Prediction of Voltage Shifts During Fretting Corrosion of Titanium Alloy: Effect of Area, Impedance and Mechanics

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Statement of Purpose: Mechanically assisted corrosion (fretting corrosion, tribocorrosion) has been recognized as a continuing concern with metallic implant materials. A common characteristic of tribocorrosion is the cathodic voltage excursion seen during abrasion. These voltage shifts change the resistance and capacitance of the oxide film, and might affect the behavior of cells surrounding the device [1]. While these voltage changes have been known for decades, to date there have been few systematic theory proposed for predicting them [2]. The extent of voltage drop depends on the extent of tribocorrosion taking place, the total exposed area of the material, and, as will be shown, the impedance characteristics of the surface. Therefore, the goals of the study are to present a theory and experimental assessment of the relationships between voltage shifts and tribocorrosion, electrode areas and impedance characteristics of Ti6Al4V interfaces.

Methods: Disks and pins made of Ti6Al4V alloy were prepared through sequential wet sanding to a 600 grit finish. All electrochemical measurements were made using a three electrode system and performed in phosphate buffered saline solution (pH 7.4). Electrochemical impedance spectroscopy (EIS) measurements were performed for disks of 3 different areas (0.8, 2.6, 6.0 cm^2) without fretting. Solution resistance (R_s), polarization resistance (R_p) and interfacial capacitance(C) were obtained by fitting the EIS spectra to the CPE modified Randle's circuit. Samples were held at Open circuit potential (OCP) for 20 min before fretting. Fixed displacement amplitude of 50 µm, load of 6 N and fretting frequency of 1.25 Hz were applied for area tests (0.8, 1, 4 cm^2) and voltage was recorded. Fretting was performed for 150 s and then voltage was allowed to recover to a stable level after fretting was ceased. The disk area of 0.8 cm^2 was used for varied load (1, 3, 6 N) and frequency tests (0.125, 1.25, 2.5 Hz).

Theory: A model of voltage excursion was proposed based on the idea that the fretting current, I_f, at the source is consumed by the remaining surface area which is acting like a Randle's circuit of the Ti-6Al-4V interface (Fig 1). The relationship between fretting current and voltage drop can be shown from the differential equation for the Randle's circuit:

$$I_f(R_s+R_p)+R_sR_pC\left(\frac{dI_f}{dt}\right)=V_d+R_pC\frac{dV_d}{dt}$$

I_f is the fretting current and V_d is the voltage drop. The other equation used is the equation previously developed for fretting currents

$$I_f=\frac{\rho nF}{Mw}\frac{A}{\Delta}m(V-V^o)\frac{d\delta}{dt}=k(V-V^o)\ [1]$$

where k is a parameter which depends on oxide properties and mechanical conditions. V^O is the onset voltage of oxide film formation. V is the interface voltage. Then, by substituting I_f into the equation and solving yields the voltage drop as:

$$V_d=-\frac{k(V_o-V_s)(R_s+R_p)}{\left[1-k(R_s+R_p)\right]}\left\{1-\exp\left[-\frac{1\text{-}k\left(R_s+R_p\right)}{(1\text{-}kR_s)R_pC}*t\right]\right\}$$

V_s is the OCP before fretting, R_s & R_p (Ω), C (F) are extrinsic impedances and are dependent on electrode area.

Results: EIS results indicate that the extrinsic R_p and R_s decrease with the increase of exposed disk area while capacitance gets larger as the disk area increases as expected. Fretting corrosion results show that during fretting corrosion, the voltage dropped dramatically at the beginning of the fretting. Voltage drop values range from -0.23V to -0.59V depending on the area size (Fig 2). Results also show that the voltage drop gets larger as the load and fretting frequency increases as predicted (Fig 3). The model has been used to look into the voltage excursion and shows excellent agreement with the experiment results (Fig 4) when appropriate values for R_p, R_s and C are used.

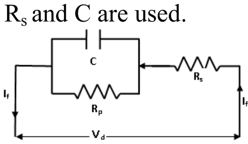

Figure 1: Randle's circuit

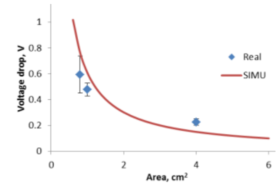

Figure 2: Absolute values of voltage drop for different areas, data (diamond marker) and theory (solid line). Load-6N, frequency-1.25Hz

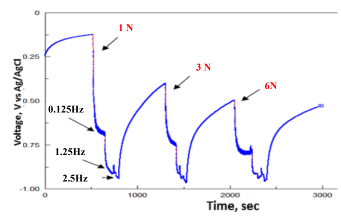

Figure 3: Voltage changes with time during fretting test of Ti6Al4V pin-disk sample (area 0.8 cm^2).

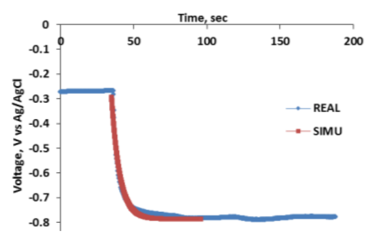

Figure 4: Compare simulation of voltage excursion with experiment results. The blue line represents the real data and the red line shows the simulated data.

Conclusion: This study developed an impedance-based model, coupled with a previously proposed fretting current model to predict voltage excursions during tribocorrosion. Experimental tests of voltage shifts show the predicted effects are electrode area, fretting load and fretting frequency on the time course and extent of the voltage shift. Extrinsic impedance (R_s, R_p, C) of Ti6Al4V depends on exposed area of disk. As exposed area increases, voltage drop decreases .Voltage drop during fretting corrosion increases as the load or frequency rises. The proposed model shows excellent agreement with the experiment data.

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Abstract #339