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Fretting corrosion of CoCrMo alloy biomaterials: Instrumentation development, heredity integral modeling and the effect of frequency

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Abstract

Mechanically assisted crevice corrosion, a process of corrosion that generally occurs in joint replacements of the hip and knee, is a major problem for metallic biomaterials. Though extensive research has already been undertaken, the basic concepts of fretting corrosion including prediction of the instantaneous current response during fretting corrosion, still needs to be understood in a systematic form. The aim of this study is to present the mechanical and electrochemical elements of a model pertaining to the process of fretting crevice corrosion and the prediction of fretting corrosion current transients. The influence of sliding speed on fretting corrosion severity of CoCrMo alloys will also be measured. To be complete, a new fretting corrosion model that predicts instantaneous current versus time during fretting was developed to better explore the effect of instantaneous mechanical and electrochemical factors on fretting corrosion current. Based on the principle that there is a direct correlation between the oxide repassivation volume and the current, the method of the Duhamel Integral (Boltzman superposition) was used to link abrasion and repassivation of oxide film and the resultant current waveform.

In addition, a new testing device was designed and built to observe fretting corrosion phenomena under microscopic conditions. The data collection and control systems that include displacement sensors and NI-DAQ board, as well as LabVIEW program, was also developed and is described.
The effect of frequency/sliding speed on fretting corrosion current was explored in this thesis. All tests were performed by varying sliding frequency in PBS solution under fixed potential, load, displacement and surface roughness.

The results demonstrated a strong correlation between model prediction and experimental data. This model gave a clear basis between fretting elements (abrasion per time) and current transients.

For frequency tests, increased sliding speed resulted in proportional increases in fretting corrosion currents over the specific range from 0 to 400 μm/sec. The current stopped linearly increasing above 400 μm/sec, which is considered the maximum CoCrMo reformation rate under the conditions of this experiment. There were more sliding and sticking events, as well as fretting currents, in a unit time with increasing frequency. The rms fretting current was narrowed at higher fretting speed. Frequency does not have a significant effect on COF, frictional force or dissipated energy per cycle.
Fretting corrosion of CoCrMo alloy biomaterials: Instrumentation development, heredity integral modeling and the effect of frequency

By

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Thesis

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Table of Contents

1 Introduction ............................................................................................................. 1
   1.1 Factors affecting fretting system .................................................................. 3

2 Structure and objectives ......................................................................................... 7
   2.1 Objectives: ..................................................................................................... 7
   2.2 Hypotheses: .................................................................................................. 8

3 2-D fretting instrument development ................................................................. 9
   3.1 Mechanical and electrochemical components ............................................. 11
   3.2 Data acquisition and LabVIEW program part ........................................... 12

4 Development of Theoretical Model for Fretting Corrosion Process .......... 16
   4.1 Determination of fretting corrosion related elements ................................ 17
      4.1.1 Oxide abrasion and reformation .......................................................... 17
      4.1.2 Determination of true contact area ...................................................... 19
      4.1.3 Other related elements ....................................................................... 23
      4.1.4 Duhamel Heredity Integral .................................................................. 27
   4.2 Materials and methods .................................................................................. 33
   4.3 Results ............................................................................................................ 37
      4.3.1 Comparison between model and experimental results ....................... 40
   4.4 Discussion ....................................................................................................... 43

5 Frequency effect on fretting corrosion ................................................................. 46
   5.1 Introduction ..................................................................................................... 46
   5.2 Materials and Methods ................................................................................. 48
   5.3 Results ............................................................................................................ 50
   5.4 Discussion ....................................................................................................... 59
   5.5 Comparison between model and fretting current ....................................... 61
   5.6 Conclusions ................................................................................................... 63
List of Figures

Fig 1: Factors have influence on fretting system .......................................................... 3
Fig 2: The schematic of the 2-D fretting system .............................................................. 10
Fig 3: The physical photo of the new fretting system (top-view) ................................. 11
Fig 4: The schematic of the configurations between different channels of DAQ board and sensors ................................................................. 13
Fig 5: The screenshot of ‘front panel’ for showing and collecting data from the fretting device ............................................................................................................... 15
Fig 6: Schematic of reformation process after oxide film is fractured and removed by pin .................................................................................................................. 19
Fig 7: The sum of the asperity contact area is assumed as a single circular area. ......... 18
Fig 8: The difference between multiple-asperity and single asperity assumptions. ... 22
Fig 9: Plot of decay in electro-field strength and current density with growing oxide film thickness ..............................................................24
Fig 10: At some specific potential above E₀, film thickness is gradually increasing to x₁ with decreasing electro-field until arriving at maximum x₄. ..................... 25
Fig 11: The dependent relationship between current response and oxide volume......28
Fig 12: The mechanism of how current varies with triangular signals and displacement during fretting process. ................................................................. 32
Fig 13: General view of the pin on disk fretting system ................................................ 34
Fig 14: Fretting Currents versus time plot of CoCrMo/CoCrMo at -0.1 V vs Ag/AgCl reference electrode in PBS solution ......................................................... 37
Fig 15: Plot of displacement varies with time at 1 Hz, 10 N for CoCrMo/CoCrMo alloys ........................................................................................................ 37
Fig 16: Comparisons of 1 Hz, 1.5 Hz and 2 Hz between model and experimental currents ........................................................................................................ 42
Fig 17: Representative picture of fretting currents from 1-20Hz at fixed load, displacement, and potential ................................................................. 51
Fig 18: The plot of RMS current versus frequency ...................................................... 52
Fig 19: The comparison of fretting currents for CoCrMo/CoCrMo at different frequencies ........................................................................................................ 53
Fig 20: Average fretting current vs. sliding speed for CoCrMo/CoCrMo alloy couple. ................................................................. Error! Bookmark not defined.
Fig 21: The plot of average COF and tangential force vs. frequency (1-20Hz). ........ 55
Fig 22: Representative plots of tangential force and COF vs. time for 1, 2 and 3 Hz tests ........................................................................................................ 56
Fig 23: The plot of average work done per cycle vs. frequency (1-20Hz) ............... 57
Fig 24: Typical energy loops for frequencies of 1-20Hz ........................................ 58
Fig 25: The data points with error bars are average fretting currents obtained from three different experimental groups ......................................................... 62
List of Tables

Table 1: The important elements pertaining to fretting process and the oxide properties of CoCrMo and Ti4Al6V alloy are listed.................................26
Table 2: List of parameter values used in the integration model. These are specific values for CoCrMo alloys and the test conditions. ...........................................40
Table 3: Units and values of all the parameters used in above equation. ...............61
1 Introduction

CoCrMo alloy is one of the main biomaterials used in medical implants in the world. This alloy is used in high load-bearing joints such as hip, knee and ankle arthroplasty because of its excellent mechanical strength and corrosion resistance [1]. Corrosion resistance mainly arises from the presence of a spontaneously formed chromium-oxide passive film on the metal surface, which prevents active reactions between base alloy and solution [2].

Most modern orthopedic devices contain multiple components that are designed to have modular self-locking taper junctions, because implants with modularity have advantages in surgical flexibility, ease of surgical revision and an ability to vary the metal combination across the junction [3]. Thus, it is important to explore and understand the reactions that may occur on metal oxide surfaces in modular interfaces of medical implants.

However, implants fabricated with modularity have exhibited evidence of corrosion-related damage mechanism. Munir et al. reported severe corrosion damage was found at head-neck taper and stem-sleeve connection [4]. In research by Makis et al., necrotic pseudotumors were observed adjacent to hip prosthesis in patients’ body through an imaging scan system [5]. Katzer et al. reported on signals and indications for early loosening of hip replacement [6]. Vundelinckx et al. recognized and showed the evidence of migration of chromium and cobalt ions from alloy into serum [7]. Numerous retrieval studies on failed implants
retrieved from the human body have revealed that the major causes for revision may be linked to corrosion and wear. In the study by Sinnett-Jones et al., debris and third body particles generated from wear caused more abrasion in the nanometer-scale and accelerated corrosion of artificial joints[8]. Santos et al. indicated that CoCrMo alloy had less wear attack with a diamond like carbon (DLC) coating [9].

