rate (CPR) for AM, CNP, and CP CoCrMo samples. The means are labeled.