Corrosion behavior of implant alloys used in total shoulder arthroplasties

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Daehan J. Yi, Mozart Queiroz Neto, Deborah J. Hall, Bianca Romay, Jennifer L. Wright, Simona Radice, Gregory Nicholson, Grant E. Garrigues, Robin Pourzal
Department of Orthopedic Surgery, Rush University Medical Center, Chicago, IL

The Robbins and Jacobs Family Biocompatibility and Implant Pathology Laboratory

Introduction

- Ti-6Al-4V (Ti64) and Co-base alloys are the two essential implant alloys used in total shoulder arthroplasty (TSA) components.
- TSA components can undergo fretting corrosion similar to that observed in total hip arthroplasties (THA), and that the alloy microstructure of both alloy types can vary broadly within the specified constrains of their respective ASTM standards with implications on corrosion behaviour [1-2].
- With the number of shoulder arthroplasties rapidly rising over the past decade and failure rates reported as high as ~17.4%, it is imperative to ensure that the microstructure of TSA implant components does not promote corrosion-related failure.
- Thus, we investigated Ti64 and Co-base alloys from different implant manufacturers to characterize microstructure and corrosion behaviour.

We hypothesized that despite identical or similar chemical composition, differences in microstructural features can dictate the corrosion behaviour of TSA implant alloys.

Materials and Methods

- We selected three TSA designs from three manufacturers (Arthrex, Tornier, Zimmer), referred to as type A, B, and C in no particular order.
- All types had a humeral stem made from Ti64. Types A and B had a humeral head made from CoCrMo alloy, while the head of type C was made from CoCrNiFeMo alloy.
- Microstructure was assessed using electron backscatter diffraction (EBSD) in a scanning electron microscope (SEM) for Ti64 and by standard metallographic etching for the Co-base alloys.
- Ti64 grain size was determined by its ECD (equivalent circle diameter), grain aspect ratio (AR), β phase volume fraction, as well as chemical distribution. For Co-base alloys we assessed grain size, presence of hard phases (e.g. carbides) and alloy segregation banding.
- Alloy samples were sectioned, embedded in epoxy resin, and mirror-polished. Then we conducted potentiodynamic polarization tests in a custom-made three-electrode cell, Fig. 1, (counter electrode: graphite; reference electrode: Ag/AgCl; testing fluid: newborn calf serum (30g/L protein) at pH 7.4 and 37°C.
- For Ti64, corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were assessed using Tafel's method. For Co-base alloys, pitting potential (E_{pit}) was determined in addition to E_{corr} and i_{corr}.
- Each alloy type was tested with N = 5 and each sample/type was tested 3 times.
- Differences between groups were determined using one-way ANOVA and Kruskal-Wallis tests.