The above studies proposed that corrosion and wear have a synergetic effect on the deterioration of medical devices. In 1993, Gilbert [10] brought forward the idea of mechanically assisted crevice corrosion (MACC) in taper junctions of modular implants. The basic concept of MACC can be interpreted as follows: The crevice formed at modular junctions, such as the cup/femoral head-femoral stem junction allows the ingress of body fluids into the taper interface. Abrasion of metal oxide occurs during loading and fretting inside of the crevice leads to repassivation reactions which consume oxygen in crevice fluids. The products of the reactions involve hydrogen ions and metal ions in solution as well as electrons inside the metal surface. Accumulation of these ions creates an acid environment and a potential drop across the interface which leads to unstable oxide at the metal surface. When a cycle of abrasion and repassivation occurs, newly formed oxide film may be easier to remove by subsequent mechanical events and the corrosion process will be accelerated. Thus, more severe corrosion can be observed at taper junctions of modular devices as a result of fretting corrosion. The final result is release of metal ions into the blood, as well as loosening of metal-on-metal junctions that may lead to ultimate implant failure.
1.1 Factors affecting fretting system

Mechanically assisted crevice corrosion is a complex phenomenon that combines mechanical and electrochemical conditions, solution environment, material properties, alloy combination as well as geometry of the interface (Fig 1).

Fig 1: Factors have influence on fretting system are categorized into five groups of mechanical elements, electrochemical aspect, material, solution and biological environment.

Fretting is a mechanical process that involves small scale cyclic motion (<100 um) that can cause fracture of oxide films on metal surfaces and electrochemical processes that lead to
the reformation of oxide film.

Mechanical factors, including contact load (stress), cyclic motion, frequency, and sliding displacement etc., have a direct influence on the severity of corrosion that develops. Contact load works [11] to rupture oxide films and affects the specific fretting regimes. Increasing load may change the contact conditions from sliding to sticking [12]. For instance, Wimmer et al. [13] studied the wear corrosion with different contact load. He found in some range the higher the applied load, the lower the coefficient of friction (COF). The research results of Yap [14] indicated that Ti-5Al-4V-0.6Mo-0.4Fe surface with lower roughness has reduced COF and frictional force during tribocorrosion. In addition, increasing contact load and sliding displacement will each lead to higher corrosion currents by increasing the fretting area. The abrasion speed of oxide film is based on the frequency of motion. The frequency of normal walking is usually between 0.5 and 2 Hz [15].

Electrochemically, potential will greatly affect the film reformation current by influencing the thickness of the oxide film [16]. At potentials lower than the passivating, or oxide film onset potential, there won’t be significant oxide film covering the metal surface and the fretting current should be low due to the lack of film-based current. When potential is set in the passivation region (i.e., above passivating potential), there is a growth in thickness of oxide film with increasing potential. Large fretting current transients will be observed as a result of the disruption and regrowth of the oxide film. For testing potentials higher than the breakdown voltage, fretting current becomes very small again due to the loss of
passivity.

Other factors such as material properties and solution conditions are also of great importance in fretting corrosion [17]. For instance, high carbon-contained CoCrMo with coarser microstructure has a better corrosion resistance than one alloyed with low carbon content [18]. Titanium of alpha (hcp) crystal structure is widely used in dental and medical device industry because of its stability at low temperature [19]. Compared to CoCrMo, titanium alloys have more biocompatibility with bone cells but less resistance to wear due to its poor surface mechanical performance. In addition, cells, proteins, inflammatory species, solution pH and temperature all play a role in affecting corrosion behavior of implants. For Co-Cr-Mo alloys in neutral PBS solution, the main reactions during fretting are presented below:

\[
\begin{align*}
\text{Cr} & \rightarrow \text{Cr}^{3+} + 3e^- \text{ (dissolution of metal ions)} \\
2\text{Cr} + 3\text{H}_2\text{O} & \rightarrow \text{Cr}_2\text{O}_3 + 6\text{H}^+ + 6e^- \text{ (repassivation of oxide film)} \\
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- & \rightarrow 4\text{OH}^- \text{ (consumption of oxygen)}
\end{align*}
\]

Reaction (1) and (2) are oxidation reactions, from where the electrons are generated. The majority of oxides formed during fretting are \( \text{Cr}_2\text{O}_3 \) along with some other complexes such as \( \text{CoO} \) and \( \text{MoO}_3 \) [1]. Reaction (3) is a reduction reaction that depletes oxygen in solution.

On the basis of these important elements involved in the fretting system, several theoretical
models used for predicting corrosion current have already been developed in prior studies. Ambrose [20] proposed a fundamental equation ‘\( I(t) = I_{\text{film}} + I_{\text{diss}} \)’ to estimate the current transient for oxide repassivation, where \( I_{\text{film}} \) is oxide formation current, \( I_{\text{diss}} \) is ionic dissolution current. This model was later modified by Gilbert et al. [21] and used to explain the current dependence on abrasion area and metal oxide properties with a method of a high-speed single asperity scratch test on Ti-6Al-4V. With the same equation, Goldberg [22] explained corrosion behavior of CoCrMo alloys and predicted the thickness of oxide film. Swaminathan and Gilbert [23] developed another mathematical model in 2012 to build a linkage between mechanical elements and electrochemical responses:

\[
I_{\text{film}} = 2 \frac{\rho nF}{M_w} \frac{A_{\text{nom}}}{\Delta} h \frac{d\delta}{dt}
\]

Where \( \frac{\rho nF}{M_w} \) denotes the charge per oxide volume, \( \frac{A_{\text{nom}}}{\Delta} h \frac{d\delta}{dt} \) is the abraded oxide volume per unit time, \( \frac{d\delta}{dt} \) represents sliding speed, \( \Delta \) is the average inter-asperity distance in the sliding direction, \( A_{\text{nom}} \), is the nominal contact area and \( h \) is the oxide thickness.

The models stated above provided good understanding of fretting corrosion phenomenon and is a solid basis for current estimation related to oxide film formation. However, these models can only predict average or peak current values. It is necessary to develop a new model to simulate the detailed abrasion-current fluctuations over time during fretting. This study presents a theory to predict the current transients that arise at any arbitrary time as a result of any arbitrary abrasion process, which will be a better basis for evaluating the
performance of metallic biomaterials and for exploring the corrosion kinetics of MACC. The effect of sliding speed/frequency on CoCrMo alloys and development of 2-D fretting device are also explained here as a part of the thesis.

2 Structure and objectives

This work consists of three sections: The first section is a description for data collection system of the 2-D fretting corrosion test device recently designed and built in the lab. In the second part, model development and verification efforts are presented in detail. The last section explores the effect of sliding speed/frequency on corrosion performance of CoCrMo sliding on CoCrMo in phosphate buffered saline.

2.1 Objectives:

The objectives of this thesis are:

1. To design and set up a 2-D fretting corrosion test system, which allows for variations in experimental conditions (e.g. Load, sliding distance and speed, potential, material combination, solution, etc.) and provides for the ability to observe fretting corrosion behavior under an optical microscope. Most of the parameters pertaining to the fretting corrosion process can be continuously controlled, monitored and measured.

2. To develop and verify a theoretical model which is capable of predicting fretting current
versus time response to any arbitrary abrasion time input with which one can correlate the mechanical and electrochemical elements with instantaneous corrosion current.

3. To observe the effect of sliding speed on fretting currents of CoCrMo/CoCrMo alloy combinations under fixed potential, load, displacement and surface roughness in PBS solution.

2.2 Hypotheses:

• Sliding speed affects fretting corrosion current by affecting oxide abrasion rate and repassivation (i.e., average currents are proportional to sliding speed). Increasing frequency will result in a proportional increase of corrosion current due to growth in volume of abraded oxide in unit time.

• Corrosion currents will stop growing at an upper limit abrasion speed when sliding speed is higher than oxide repassivation rate because no more film-based current will be generated under this condition.

