Toward a Better Understanding of Fretting-Crevice Corrosion of Titanium and Its Alloys

Paul Kovacs
SynergEthics, Louisville, KY

Statement of Purpose: Ever since the introduction of modular orthopaedic implants, the fretting-crevice corrosion of their metallic components has been extensively studied. In addition to occasionally severe corrosion in the form of etching and pitting, a recent study of retrieved hip-implants with Ti-6Al-4V/Ti-6Al-4V modular tapers has shown that hydrogen embrittlement can also be a mechanism of degradation in modular connections (Rodrigues DC, JBMR-B, 2009, 88(1): 206-219). As the biocompatibility of implant metals can be directly related to the protective ability of their surface oxides/hydroxides – and interpreted very well on the basis of their thermodynamic stability in aqueous environments (Kovacs P, ASTM STP 1272, 1996, 163-178) –, the propensity of titanium alloys for the various forms of hydrogen damage could also be better understood based on the same thermodynamic considerations. This study estimates the relative differences in this regard between two titanium alloys, Ti-6Al-4V and Ti-13Nb-13Zr.

Methods: The potential-pH equilibrium diagram for water (Pourbaix M, NACE, 1974), including the Kovacs-Freeman line for crevice conditions (Freeman MH, FPS 64th IC, 2010, 6-22; P-37), was used to identify the domains of fretting-crevice corrosion and hydrogen damage (Figure 1). The Kovacs-Freeman line, which represents the separation of the relative oxidizing-reducing power of water under localized corrosion conditions in crevices and pits – and along which both the local pH values and corresponding partial gas pressures change gradually when the system is at steady state –, is described by the following equation:

$$E\,(H_2/O_2)_{redox\ active} = -0.013 + 0.059\ pH \quad \text{(Eq. 1)}$$

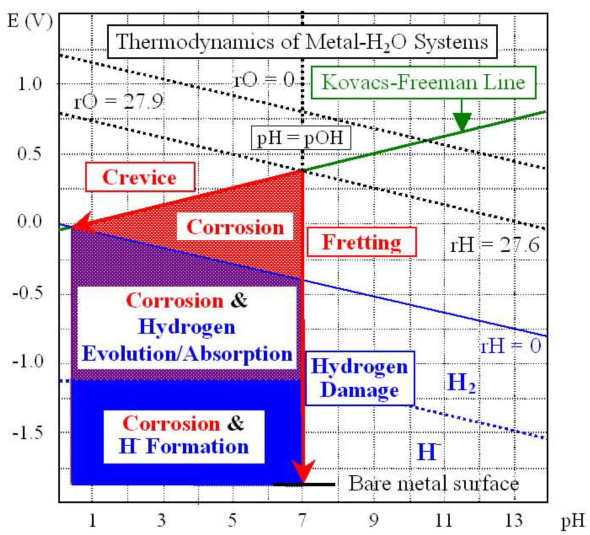

Figure 1

The potential-pH equilibrium diagrams for Ti, Al, V, Nb, and Zr at various pH and metal ion concentration values were generated by the MEDUSA software program (Puigdomenech I, KTH, 2009). The characteristic crevice pH values were given by the Kovacs-Freeman equation (Eq. 1) as 0.11('maximum'), 3.555 ('medium'), and 7.0 ('mimimum'), while the total concentrations of M^{n+} or $M(OH)_m$ in solution under these conditions were selected as 7.8×10^{-1} M, 2.8×10^{-4} M, and 1.0×10^{-7} M, respectively.

Results and Discussion: The stability domains of the protective oxides/hydroxides as well as the domains of different forms of hydrogen damage under the three simulated crevice conditions are summarized in Figure 2.

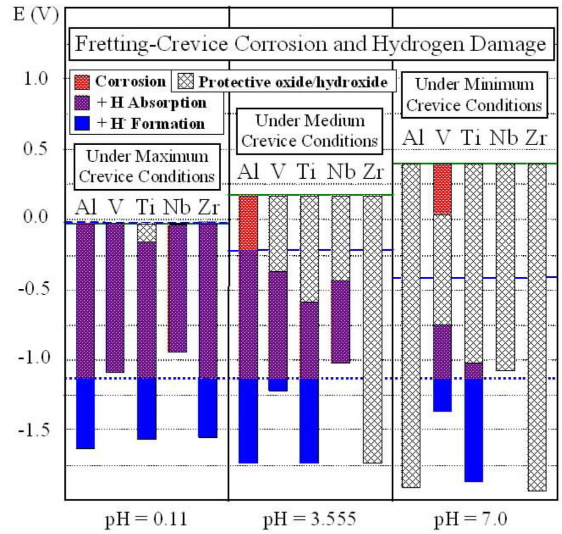

Figure 2.

In the absence of crevice conditions, Ti shows a relatively small region for active corrosion and concurrent hydrogen absorption. The domain of hydride formation, however, is considerably large. In case of the alloys, the protective oxides and hydroxides of the alloying metals, which act as barriers against both hydrogen absorption and hydride formation, may successfully protect the bulk alloy, except for V. Under medium crevice conditions, this kind of protection is shown to be provided only by Zr. Finally, the most severe (max.) crevice conditions make both alloys unprotected from damages by corrosion and hydrogen. Overall, in paired comparison, Nb is more preferable than V, while Zr is more protective than Al under medium crevice conditions. Considering everything else equal, e.g. taper design and patient activity, the signs of considerable corrosion and hydrogen embrittlement seen on retrieved Ti-6Al-4V tapers could be expected to be far less severe if they were made of Ti-13Nb-13Zr. Nevertheless, the complete elimination of these phenomena is impossible as long as the protective oxide/hydroxide layer on the alloy is repeatedly removed/damaged mechanically.

Conclusions: The fretting-crevice corrosion of titanium and its alloys – both *in vitro* and *in vivo* – can be much better understood by the thermodynamic considerations employed in this study. Future work in this area calls for the integration of such considerations with those of the corresponding reaction mechanisms and kinetics.