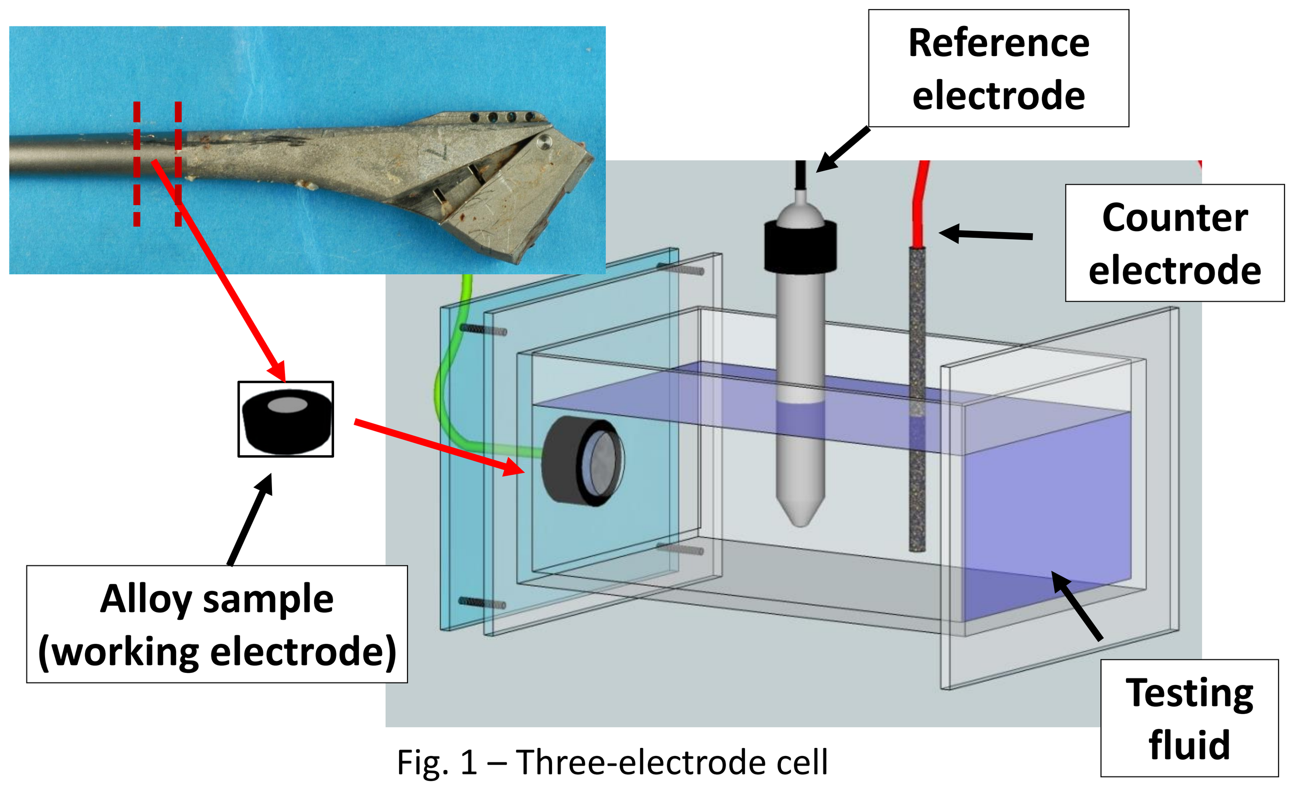


Fig. 1 – Three-electrode cell

Results

Ti64

All Ti64 TSA components were made from wrought alloys. However, microstructure varied between types: A) fine equiaxed grains, B) coarse equiaxed grains, and C) a bimodal microstructure with fine and coarse grains (Figs. 2 and 3). The difference of vanadium content across phases was <10% in all cases.

Corrosion tests did not reveal any meaningful difference between the 3 alloy types for neither E_{corr} (p=0.2) nor i_{corr} (p=0.25) (Fig. 4)