• An increase in frequency will influence the COF and tangential force at a constant normal load. These two parameters are primarily influenced by contact load and surface roughness. Increasing frequency may not be able to dramatically change the fretting regime of the metal interface.
• Similarly, dissipated energy per fretting cycle will be almost unchanged with increasing frequency. Because the hysteresis energy will be based on tangential force if a fixed displacement is applied.

3 2-D fretting instrument development

Many different test devices have already been designed and built in prior studies that focused on fretting corrosion or tribocorrosion. Komotori et.al [24] developed a scratch test system to evaluate the repassivation behavior of Ti4Al6V biomaterials. Yan et al. [25] set up a new tribocorrosion device to explore the wear damage difference between high and low carbon-contained CoCrMo alloys. Another fretting test instrument devised by Kumar et al. [26] was used on thermal oxidation study during fretting of commercially pure Titanium (CP Ti). These test devices are in the similar design principles that the complete system consists of electrochemical cell as holder for samples and solution, counter and reference electrode for forming circuit, piezo-actuator for movement actuation, normal load control for providing surface contact, and computer for data collection and analysis.

This new test system described below (Fig 2 and Fig 3) was designed in the similar pattern: The thin slice sample disk is fixed in the electrochemical cell (made of two glass slides) of the pin-on-disk fretting system. The normal load is applied or removed by the screw at the
end of the pin. There is a piezo-actuator assembled below the glass slide holder to apply lateral cyclic movement (fretting). The related data are measured by different sensors and are transferred to A/D converter.

Fig 2: The schematic of the 2-D fretting system. Phosphate buffered saline (PBS) solution is maintained in the middle space created by the two glass slides. Pin and disk samples are coated with insulating layer except the fretting part. Displacement sensors are calibrated and are used for signal measurement.
The main purpose of the instrument is to observe the fretting corrosion phenomenon of metal-on-metal (M-O-M) contacts under the microscope in real-time, and to meet the needs of simultaneously controlling and monitoring fretting corrosion related parameters. Variations in materials and solution will be feasible as well. To be clear, the system is categorized into three parts: mechanical and electrochemical components, data acquisition part, as well as sample and solution.

Fig 3: The physical photo of the new fretting system (top-view).

3.1 Mechanical and electrochemical components

The driving actuator of this laboratory test device is a piezoelectric actuator (Piezo-Jenna
System, Germany), which has the capability to provide movement amplitude up to 80 microns. A non-contact differential variable reluctance transducer (DVRT, eddyNCDT 3010, MICRO-EPILSON., USA) is used for measuring lateral pin displacement and tangential force. Normal load is based on deflection of the double cantilever (load cell), which is directly connected to and measured by a linear variable differential transformer (LVDT, MICRO-SENSORS., USA). Another LVDT for the purpose of measuring disk displacement, is rigidly mounted in a plastic sample holder stage that has an extremely tight connection with the piezoelectric actuator. The difference between pin displacement measured by the non-contact DVRT, and disk displacement measured by the stage LVDT is determined as the true pin-disk displacement of the fretting sample.

The electrochemical aspects of the system include potentiostatic control (263A, EG&G INSTRUMENTS., USA) along with a three-electrode system, which consists of a reference electrode (Ag/AgCl), counter electrode (gold) and working electrode (samples including pin and disk).

3.2 Data acquisition and LabVIEW program part

All electrochemical and mechanical data are collected with one 14-bit B series multifunction (NI-USB-6009) National Instruments data acquisition device that contains eight differential analog input (AI) channels and two analog output (AO) channels. As shown in Fig 4 of hardware connection, analog input channels 1 to 4 are used for data
collection of stage displacement, normal load, frictional force & pin vibration, and corrosion current respectively. The computer user interface presented in Fig 5a and 5b was developed in National Instruments LabVIEW.

![Diagram](image)

Fig 4: The schematic of the configurations between different channels of DAQ board and sensors

LabVIEW, full name is Laboratory Virtual Instrument Engineering Workbench, functions as a powerful tool for data acquisition in academic research and industry development because of its ease of flexibility in programming, versatility in different disciplines, and simplicity in visualization & editing. There are two parts of a LabVIEW program. One is graphical user interface named ‘Front Panel’, which includes ‘controls’ for input operations and ‘indicators’ for output displays, another one called ‘Block Diagram’ which consists of different nodes for the purpose of defining functionality of LabVIEW program. Compared to traditional text-based programming language, the graphical program of LabVIEW transfers signals in the form of data flow starting from virtual channels, going through
nodes and ending in indicators, which is a process that could be monitored and tracked in the ‘Block Diagram’.

The ‘Front Panel’ and ‘Block Diagram’ are presented in Fig 5a and Fig 5b separately. In ‘Front Panel’ section, all ‘controls’ that allow user to define sampling condition and to save collected data are gathered in the input box on the right side of the picture, and on the left side are four waveform charts for data display of normal load, tangential force, displacement amplitude and corrosion current, respectively.

The main frame of ‘Block Diagram’ is a three-section flat sequence structure that ensures codes inside it to execute from left to right sequentially. In the first sequence piece is a property node ‘reinitialize all’ that resets values of all ‘controls’ and ‘indicators’ to default. The main functional code in the second part is a file dialog VI that prompts user to define desired file save location, which will be displayed in the file path indicator of the ‘Front Panel’. The third section deals primarily with data collection and processing. Signals are collected with an express DAQ assistant that works to configure all the physical analog input channels as figure 4 listed, and processed in a ‘for loop’ structure. Processed data can flow into waveform charts as well as being saved in comma separated variable (CSV) format once the ‘save button’ on the front panel is clicked. Users are able to choose how many data points to be saved. All the nodes mentioned above are placed in a while loop which makes the codes inside it run continuously. The LabVIEW program will stop running after the ‘stop Boolean control’ of front panel is pressed.
Fig 5: The Screenshot of ‘front panel’ (a) for waveform display and ‘block diagram’ (b) for functionality of this VI.
Samples and solution preparation

Samples include a cone-shaped CoCrMo (ASTM F-1537) pin with flat bottom fixed in a holder and a rectangular CoCrMo disk with about 0.1 mm thickness secured to a glass stage. Standard phosphate buffered saline (PBS) simulating human body fluids is used as the experimental solution.

4 Development of Theoretical Model for Fretting Corrosion Process

Fretting corrosion currents are some of the most important factors in evaluating corrosion severity of metallic biomaterials. As discussed above in the introduction part, there are many mechanical aspects, such as normal load, abrasion rate, sliding distance, surface contact conditions, and metal properties, that work together to have a synergetic influence on the corrosion currents under potentiostatic condition. A clear correlation between instantaneous corrosion current and integration of all the mechanical and electrochemical elements involved in the fretting system is given by the model discussed below. This model should provide a more accurate and reliable basis for exploring the mechanism of fretting corrosion.
4.1 Determination of fretting corrosion related elements

Fretting is a small scale (<100um) cyclic relative movement process between two surfaces in the presence of normal load that makes asperities contact. The mechanical, material (surface) and electrochemical parameters that prove to be the most influential are listed here.

**Oxide abrasion and reformation:** During fretting, the unit removal of oxide volume is determined by abrasion rate \( \frac{dV}{dt}(ab) \), while the unit gain of oxide film is determined by repassivation rate \( \frac{dV}{dt}(repass) \), and the difference between these two rates is instantaneous net V amount of missing oxide on the surface (see Fig. 6). This relationship is given by equation:

\[
\frac{dV_{net}}{dt} = \frac{dV_{abrasion}}{dt} - \frac{dV_{repassivation}}{dt} = w \cdot h \left( \frac{d\delta}{dt} - \frac{dx}{dt} \right)
\]

Where ‘w’ is diameter of true contact area and ‘h’ is thickness of oxide film. Note, the rate of repassivation (or regrowth) cannot exceed the rate of abrasion (or removal), so the net \( \frac{dV_{net}}{dt} \) must be greater than, or equal to zero.

