Classifying the Severity of Grain Boundary Corrosion in CoCrMo Biomedical Implants

Alex Lin¹, Emily Hoffman¹ and Laurence D. Marks¹

¹Department of Materials Science and Engineering, Northwestern University, Evanston, IL

Cobalt-chromium-molybdenum (CoCrMo) alloys with the addition of carbon are popular for biomedical devices, specifically total hip replacements, due to their superior wear resistance, longer service duration and reduced inflammation resulting from such devices. In the mid-2000s, approximately 35% of the hip replacements in the US were metal-on-metal hip replacements based on CoCrMo alloys.[1] Despite its superior mechanical properties and wear resistance compared to metal-on-plastic or ceramics systems, CoCrMo is susceptible to corrosion due to tribological events such as joint movements and its constant exposure to corrosive body fluids.

Grain boundaries have been commonly associated with the mechanical behaviour of alloys and their structure is especially significant. The coincidental site lattice (CSL) model is a powerful mathematical tool to characterize grain boundaries and identify 'special' boundaries that display superior mechanical behaviour compared to regular high angle grain boundaries.[2] Previous work on stainless steel, copper, nickel, and aluminum alloys has demonstrated that, in accordance with CSL theory fitted with the Brandon criterion ($\Delta \theta_m \leq \frac{15^{\circ}}{\sqrt{\Sigma}}$), grain boundaries with a low reciprocal coincident lattice density (Σ) have a relatively low energy compared to 'general' high angle grain boundaries and high Σ boundaries.[3]

Solution-annealed high carbon CoCrMo hip implants are imaged using scanning electron microscopy (SEM) to investigate the grain boundaries in the retrieved sample. As shown in Figure 1 (A) and (B), the SEM images containing the grain boundaries at varying degrees of corrosion are classified via electron backscatter diffraction (EBSD) in order to index the crystallographic misorientations of the grains. The grain boundaries identified as special CSL boundaries (Σ 3-49) are then analyzed using a 3D optical microscope for their depth profiles.

Preliminary EBSD scans show that there is some relation between the corrosion depth of grain boundaries and their geometry given by the Σ parameter. We report that 50 out of the 85 nontwin CSL grain boundaries examined exhibited some form of corrosion resistance and 24 of these grain boundaries are above $\Sigma 11$, which has been previously determined as a threshold for corrosion resistance.[4] By SEM imaging and visual analysis, we are able to differentiate between immune, corroded and semi-corroded boundaries which contain shallow, irregular divot-like features as shown in Figure 2. However, upon further examination of the grain boundary statistics, $\Sigma 17$ and $\Sigma 29$ boundaries seem to display stronger corrosion resistance behaviour than what its geometry predicts. From this observation, it is clear that there is a quantifiable correlation between the severity of corrosion at a grain boundary and its corresponding interfacial energy. Using the depth profiles of these CSL grain boundaries, a relationship between the depth of the divots, semi-corroded and severely corroded grain boundaries and the geometry of these respective grain boundaries can be established. This relationship is crucial as it provides a more refined understanding of the exact geometries that show corrosion resistant behaviour and how to reduce corrosion in CoCrMo hip implants by using grain boundary engineering.

References:

[1] S. Pramanik, A. K. Agarwal, and K. N. Rai, *Trends in Biomaterials and Artificial Organs*, **19** (2005), p. 15-26.

[2] M. D. Sangid, et al, Materials Science and Engineering: A, 527 (2010), p. 7115-7125.

[3] G. Palumbo, K. T. Aust. Acta Metall Mater, 38 (1990), p. 2343-2352.

[4] P. Panigrahi, et al, J Biomed Mater Res Part B, 104 (2013), p. 850-859.

[5] The authors acknowledge funding from the NSF on grant number CMMI-1030703.



Figure 1: (A) A SEM image showing preferentially corroded grain boundaries and different grain boundary geometry. (B) The corresponding EBSD map showing the crystallographic orientations of the grains in order to determine grain boundary geometry.



Figure 2: A SEM image showing the semicorroded boundaries and asymmetrical divot-like features.