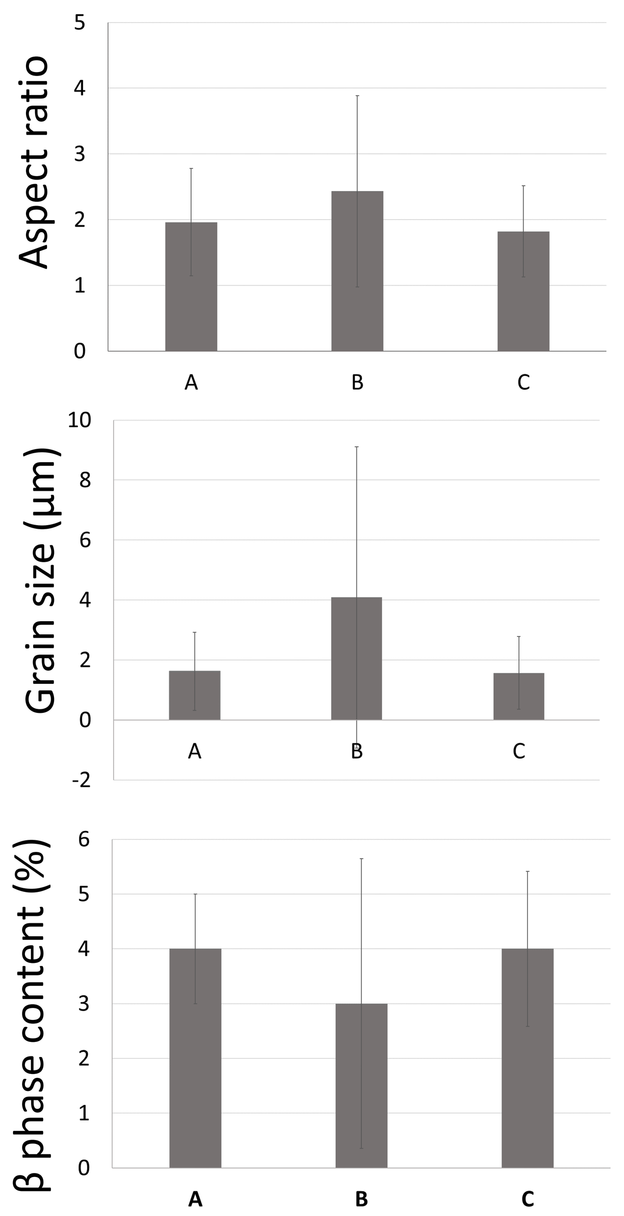


Fig. 3 – Comparison of microstructural metrics of the Ti64 alloys

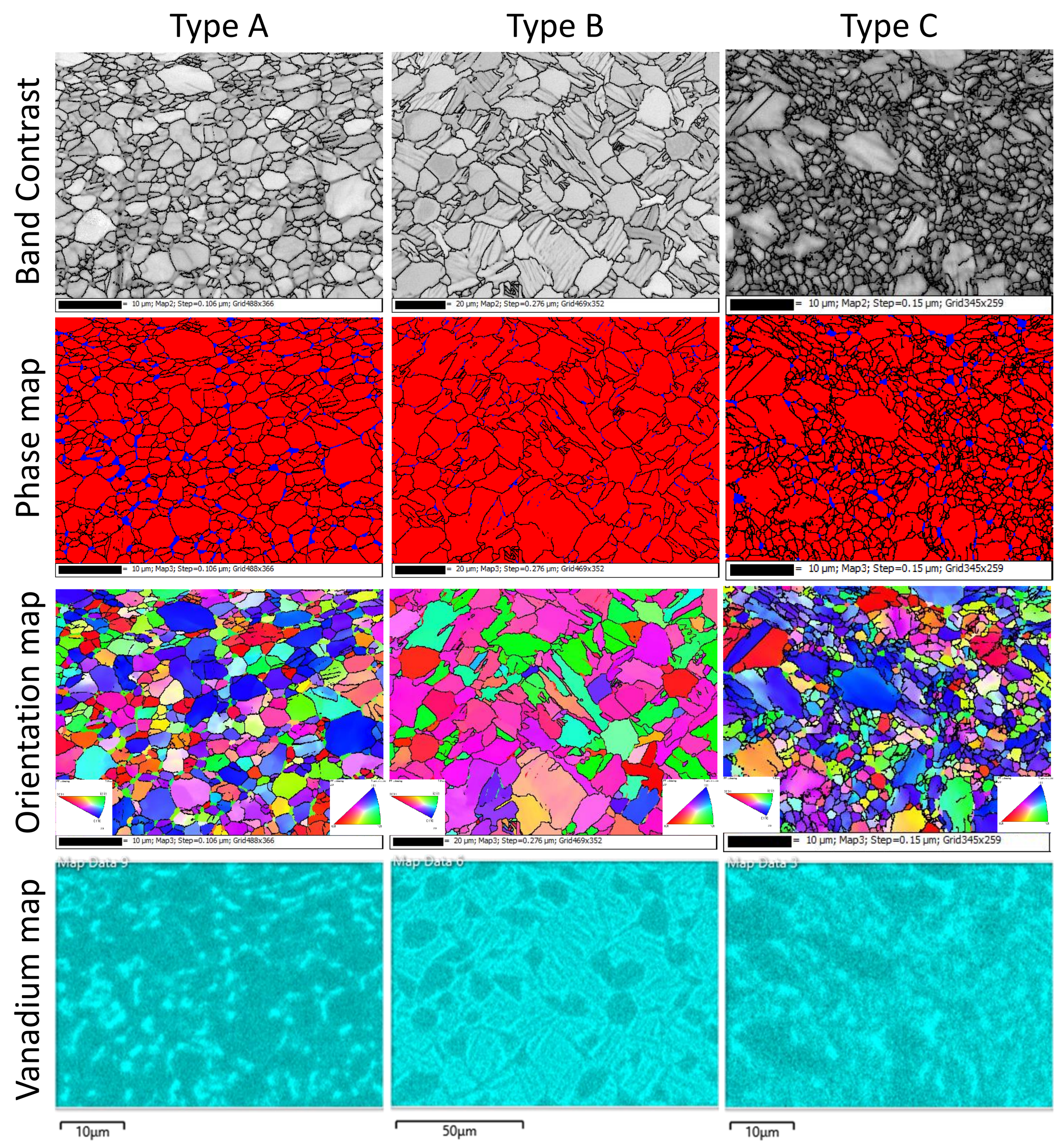


Fig. 2 – Band contrast, phase (red: α, blue: β), orientation and vanadium maps of all Ti64 alloys exhibiting grain size and shape, phase distribution, texture and chemical homogeneity.