For the case when the oxide removal rate doesn’t exceed the maximum oxide repassivation rate, which is the most common situation for metallic implants in human body, net oxide film volume rate \( \frac{dV_{net}}{dt} \) will be zero, and the rate of abrasion will equal the rate of
repassivation. However, it is possible that abrasion rate could be higher than oxide reformation rate at very fast fretting speed, where $V_{\text{net}}$ is bigger than 0. In this case the maximum oxide growth velocity will be determined at the rate where film currents stop increasing with increasing sliding speed. This will be discussed in the third section ‘effect of sliding speed and frequency on CoCrMo alloys’ of this thesis. The two rates are considered to be equal in this model since normal walking frequency is usually in the range of slow abrasion compared to repassivation, however, this assumption also implies that the fretting currents should scale directly with the sliding velocity if the two rates are equal.

In addition, one can envision that $\frac{dV_{\text{repassivation}}}{dt}$ can be viewed as being comprised of the width, $w$, height, $h$ of the oxide to reform and an effective repassivation velocity $\frac{dx}{dt}$.

Fig 6: Schematic of reformation process after oxide film is fractured and removed by pin. Abrasion volume is calculated by $w \ h \ \frac{d\delta}{dt}$. Note, for most cases (i.e., ‘slow’ abrasion rate), the repassivation rate will equal the disruption rate. That is, for each infinitesimal step in oxide removal, that exposes region will repassivate almost instantly, so the two rates will be approximately equal.
**Determination of true contact area:** Samples studied here are Co-Cr-Mo and the contact situation fits the plastic deformation multiple asperity concept (see Fig 7). In this model, the true contact area is randomly distributed over multiple contacting asperities and all of these contacts sums up to be the normal load across the contact surfaces divided by the effective hardness of the surface.

![Diagram of contact area](image)

**Fig 7:** In real cases there are a certain number of asperities distributed on the fretting interface. The sum of the asperity contact area is assumed as a single circular area. Note the true contact area is much smaller than the nominal contact area.

As shown in figure 7, if the true contact area $A_{true}$ is assumed as a single circular area, $F_N$ is the normal load, $H$ is the hardness of material, then the true contact area can be calculated as:

$$A_{true} = \frac{F_N}{H} = \pi a^2$$  \hspace{1cm} (1)

radius $a$ is:

$$a = \sqrt{\frac{F_N}{\pi H}}$$  \hspace{1cm} (2)
diameter \( w \) will be:

\[
    w = 2a = 2\sqrt{\frac{F_N}{\pi H}}
\]  \hspace{1cm} (3)

which is used to determine the abraded oxide volume along with oxide thickness ‘h’ and fretting velocity \( \frac{d\delta}{dt} \), as depicted in Fig 6. That is, the volume of oxide abraded per unit time is given by:

\[
    \frac{dV_{abrasion}}{dt} = h 2\sqrt{\frac{F_N}{\pi H}} \frac{d\delta}{dt}
\]

If multiple circular asperities are assumed, then a slight modification to this analysis is needed (see below and discussion).

To clarify this problem (Fig 8a & b), one can consider each single asperity contact area to be approximated as a fixed single circular area \( A_i \), and the diameter of this area can be calculated as:

\[
    d_i = 2\sqrt{\frac{A_i}{\pi}}
\]

Assuming all \( A_i \) are equal and the amount of contacted asperities is \( n \), then true contact area will be:

\[
    A_{sum} = \sum_{i=1}^{n} A_i = n A_i
\]

If \( \bar{d} \) is the sum of the diameters (\( d_i \)) of all asperities in contact, then there is:

\[
    \bar{d} = n d_i
\]
\[ \bar{d} = 2 \, n \, \sqrt{\frac{A_i}{\pi}} \]

For a specific sliding distance, \( \delta \), the abrasion area is:

\[ A_{\text{abrasion}} = \bar{d} \, \delta = 2 \, n \, \delta \, \sqrt{\frac{A_i}{\pi}} \]

But from the single asperity theory, the true contact area \( A_{\text{sum}} \) can be calculated by:

\[ A_{\text{sum}} = n \, A_i = \frac{F_N}{H} \]

Then,

\[ A_i = \frac{F_N}{Hn} \]

The effective diameter \( d_{\text{sum}} \) is:

\[ d_{\text{sum}} = n d_i = 2 \, n \, \sqrt{\frac{F_N}{\pi H n}} = 2 \sqrt{n} \, \sqrt{\frac{F_N}{\pi H}} \]

If one uses \( d_{\text{sum}} \) to calculate the abrasion area, the equation will be:

\[ A_{\text{abrasion}} = d_{\text{sum}} \delta = 2 \, \delta \, \sqrt{n} \, \sqrt{\frac{F_N}{\pi H}} \]

Calculations of which lead to \( \sqrt{n} \) smaller than the true abrasion area. And this may lead to inaccuracy in current prediction with the model.
Fig 8: (a) The multiple-asperity and single asperity assumptions. (b) The CoCrMo disk surface photo of post-fretting taken under optical microscope. It is clear to see the multi-scratch traces caused by fretting motion in the abraded area.
Other related elements: The oxide film thickness is given by:

\[ h = m (E - E_{\text{onset}}) \]  \hspace{1cm} (4)

where \( m \) is anodization rate, \( E \) is the potential held for experiment, \( E_{\text{onset}} \) is the potential where oxide film begins to form (i.e., passivating potential, or onset potential).

The equation (4) of calculating oxide thickness is based on high field growth theory proposed by Gunterschulze and Betz [27] in the form as:

\[ i = A \exp \left( B \frac{E - E_0}{x} \right) \]

where \( i \) is the film formation current density, \( x \) is the thickness of oxide film, \( A \) and \( B \) are material-dependent constants which are determined by hopping ion attempt frequency, activation energy and charge number of the mobile species. \( E_0 \) is the oxide onset potential, \( E \) is the potential above \( E_0 \).

In this theory, film current density decreases with increase in oxide thickness. As shown in Figure 9, if one assumes there is a limiting current density \( i_L \) below which the oxide thickness will no longer grow, and the film thickness at \( i_L \) is \( x_L \). Then rearranging above equation with these two parameters yields:

\[ x_L = \ln \left[ \frac{i_L}{A} \right] B (E - E_0) \]

\[ \downarrow \]

\[ h = m (E - E_{\text{onset}}) \]

where \( m = B \ln \left( \frac{i_L}{A} \right) \).
The high field theory assumes current can go to infinity when there is zero thickness of oxide covers on metal surface, but it will drop quickly to limiting current ($i_L$) as the film is thickening to $x_L$ (Fig. 9). This equation also means that in the repassivation region of metal, increases in potential will lead to a linearly thicker oxide film formed on metal surface (Fig 10).

Fig 9: Plot of decay in electro-field strength and current density with growing oxide film thickness. Limiting current $i_L$ is about 1.2E-6 A/cm$^2$, and limiting oxide thickness $x_L$ is about 2.35 nm. ($A=10^{-18}$ A/cm$^2$, $B=3*10^{-6}$ cm/V, $E=E_0=2$ V).
Fig 10: At some specific potential above $E_0$, film thickness is gradually increasing to $x_L$ with decreasing electro-field until arriving at maximum $x_L$. Higher potential in passivation region leads to thicker oxide film.

The charge per volume of oxide, $\Phi$, is calculated as:

$$\phi = \frac{\rho n F}{M_w} \text{ (C/cm}^3\text{)} \quad (5)$$

where $\rho$ is oxide density, $n$ is valence, $F$ is Faraday’s constant and $M_w$ is the oxide molecular weight. Each of these are constants or physical properties of the specific oxide for specific metal alloys. For an alloy with multiple oxide forming constituents, the values of $\rho$, $n$ and $M_w$ can be estimated from a volume fraction of the alloy oxide forming constituents. For instance, according to the alloying factor, the molecular fraction of Co, Cr and Mo in CoCrMo alloy is 65.80%, 31.19% and 3.01%, respectively. The oxide film of the alloy mainly consists of CoO, Cr$_2$O$_3$ and MoO$_3$. If one multiplies the molecular weight,
density and valence of the 3 oxide with the molecular fraction respectively, and the addition results of each parameter are the oxide film properties of CoCrMo alloy (Table 1).

