Titanium Electrochemistry in the Presence of the Inflammatory Species H_2O_2

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Statement of Purpose:
During implantation most alloys, including titanium (Ti), are exposed to an initial electrochemical environment that includes inflammatory species like H_2O_2. Many inflammatory species, including H_2O_2, are electrochemically active, and metal-implant surfaces may interact with these species by way of oxidation and/or reduction reactions. Since metal surfaces can undergo large changes in potential due to a variety of surface events (e.g., mechanically assisted corrosion), it is likely that the interaction of metals with inflammatory species also varies with potential. While there have been several studies[1] investigating the effects of H_2O_2 on titanium, very few have sought to explore the electrochemical behavior of these surfaces when potentials are applied in the presence of H_2O_2. Furthermore, surface modification of titanium alloys using H_2O_2 has also been investigated[2], but again in the absence of applied potentials. Thus, the goal of this study is to explore the electrochemical behavior of Ti-6Al-4V in the presence of a wide range of H_2O_2 concentrations. The underlying hypotheses of this study are: 1. cathodic surface potentials can accelerate the consumption of H_2O_2 and reduce inflammatory species concentration; 2. the combination of potential and H_2O_2 can alter the surface structure of Ti-6Al-4V.

Methods: Samples of Ti-6Al-4V were mechanically polished to 600 grit followed by 1, 0.5 and 0.03 µm alumina and were cleaned using deionized water, ethanol and again with DI water for 10 min each. Electrochemical tests of open circuit potential (OCP) vs. time and potentiodynamic polarization at 1 mV/s from –1V to +1V were run (n>2) on polished surfaces of Ti-6Al-4V alloy immersed in different concentrations of H_2O_2 along with 0.154 M phosphate-buffered saline. Concentrations of hydrogen peroxide solutions ranging from 0.003 M to 5 M were prepared and used for testing. After electrochemical testing, the samples were analyzed using scanning electron microscopy (SEM). For comparison, polished samples were etched using Kroll's Reagent (5% wt HNO_3 + 2% wt HF in water) in order to show the difference between α and β grains of the Ti-6Al-4V in the corroded and etched conditions.

Results and Discussion: Figure 1 shows the polarization curves for Ti-6Al-4V in different concentrations of hydrogen peroxide. It shows several trends of importance. First, there is a 200-fold increase in the current density with increasing H_2O_2 concentration. There is also a move from a passive material to one that exhibits an active-to-passive transition. Ecorr and current density shift with H_2O_2 concentration (Ecorr becomes more cathodic with H_2O_2, and current densities increase). After testing, the surfaces of the Ti-6Al-4V appeared grayish to blue-green in color, and SEM analysis indicated a significant change in the surface microstructure of the alloy. There was a preferential etching of the beta grains from the surface at high concentrations of H_2O_2.

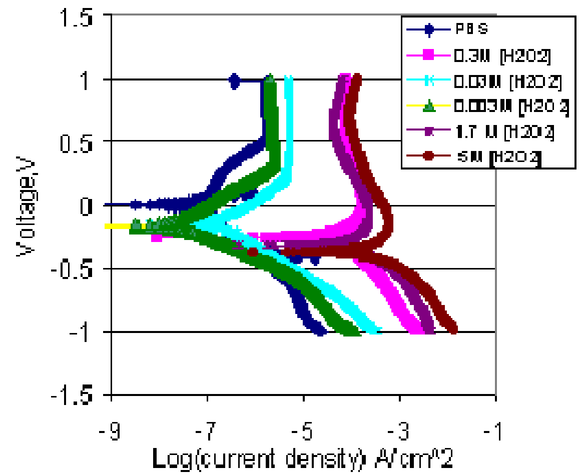

Figure 1: Polarization curves for Ti-6Al-4V in H_2O_2.

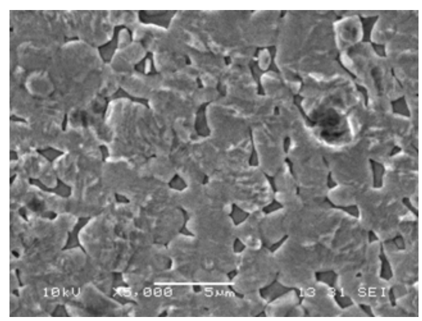

Figure 2: SEM micrograph of Ti-6Al-4V after polarization testing in 0.3M H_2O_2. Note the preferential etch of the beta phase.

It is clear from these tests that, even at relatively low concentrations ($3x10^{-3}$ M), there were changes in the electrochemical behavior of the surfaces. This was true in both the anodic and cathodic regions of the electrochemical testing. Thus, it is likely that electrochemical reactions of H_2O_2 at, and with, the surface are taking place. These indicate that Ti surfaces may act to reduce this inflammatory species by electrochemical processes. The visual and SEM micrographic analysis shows that, at least for some conditions of testing, there is a preferential attack of the beta grains of the surface by H_2O_2. This may potentially serve as a treatment process for preparing micron-submicron-scale surface topography for these alloys.

Conclusions: Ti-6Al-4V/H_2O_2 electrochemical interactions occur that both react to inflammatory species and affect the corrosion behavior of Ti-6Al-4V.

References: 1. J. Pan et al. JBMR.1998; 40: 244-256.
2. X.X.Wang. et al. J Biomaterials.2002; 23: 1353-1357.