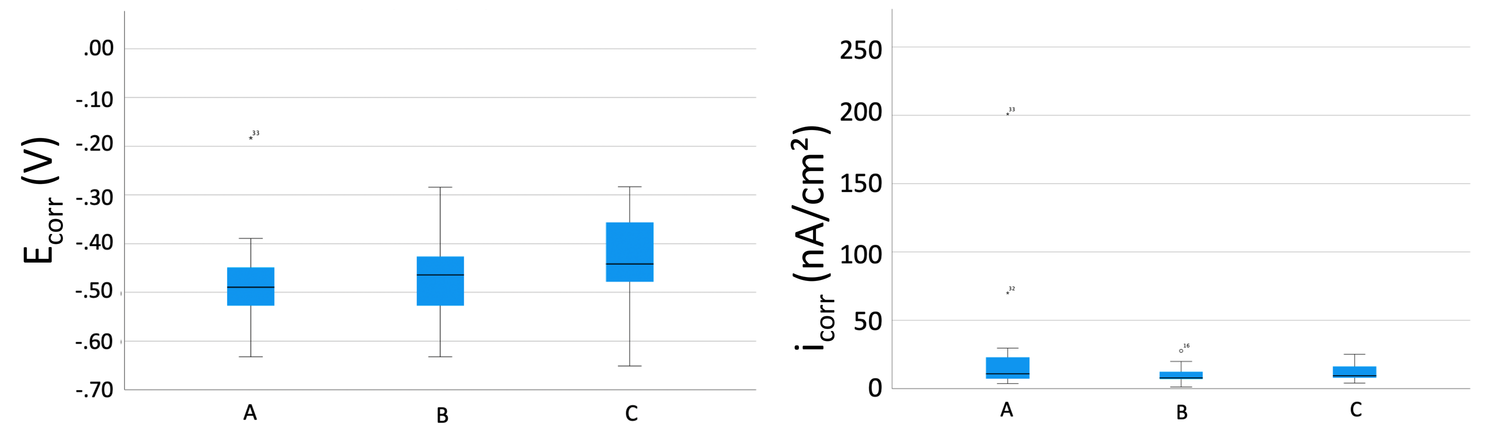


Fig. 4 – Comparison of corrosion potential and corrosion current density for the Ti64 alloys. No significant difference was observed between fine equiaxed and bimodal alloys

Co-base

Co-base alloys were fundamentally different from each other

A. fine grained CoCrMo wrought alloy with no hard phases and a mild presence of segregation banding
B. coarse grained (mm-range) CoCrMo cast alloy with hard phases (carbides + intermetallic phases) along the grain boundaries
C. fine grained CoCrFeNiMo wrought alloy with severe segregation banding (Fig. 5)

The CoCrFeNiMo alloy exhibited a higher E_{corr} compared to the CoCrMo alloys but had the lowest i_{corr} (Figs, 6 and 7). The two CoCrMo alloys exhibited the same corrosion tendency and rate, but the wrought alloy (Type A) had a superior pitting behaviour indicated by a higher E_{pit} compared to the cast alloy (Type B).