The above parameters affect Φ and the magnitude of corrosion current. Below is a summary listing of these parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Unit</th>
<th>Oxide</th>
<th>Mole fraction</th>
<th>Mw (g/mol)</th>
<th>ρ (g/cm³)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abrasion velocity</td>
<td>dδ/dt</td>
<td>cm/s</td>
<td>CoO</td>
<td>65.80%</td>
<td>75</td>
<td>6.45</td>
<td>2</td>
</tr>
<tr>
<td>Repassivation velocity</td>
<td>dx/dt</td>
<td>cm/s</td>
<td>Cr₂O₃</td>
<td>31.19%</td>
<td>152</td>
<td>5.21</td>
<td>3</td>
</tr>
<tr>
<td>Test potential</td>
<td>E</td>
<td>V</td>
<td>WO₃</td>
<td>3.01%</td>
<td>128</td>
<td>6.47</td>
<td>6</td>
</tr>
<tr>
<td>Onset potential</td>
<td>E onset</td>
<td>V</td>
<td>Total</td>
<td>CoCrMo oxide</td>
<td>76.91</td>
<td>6.06</td>
<td>2.43</td>
</tr>
<tr>
<td>Anodization rate</td>
<td>m</td>
<td>nm/V</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxide film thickness</td>
<td>h</td>
<td>nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>True contact area</td>
<td>A₀</td>
<td>cm²</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radius of A₀</td>
<td>a</td>
<td>cm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diameter of A₀</td>
<td>w</td>
<td>cm</td>
<td>TiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardness</td>
<td>H</td>
<td>Pa</td>
<td>Ti₄Al₆V oxide</td>
<td>79.9</td>
<td>4.45</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Normal load</td>
<td>F₅</td>
<td>N</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>ρ</td>
<td>g/cm³</td>
<td></td>
<td></td>
<td></td>
<td>21498</td>
<td></td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>Mw</td>
<td>g/mol</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Valence</td>
<td>n</td>
<td>NA</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Faraday constant</td>
<td>F</td>
<td>C/mol</td>
<td></td>
<td></td>
<td></td>
<td>96485</td>
<td></td>
</tr>
<tr>
<td>Charge per oxide volume</td>
<td>ϕ</td>
<td>C/cm³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relaxation time</td>
<td>τ</td>
<td>s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: The important elements pertaining to fretting process and the oxide properties of CoCrMo and Ti₄Al₆V alloy are listed.
4.1.1 Duhamel Heredity Integral

The Duhamel integral, also called ‘The Boltzmann superposition principle’, is an integral that allows determination of time-dependent outputs resulting from an arbitrary input. It shows that summed effects caused by multiple infinitesimal inputs can be integrated to predict an output over time.

The proposed model will use a Duhamel integral to link the oxide abrasion as a function of time to the predicted fretting current variation with time. That is, there are time-dependent relationships between current transient $I(t)$, and oxide reformation volume $V_{\alpha}(t)$ (or abrasion volume). As shown in figure 11, if the oxide volume reformed during fretting is partitioned equally into multiple small pieces, $dV_0$, and each of them will lead to a single current response. According to the concept of Duhamel integral, the addition of all the single current responses will be the experimental current observed in the fretting corrosion test. So the current transient can be predicted at any arbitrary time as long as one knows the time-dependent reformation of the oxide volume.
Fig 11: The dependent relationship between current response and oxide volume. Each step of repassivation oxide volume leads to the corresponding current response.

Based on prior research [21] [22] the current response to an instantaneous disruption of the oxide results in an exponential spike and decay function of the form:

$$I(t) = I_{\text{peak}} e^{-\frac{t}{\tau}}$$

(6)

where $I_{\text{peak}}$ is the peak current value, $\tau$ is relaxation time for decay of the current transient. The parameter $\tau$ is measured in the experiment as the time for the current decay to $\frac{1}{e} I_{\text{peak}}$ after stopping abrasion and is likely affected by the geometry of the system.
From Faraday’s Law, film-based current is related to oxide properties and oxide volume as shown in following:

\[ I(t) = \frac{\rho n F}{M_w} \frac{dV_{ox}}{dt} \tag{7} \]

where \( \frac{dV_{ox}}{dt} \) can be taken as excitation signal and \( I(t) \) is the corresponding current response.

On the assumption that the film current is close to total current [21] [22], connecting Eq. (6) and (7) one can get an equation for instantaneous repassivation:

\[ I(t) = I_{peak} e^{-\frac{t}{\tau}} = \frac{\rho n F}{M_w} \frac{dV_{ox}}{dt} \tag{8} \]

The total charge can be determined with:

\[ Q = \int_0^\infty I(t)dt = \int_0^\infty I_{peak} e^{-\frac{t}{\tau}} dt = \int_0^\infty \frac{\rho n F}{M_w} dV_{ox} = I_{peak} \tau = \frac{\rho n F}{M_w} V_{ox} \tag{9} \]

\[ \downarrow \]

\[ I_{peak} \tau = \frac{\rho n F}{M_w} V_{ox} \tag{10} \]

If \( A_T(t) \) is defined as repassivation admittance, substituting Eq. 5 and 8 into Eq. 10 one will get the expression:

\[ A_T(t) = \frac{I(t)}{V_{ox}} = \frac{\Phi}{\tau} e^{-\frac{t}{\tau}} \tag{11} \]

Then current response should be the addition of a series of impulses from \( t_0 \) to \( t \) determined by:

\[ I(t) = A_T(t)V_{ox}(t = 0) + \int_0^t A_T(t - \lambda) \frac{dV_{ox}(\lambda)}{d\lambda} d\lambda \tag{12} \]

The expression ‘\( A_T(t)V_{ox}(t = 0) \)’ on the right side of Eq. 12 is the current at the starting
point \((t=0)\). Usually this part is zero because there is no oxide abrasion before initiation of fretting. Replacing repassivation admittance \(A_T(t)\) of Eq. 12 with Eq. 11, the result presents in below form:

\[
I(t) = \int_0^t \frac{\phi}{\tau} e^{-\frac{t-\lambda}{\tau}} \frac{d\Delta V_{ox}(\lambda)}{d\lambda} d\lambda
\]

(13)

From the previous discussion, the repassivation of oxide volume during low speed fretting is determined by:

\[
V_{ox}(t) = V_{abrasion}(t) = w \times h \times \delta(t)
\]

(14)

Integrating Eq. 3, 4, 13 and 14, the model for predicting instantaneous fretting current can be expressed as:

\[
I(t) = 2 \sqrt{\frac{FN}{\pi H}} \frac{\phi}{\tau} m (E - E_{onset}) \int_0^t e^{-\frac{t-\lambda}{\tau}} \frac{d\delta}{d\lambda} d\lambda
\]

(15)

This model builds a linkage between fretting current transient and oxide properties, system relaxation time, mechanical force and electrochemical potential, material hardness, and abrasion velocity. For a known normal load, material and voltage, one can predict the corrosion behavior and track the variations of current transients during fretting process on the basis of removal rate of oxide volume.

The following assumptions are made for this equation: (1) oxide reformation rate equals to abrasion rate. (2) Asperities dispersed on the contact surface can be approximated as a single circular spot. (3) Most of the current transient measured from experiment is film-
Based current. (4) Fretting current will not be influenced or changed by metal debris and other substance released from fretting process, such as oxide complexes and third body particles.

Based on this equation, fretting current is primarily influenced by frequency, displacement, type of oxide film, relaxation time \((\tau)\) of the system and voltage. Increasing frequency, displacement magnitude and voltage will lead to growth of corrosion current.

The relationship between the excitation signal from function generator during motion, the actual amplitude of the displacement, the abrasion velocity and the fretting current vs. time is presented in figure 12.
Fig 12: mechanism of how current varies with triangular signals and displacement during fretting process.

