Tribocorrosion Heredity Integral Modeling of Abrasion-Current-Impedance-Voltage Relationships

Jeremy L. Gilbert, Ph.D., Zhe Li, Dongkai Zhu, Gregory W. Kubacki
Syracuse Biomaterials Institute, Department of Biomedical and Chemical Engineering, Syracuse University, Syracuse, NY 13244

Statement of Purpose: Mechanically assisted crevice corrosion in orthopedic implant alloys is a major ongoing concern. There have been limited theoretical approaches available to model or predict both the currents and the potential shifts associated with disruption and repassivation of the oxide film covered surfaces of these alloys. This study provides new insights and research directions into modeling and prediction of fretting corrosion processes taking place in more complex conditions and geometries.

Theoretical Model:

The Current-Oxide Volume Abrasion Heredity Integral is

$$I(t) = A^T(t)\Phi(0) + \int_0^t A^T(t-\lambda)\frac{d\Phi}{d\lambda}\,d\lambda \text{ , where} \qquad \text{Eq. 1}$$

$$A^T(t) = \frac{I(t)}{\Phi_o} = \frac{\theta}{\tau}e^{-\frac{t}{\tau}} \text{ , and } \frac{d\Phi}{d\lambda} = 2m(V - V_0)\sqrt{\frac{F}{\pi H}}\frac{d\delta}{d\lambda} \qquad \text{Eq. 2}$$

where I(t) is the current resulting from abrasion (or fretting), Φ is the volume of oxide abraded (and repassivated), which depends on contact mechanics, oxide thickness, and sliding speed, A^T is defined as the tribocorrosion transfer function which depends on the charge per volume of oxide, θ, and the time constant, τ, for repassivation, and λ is a dummy variable in time.

The Potential-Impedance-Current Heredity Integral is

$$Z(t-\lambda) = R_s + R_{ox}\left(1 - e^{-\frac{t-\lambda}{\tau_{ox}}}\right), \qquad \text{Eq. 3}$$

$$V(t) = Z(t)I(0) + \int_0^t Z(t-\lambda)\frac{dI}{d\lambda}\,d\lambda \qquad \text{Eq. 4}$$

where R_{ox} is the lumped representation of the electrode oxide resistance, R_s is the lumped solution resistance (between the abraded region and the remaining electrode) and τ_{ox} is the impedance-based time constant ($R_{ox}C_{ox}$)[1]. Eqs. 1 and 4 can be numerically integrated in a coupled fashion over time to predict V(t) and I(t) for known oxide mechanics and impedance behavior for specific tribocorrosion conditions.

Materials & Methods: Fretting corrosion pin-on-disk experiments were performed at room temperature to evaluate the proposed model. Pins and disks (CoCrMo, ASTM F1537) and isotonic (0.154 M) phosphate buffered saline (PBS) were used. Two fretting tests were performed. First, samples were held at -100 mV vs Ag/AgCl, 5.0 N load (1.0 Hz) and the fretting corrosion currents and sliding displacements were captured. Second, freely corroding conditions under 0.5 N load were used and the frequency of fretting sliding was varied between 10 Hz to 0.2 Hz (45 µm). Fretting currents and electrode potentials were captured. R_{ox} and C_{ox} were measured using impedance methods. The model, using fixed known or measured parameters (e.g., load, hardness, anodization rate, R_{ox}, C_{ox}, etc), integrated sliding displacement-time data to determine currents and voltages for experimental comparison. V and I vs time, I_{avg}, I_{rms} and ΔV_{fret} were determined across frequencies and compared to theory.

Results: Sliding displacement and fretting current vs time are presented (Fig. 1). In addition, the calculated fretting currents using Eq. 1 is superimposed on Fig. 1. For freely corroding conditions, both fretting currents and potential shifts over the range of frequency (Fig. 2) show high correlation between theory and experiment. Fig. 3 compares the I_{avg}, I_{rms} and ΔV_{fret} for experimental and model results. Note the close correlation in response.

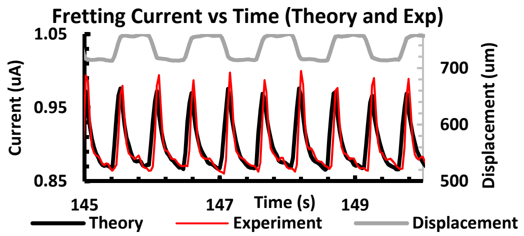

Fig. 1. Fretting currents and sliding displacements under potentiostatic conditions (1.0 Hz), theory and experiment.

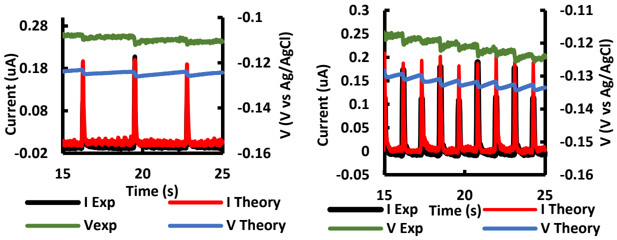

Fig 2. Currents and potential at 0.2 (left) and 0.5 Hz (right)

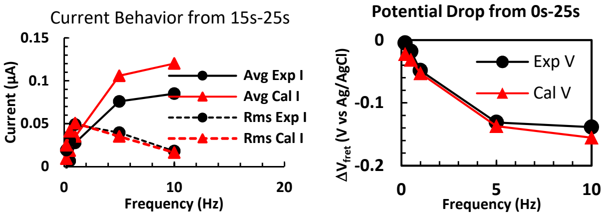

Fig. 3. Average (I_{avg}) and root mean square (I_{rms}) currents from 15s-25s (left) and potential drop, ΔV_{fret} from 0s-30s (right) of fretting for 0.2 to 10 Hz frequency. Theory and experiment.

Discussion: Detailed and specific tribocorrosion responses (I and V vs t) can be predicted from knowledge of the sliding, contact mechanics, voltage-dependent oxide film thickness, and impedance behavior of the electrode. Excellent correlation between the model and experiments were observed for fixed parameters of fretting and impedance.

Conclusions: A proposed heredity integral-based model of fretting corrosion predicted the current and potential response based on fixed and known parameters of the system. With knowledge of the contact mechanics, sliding mechanics, hardness of the alloy, area and impedance, as well as the high-field growth mechanism for the oxide, this approach can be used to model tribocorrosion currents and voltages. **Acknowledgement:** DePuy Synthes.**References:** 1. Gilbert et al, STMP, 2016.