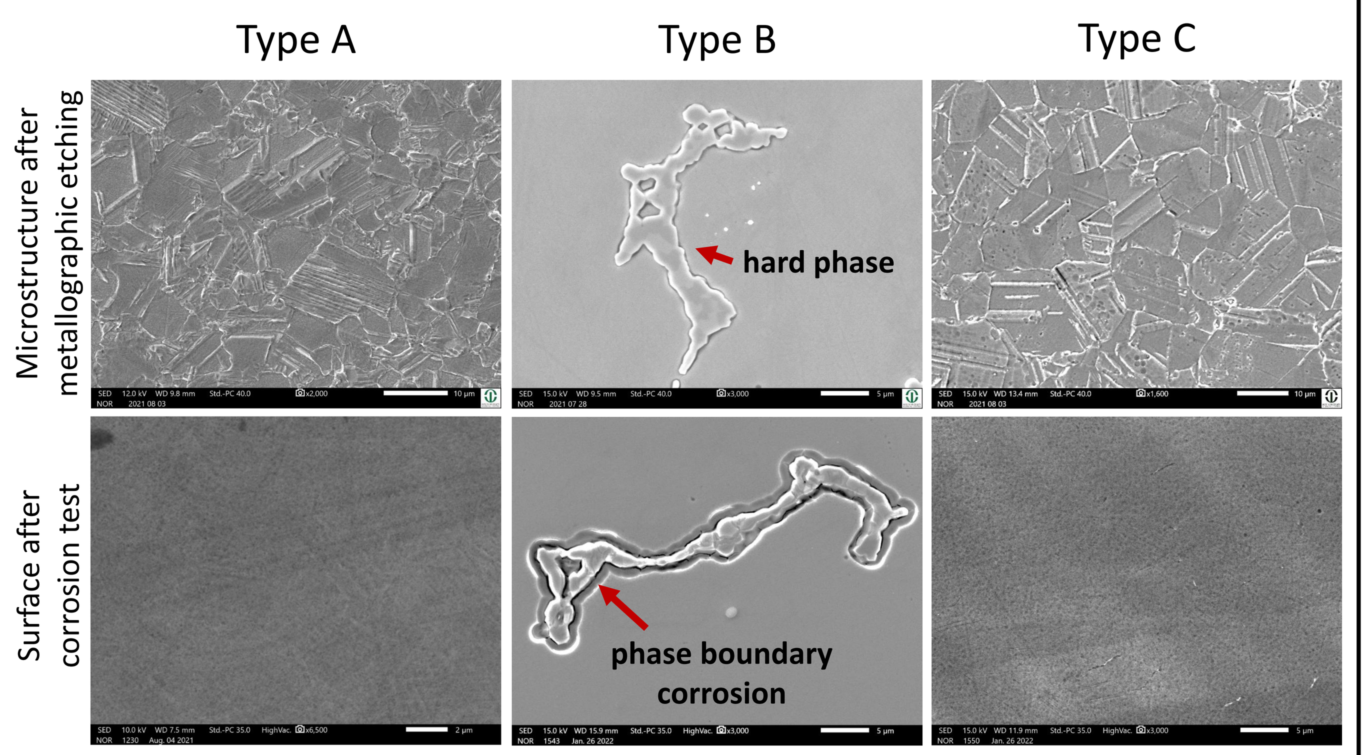


Fig. 5 – Co-based alloys: type A is a low carbon CoCrMo wrought alloy, Type B is a CoCrMo cast alloy with large hard phases, and Type C is a CoCrFeNiMo wrought alloy. After corrosion testing, Type A and C exhibit very fine pitting on the surface, while Type B mainly exhibited phase boundary corrosion.

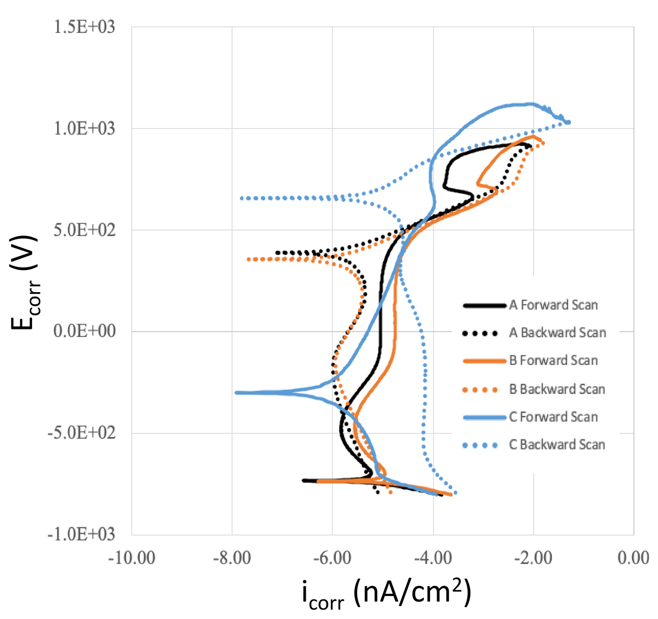
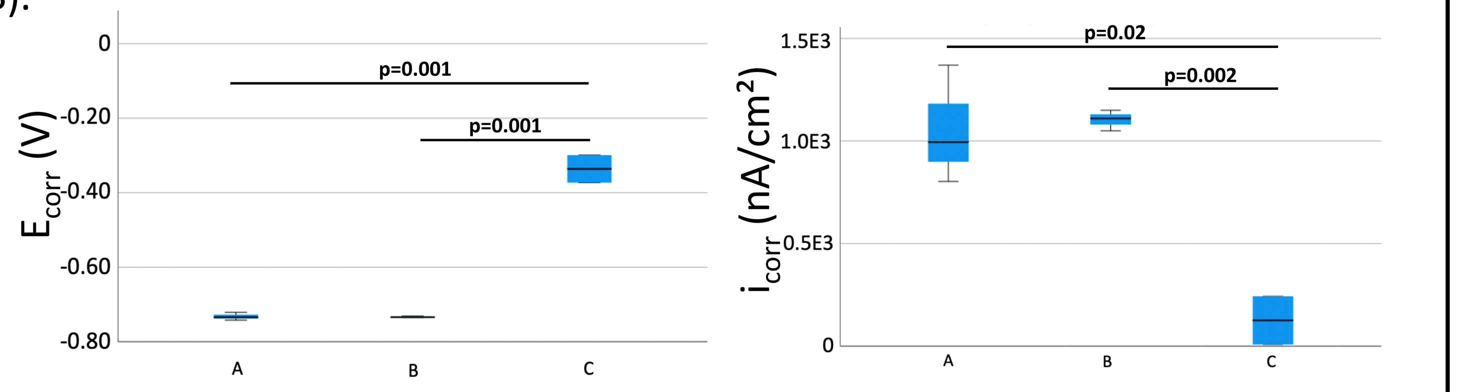