The plot on the top of figure 12 is one pulse of triangular wave forcing function that experiences linear increase and decrease periodically. This is the input voltage waveform.
during motion. The second plot is a schematic of the true variation of displacement \( \delta(t) \), which typically experiences sticking followed by linearly sliding with signal excitation until full displacement is reached when it comes to maximum amplitude of triangular wave. The plateau represents the sticking condition where reversing of the direction occurs during the back and forth movement. The next one is a schematic plot of the anticipated abrasion velocity vs time. Abrasion velocity keeps constant during sliding but drops quickly to zero in sticking section in this example. On the bottom is the schematic of the current plot, I(t). Sliding results in current growth because of the oxide removal while sticking leads to current relaxation to baseline as a result of zero oxide reformation during this time.

### 4.2 Materials and Methods

Experimental materials include flat circular CoCrMo disks (diameter is around 35mm, ASTM F-1537) and cone shaped flat bottom CoCrMo pins (with about 0.6mm diameter, ASTM F-1537) that were polished to 600 grit with emory sand paper. Ethanol and DI water were used to clean the metal surface before samples were mounted on test device. Acrylic material intended for electrical insulation was coated on both pin and disk except exposure of a small test region (nearly 0.25 cm\(^2\)) to the surrounding solution. Tests were carried out with the following pin-on-disk fretting system in PBS solution at room temperature.
Fig 13: General view of the pin on disk fretting system. (The plot is adopted from paper [23] published by Swaminathan and Gilbert.)

The fretting test system (Fig 13) is an integration of actuation, control and measurement elements that pertain to both electrochemical and mechanical elements of the system.

The magnitude of normal load between pin and disk is controlled by a micrometer that is rigidly mounted to Z-stage of the dimensional stages. Load data are measured by a six axis load cell (MINI 45 F/T six axis load cell, ATI Measurement Inc., USA) on the bottom of which there is a chamber used to fasten CoCrMo pin. This load cell also helps to measure transverse forces, which are of great importance in determining coefficient of friction, interfacial energy dissipated and other parameters related to fretting system.

The movement of the electrochemical cell mounted on an X-Y linear stage is provided by a piezoelectric actuator (Piezosystems Jena, Germany) which can go up to 140 microns. A
function generator works to control the type of waveform and amplitude of signal in order to regulate displacement magnitude during abrasion. In this research, a triangular waveform was used as the excitation signal and displacement magnitude was approximately 140 microns. Motion differences between pin and disk were measured by a contact differential variable reluctance transducer (DVRT, Microstrain Inc., USA).

Potential control and current measurement functions were performed with a three electrode testing system consisting of a working electrode (pin and the disk), reference electrode (standard Ag/AgCl) and counter electrode (carbon). Samples were isolated from other metal sections of the device by mounting in a delrin electrochemical cell. An electrical connection was established between the pin and disc using a wire. A potentiostat (263A, Princeton Applied Research, USA) applied a fixed potential and NI-USB-6009 DAQ board was used for current data collection. Samples were immersed for 30 minutes before each test started to equilibrate the electrochemical interface. Experiments were designed to measure the parameters that were necessary in model verification. All the fretting tests were carried out at a constant potential of -0.1 V vs. Ag/AgCl and a fixed normal load of 10 N. Mechanical data such as normal load, coefficient of friction, tangential force, displacement were saved in the form of a comma separated variable (CSV) file with a custom coded LabVIEW™ program. Corrosion current data were collected at a sampling rate of 600 points/second with LabVIEW™ Express DAQ system.

Two seconds of raw current data were extracted from saved files for model comparison.
Displacement data were running average smoothed every 10 points step to cut down noise.

Instantaneous abrasion rate was calculated from acquired sliding displacement-time data with the equation:

\[
\frac{d\delta}{dt} = \frac{\delta_2 - \delta_1}{t_2 - t_1}
\]

Where ‘\(\delta_2 - \delta_1\)’ is the variation of DVRT data, ‘\(t_2 - t_1\)’ is the time interval.

Plots of typical fretting current behavior vs. time of metallic biomaterials, load/force variations vs. time, smoothed DVRT and abrasion velocity data vs. time, and comparison between experimental and model currents were made in the results portion. Regression analysis was performed using least square fitting method to evaluate the association between the theoretical equation and the experimental data.

Regression analysis:

\[
R^2 = 1 - \frac{SSE}{SSTo}
\]

(SSE: sum of squared errors, SSTo: total sum of squares)

Where \(SSE = \sum \epsilon^2\), \(\epsilon = y_i - f(x)\), and \(SSTo = \sum(y_i - \bar{y})^2\).

\(\epsilon\): The difference between model prediction and experimental value (residual)

\(y_i\): The experimental current value

\(\bar{y}\): The total average current value

\(f(x)\): The current value predicted by the model
4.3 Results

An example of corrosion current behavior of CoCrMo/CoCrMo materials during fretting corrosion testing shows the characteristic cyclic increase (Fig 14) in current due to fretting. The baseline is approximately zero prior to test, while the currents rise quickly when fretting begins. The difference between elevated and baseline current is the fretting current, because baseline current is not necessarily zero. After the back and forth movement stops, currents experienced a recovery to the same baseline currents prior to fretting. The plot on the right upper side of Fig 14 shows currents during 1 cycle in the fretting test.

Fig 14: Fretting currents versus time plot of CoCrMo/CoCrMo at -0.1 V vs Ag/AgCl reference electrode in PBS solution. Applied load was 10 N, frequency was 1.5 Hz, and displacement was 140 μm. Test lasted for about 50 seconds.
The DVRT movement and corresponding abrasion velocity data over two seconds are presented (Fig 15a). The displacement curve consists of 2 portions. The first one is the sliding portion, where oxide abrasion occurs in a constant rate. Growth of current is mainly associated with this part. The second is the flat lines where sticking of the CoCrMo pin occurs during the reversal of the direction at the end of one stroke (Note, the sliding velocity is zero during sticking). The fictional force also changed direction as a result of sliding reversal (Fig 15b, positive to negative, or vice versa). The sticking portion is responsible for current relaxation. The curve of abrasion velocity (dδ/dt) vs. time captures the instantaneous sliding speed during pin motion. The abrasion rate is zero during the sticking portion. For the period of transition from sticking to sliding, the speed increases quickly to a maximum rate of about 0.07 cm/s and keeps roughly constant until it drops quickly to zero during the conversion from sliding to sticking. Fretting currents show similar behavior as abrasion rate.

The interrelated normal load, coefficient of friction (COF) and tangential force involved in fretting corrosion are displayed as well (Fig 15b). The horizontal portions of the curves are full sliding and the flat lines and the ‘V’ shapes are where sticking occurs.
Fig 15: Plot (a) is the displacement varies with time at 1 Hz, 10 N for CoCrMo/CoCrMo alloys. The magnitude is about 140 μm. Red curve is the corresponding abrasion rate $\frac{d\delta}{dt}$. The highest velocity is about 0.07 cm/s during full sliding. Plot (b) is the corresponding force data. The variation range of the normal load, COF and frictional force is about 9 to 12 N, 0.25 to 0.42, and 3.8 to -3.8 N, respectively (the change of sign denotes direction reversal).
4.3.1 Comparison between model and experimental results

The model generated in the preceding part of the thesis to estimate the current-time behavior is presented here:

\[
I(t) = 2 \sqrt{\frac{F_N \Phi}{\pi H \tau}} \cdot m \cdot (E - E_{\text{onset}}) \int_0^t e^{-\frac{t-\lambda}{\tau}} \frac{d\delta}{d\lambda} d\lambda
\]