Fig. 6 – Representative potentio-dynamic curves (forward/anodic and reverse/cathodic scans) for all three alloy types



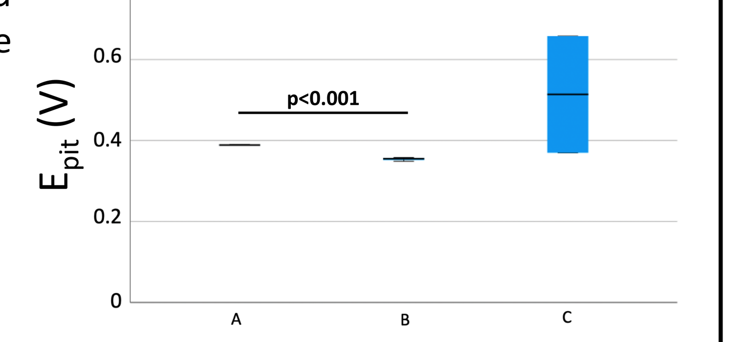


Fig. 7 – Comparison of corrosion potential, corrosion current density, and pitting potential for Co-base alloys. Type C exhibited a superior corrosion tendency (high Ecorr) and corrosion rate (low icorr) compared to Types A and B. While the pitting potential was more variable, it also appears superior for Type C. For the CoCrMo alloys, Type A (wrought) exhibited a superior pitting potential compared to Type B (cast).

Discussion

- For Ti64 alloy we found that all stems were made from wrought alloy with different grain sizes. Yet, we found no difference in the electrochemical behaviour. This finding is in line with our previous work showing broad differences between wrought, cast and additively manufactured alloys used in hips and knees, but no meaningful difference between wrought alloy apart from those with large β phase fractions with a V content of >10% [1].
- CoCrFeNiMo exhibited a favourable corrosion tendency and rate compared to CoCrMo likely to the presence of Ni in addition to Cr and Mo. Additionally, it is reported that high entropy alloys such as CoCrFeNiMo have higher corrosion resistance [4]. However, this alloy also exhibited microstructural banding aligning with a previous finding of column damage corrosion of retrieved implants [5]. Thus, this alloy still can corrode *in vivo* despite Ni content.
- Between the two CoCrMo alloys, the wrought alloy exhibited a better pitting behaviour which also agrees with previous findings on similar alloys from THAs. The difference in corrosion behaviour can be explained by a more homogenous chemical distribution of this low carbon wrought alloy (despite some mild banding) and the absence of hard phases, which were shown to be preferential corrosion sites [2].
- Overall, the wrought CoCrFeNiMo alloy exhibited the most favourable electrochemical behaviour, yet one has to consider the biological impact of Ni release during corrosion.
- The impact of microstructure on the mechanical and tribological behaviour will be subject of future research.

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Contact: mozart_q_neto@rush.edu

References: [1] Neto MQ et. al, J Bio Tribo Corros 8, 26 (2022); [2] Pourzal R et. al, CORR 2017, 475(12):3026-43; [3] Roberson TA et. al, J Shoulder Elbow Surg. 2017:1–9; [4] Qiu Y et. al, npj Mater Degrad 1, 15 2017; [5] Hornung A et. al, Trans ORS 2021, 0123.