The experimental data and the model prediction of 1 Hz, 1.5 Hz and 2 Hz cases (Fig 16) can be compared using the parameters listed in Table 2. The $\Phi$, ‘charge per volume of oxide’ is calculated as $\rho n F / M_w$, each parameter is either calculated and measured experimentally or obtained from the literature for CoCrMo oxide properties. Hardness (H), anodization rate (m) and onset potential ($E_{\text{onset}}$) are from prior studies [28, 29]. The normal load ($F_N$) and potential (E) are set by the test conditions. The time constant ($\tau$) and sliding speed ($\frac{d\delta}{d\lambda}$) are parameters calculated respectively from current recovery data and displacement-time data collected during the test. The variable $t$, is the time of interest and $\lambda$ is a dummy variable for time in the integral.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi$</td>
<td>18477</td>
<td>C/cm³</td>
</tr>
<tr>
<td>H</td>
<td>2</td>
<td>GPa</td>
</tr>
<tr>
<td>$F_N$</td>
<td>10</td>
<td>N</td>
</tr>
<tr>
<td>m</td>
<td>2</td>
<td>nm/V</td>
</tr>
<tr>
<td>$E_{\text{onset}}$</td>
<td>-0.5</td>
<td>V</td>
</tr>
<tr>
<td>E</td>
<td>-0.1</td>
<td>V</td>
</tr>
<tr>
<td>$\tau$</td>
<td>0.1</td>
<td>s</td>
</tr>
</tbody>
</table>

Table 2: List of parameter values used in the integration model. These are specific values for CoCrMo alloys and the test conditions.
The shape and magnitude of the fretting currents are primarily determined by the abrasion velocity $\frac{d\delta}{dt}$ when the same constants from Table 2 are used in the equation for each frequency. For instance, the model currents of 1 Hz (Fig 16a) rises up with the growth of $\frac{d\delta}{dt}$ and decays exponentially as the abrasion velocity drops to zero. At 1.5 Hz and 2 Hz (Fig 16b and 16c), the higher $\frac{d\delta}{dt}$ leads to an increase in the magnitude of the modeled current and there is greater up and down behavior generated in a unit time.
Fig 16: Comparisons of 1 Hz (a), 1.5 Hz (b) and 2 Hz (c) between model and experimental currents. The normal load, hardness, charge per oxide volume, relaxation time and oxide thickness are the same values listed in the Table 2 for each plot. The model currents exhibit similar trends as the abrasion velocity. The model made reasonably good predictions of the fretting currents ($R^2=0.86$).
A regression analysis was performed between the experimental and theoretical currents and showed that current calculated from the model is strongly correlated to the experimental data for all the samples (R²=0.86). This also gives the fact that film current dominates the total current while dissolution current is just a small proportion.

4.4 Discussion

This thesis developed and assessed the heredity integral approach for predicting fretting corrosion behavior. With this equation, one can predict current versus time response at any arbitrary abrasion-time function by measuring and calculating normal load, surface hardness, oxide properties, relaxation time, test potential, time parameters and abrasion velocity. A new element AT(t) defined as “repassivation admittance” is used to set up a linkage between oxide reformation equations (6) and (7) for the purpose of generating new repassivation model.

The model was used to predict the film currents and the results were a good match with the experimental currents. This result is consistent with the prior conclusions from the studies of Gilbert [21] and Goldberg [22] that the film-based current is dominant in the total current. The reason is that in the passive region, the reformation rate of oxide film is fast enough to cover the base alloy surface and stop the dissolution of metal ions. So the dissolution current is limited.
The relaxation time $\tau$ was taken as 0.1 second in this study. Determination of this parameter is based on the calculation of the duration of time for the current to drop from $I_{\text{peak}}$ to $(1/e)I_{\text{peak}}$ after scratching or fretting was stopped. There are many factors that may affect the time constant value, such as cathodic area, surface geometry, solution resistance, surface conditions and oxide complexes formed during fretting process. Calculating with higher relaxation time will lead to lower model currents. Thus for different testing systems, materials, solution environment and fretting area, the time constant should be measured and used for specific conditions to obtain more accurate estimation of fretting current.

Another factor worth discussing is the true abrasion area. Failing to correctly understand this concept may lead to underestimation of the corrosion currents. In this model the mechanism of CoCrMo pin and disk contact is considered to result in a plastic contact due to two hard surface bodies. The true contact area is assumed as a single circular area and calculated with equation `$A_{\text{true}}=\frac{F}{H}$`, which works well for single asperity contact. However, for the multiple-asperity fretting case, all contact asperities can be ground smooth and it is possible that the true contact area will become larger and more asperities can be brought into contact. Besides, adjacent abrasion areas may overlap on each other and cause the overlapped zone to be fretted twice. As discussed in the previous part, it is necessary to figure out the number of contact asperities on the interaction surface, which is related to normal load, surface roughness and system compliance.

In addition to this point, the material combinations used in this work are CoCrMo-on-
CoCrMo, which is a hard on hard metal contact. However, the mechanism of hard on soft or soft on soft metal contact might be different, in which case the Hertzian model or other surface contact model (e.g. Johnson, Kendall, Roberts model of adhesive contact, JKR model) might be more effective than the plastic contact equation used above to calculate radius of true contact area (Hertzian equation: $a^3 = \frac{3FR}{4E}$, where $F$ is applied load, $R$ is the indentor radius, $E$ is elastic modulus associated with two contact substances).

There are some other aspects that need to be further explored that this model has not considered. First, it does not include the dissolution current, which has been ignored at low speed fretting when oxide repassivation rate is much higher than abrasion velocity. But as frequency or sliding speed approaches a high level, the experimental current can be higher than the model prediction because more area of active metal is exposed to solution and dissolution currents will increase, even though film-based currents remain the same. Goldberg [22] studied both dissolution and film current of CoCrMo alloy based on the Ambrose model. In his research, dissolution current was about 10% of the total current while film current was 90%. But his study was just for a high speed single asperity scratch test, fretting corrosion was different because it is a continuous process and the dissolution current keeps changing due to variations in area of exposed metal surface per unit time to the solution.

Second, cathodic shifts in electrode potential during the fretting process are not considered in this model. During fretting, the voltage will drop [30] to more cathodic values because
more electrons are released into the metal surface. The potential will influence the thickness and stability of oxide film.

Third, a great quantity of H$^+$ ions can be generated in solution, which also has influence on the surface oxide condition [31]. When it comes to the biological environment, cells, proteins, inflammatory species all play a role in affecting corrosion process [32].

Thus, even though the model discussed in this thesis gives a good prediction for corrosion behavior of metallic biomaterials in the in vitro environment, all of those elements need to be explored to understand how the metal works in human body.

5 Frequency effect on fretting corrosion

5.1 Introduction

The corrosion resistance of CoCrMo alloys is primarily dependent on the nanometer thickness Cr$_2$O$_3$ oxide layer that covers the metal surface and prevents the reactive base metal from coming into contact with solution. The electrode potential plays the most important role in forming and thickening this oxide film. However, metal dissolution and repassivation reactions that can accelerate corrosion severity will happen when oxide films are disrupted and removed by mechanical events such as load and fretting involved in
mechanically assisted crevice corrosion (MACC). Increasing the fretting sliding frequency leads to increased removal rate of oxide films from metal surfaces and in the amount of electrochemical reactions that take place [16]. More cathodic drops in voltage will occur lowering the oxide stability and raising the corrosion rate. Thus, there is a significant need to understand how fretting corrosion currents vary with frequency.

There is a need to systematically explore the effect of frequency on the fretting behavior of metallic biomaterials from the prior literature. Most studies mainly focused on weight loss of the material that is caused by wear damage. In the study of Feng et.al, torsional fretting tests were performed on mild steel cylinders, and he found that wear rate decreases with increasing frequency from 1- 30 Hz [33]. Toth performed a similar research on steel from 0.01 to 60 Hz and indicated that less metal was release with higher frequency [34]. Schaaff et al. in his research of fretting tests between Ti6Al4V and CoCrMo alloys found there is a dependent relationship between metal wear rate and fretting frequency. The lower the frequency, the higher the wear rate [35]. Brown et al. performed cyclic fretting tests between CoCrMo head and Ti6Al4V stem from 1 to 10 Hz for hip implants. He reported higher corrosion current (maximum and minimum peak current, not a linear increase) were observed at higher frequency [15].

In this thesis, a series of tests with varying frequencies was carried out to study the effect of frequency on fretting behavior of CoCrMo coupled with CoCrMo alloys in phosphate buffered saline solution.
This thesis hypothesized that at a fixed load, displacement, and potential, an increase in the frequency will lead to a linear increase in the fretting current density because of a linear increase in the rate of oxide removal and reformation per second. However, at a specific frequency when abrasion rate equals or is greater than the oxide repassivation rate, the current density will not continue to linearly increase and will plateau.

5.2 Materials and Methods

The testing system was identical to the device used in chapter 4. CoCrMo (ASTM F-1537) pin and disk were polished to 600 grit and used as the testing couple. Samples were isolated with acrylic coating and fixed to an electrochemical cell. Fretting tests were conducted in phosphate buffered saline solution at a normal load of 10 N, a potential of -0.1 V vs Ag/AgCl reference electrode, and a displacement of around 10 microns at frequencies from 1 to 20 Hz. Frequency control was provided by a function generator (FG-8002, EZ Digital Co., Ltd). Potential was controlled potentiostatically (Solartron 1280C). At least 3 trials were performed per condition. Fretting lasted 150 seconds at each frequency, and the current relaxation after fretting stopped was 50 seconds.

Force and displacement data were monitored and captured by a custom-written LabVIEW program. Current data were collected by the potentiostat, and showed in CorrWare™.

Calculation of the average current at each frequency was conducted by a LabVIEW analysis
program written by Swaminathan [23]. Baseline current was subtracted from raw current data before the averaging process. Twelve hundred DVRT data points (2 seconds) at each frequency were collected and smoothed by making running average step every 10 points. Then, the difference between maximum and minimum value was taken as the displacement. Calculation of the coefficient of friction and the tangential force involved extracting the data of the sliding portion of the force plot at each frequency and averaging them from the saved file. One-way ANOVA was used to evaluate the correlations between frequency and the parameters involved in the fretting process.

Plots of variations of raw current data with increasing frequency, comparison of currents’ shape at different frequencies, averaged currents vs. sliding speed, averaged COF and tangential force vs. frequency, loops of work done per cycle and dissipated energy per cycle vs. frequency were generated and are presented.
5.3 Results

Typical raw fretting currents of CoCrMo coupled with CoCrMo alloy is presented with varying frequency from 1 to 20 Hz (Fig 17). Elevated currents from the baseline are identified as fretting currents. It is clear to see the fretting currents initially increase with increasing frequency, until about 15 to 20 Hz where there is no continued increase in the currents. The RMS current (Fig 18) also increases from low to intermediate sliding frequency while gradually decreasing at fast fretting rate (e.g. 1Hz: 1.01E-7 A, 4Hz: 1.54E-7 A, 18Hz: 0.54E-7 A). The current spikes at the initial and end of the fretting tests are due to the load applied to and removed from the oxide film on metal surface. From this figure there is also a slight decrease in baseline current density with increasing time and frequency.
Fig 17: Representative fretting currents from 1-20Hz at fixed load, displacement, and potential. Note: These data were collected with potentiostat (Solartron 1280C) at a very low sampling rate of 5 points/second, which resulted in the shape loss of the fretting currents. But the average currents calculated from these data should be close to the real values.

The deviation of the fretting currents from the mean current is calculated with the root mean square equation (RMS, Fig 18). The value increases from 1 Hz and reaches the peak at 4 Hz. Then it begins to decrease with increasing frequency from 4 to 20 Hz. This result also denotes that the current band is narrowed at high sliding frequency.
The plot of RMS variations with frequency. The equation used here is
\[ x_{RMS} = \sqrt{\frac{1}{n} [(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + \cdots + (x_n - \bar{x})^2]}, \]
where \( n \) is the number of the samples, and \( \bar{x} \) is the average current value (Mean and SD for \( n=3 \)).

Fig 18: The plot of RMS variations with frequency. The equation used here is
\[ x_{RMS} = \sqrt{\frac{1}{n} [(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + \cdots + (x_n - \bar{x})^2]}, \]
where \( n \) is the number of the samples, and \( \bar{x} \) is the average current value (Mean and SD for \( n=3 \)).

The fretting currents over 5 seconds of 1Hz, 5Hz, 10Hz, 15Hz and 20Hz were collected at a sampling rate of 600 points/sec and were compared with each other (Fig 19). Higher fretting currents are observed at higher frequency in the case of 1Hz, 5Hz, 10Hz and 15Hz, but the magnitude of the currents is almost identical between 15 Hz and 20Hz. While the average fretting currents continue to rise with frequency, the RMS currents decrease at the same time. It seems at high frequencies (15Hz, 20Hz) the fretting currents are unsteady. The reason might be the very limited time for current relaxation and the machine compliance which cannot provide stable fretting interface conditions at a very fast sliding speed.
Fig 19: The comparison of fretting currents for CoCrMo/CoCrMo at different frequencies. The applied load was 10 N and the displacement was about 10 μm. These data were collected at a high sampling rate to ensure the complete current shape.

Figure 20 displays the average fretting current vs. sliding speed of the CoCrMo/CoCrMo alloys combination. Sliding speed (determined from the measured displacement times the frequency) and fretting currents data were made an average from three different testing groups. From the plot, the current starts at 2.5E-9 A and linearly increases with a slope of 2.0E-9 A/sec/μm, until reaching a peak value 8.99E-7 A at a sliding speed of approximately 400 μm/sec. At this sliding speed, the current begins to plateau indicating that the maximum repassivation rate has been reached at this speed. This is considered as maximum oxide
film reformation rate of CoCrMo alloys under these experiment conditions, because there is no obvious growth in currents with increasing sliding speed above this point.

Fig 20: Average fretting current vs. sliding speed for CoCrMo/CoCrMo alloy couple. Mean/SD for n=3. The error bars in the X and Y direction are the variations in sliding distance and in average current, respectively.

The average coefficient of friction (COF) and tangential force variations vs. frequency for the same material combination ranged from 0.203 to 0.251, and 1.989 to 2.618 N respectively (Fig 21). The COF starts at 0.25 and slightly decreases from 1 to 6 Hz. It is close to 0.22 at the frequency of 7-12 Hz. In the range of higher frequency (13-20 Hz) a slight increase in the magnitude of COF from 0.22 to 0.24 was observed. Similar trends are seen for the plot of tangential force versus frequency. The Ft decreases from 2.55 to 2.20 N (1-6Hz), and keeps almost constant at 2.24N (7-12Hz), then gradually increases to 2.618N (13-20Hz).
Fig 21: The plot of average COF and tangential force vs. frequency (1-20Hz). No significant variations are observed in COF and Ft. Data were obtained and averaged from 3 different test groups. Mean and SD for n=3.

The COF and tangential force behavior from 1 to 3 Hz (Fig 22) demonstrates the plateau parts correlated with the sliding and the ‘V’ shape parts where sticking occurs. The plot of COF and tangential force exhibits similar phenomena where more sliding and sticking occurs per unit time with increasing frequency (e.g. the sliding/sticking time for 1 cycle at 1 Hz is about 2 times longer than the time at 2 Hz, and 3 times longer than the one at 3 Hz, etc.). However, the magnitude of the tangential force is relatively constant at the 3 different frequencies. One-way ANOVA analysis was performed to explore the significant influence of fretting frequency as a factor on the COF and tangential force. The results showed these two elements are not significantly affected by frequency.
Fig 22: Representative plots of tangential force and COF vs. time for 1, 2 and 3 Hz tests.

The horizontal portions are during sliding, and the transition portions and the ‘V’ shapes represent sticking at the end of the stroke where displacement reversal occurs. Note: with higher fretting frequency, less time is spent on sliding and sticking in one cycle (e.g. 1 Hz: 0.5s, 2 Hz: 0.25s, 3 Hz: 0.13s).
Dissipated energy is calculated with the following equation:

\[ U_f = \oint F_s \, d\delta \]

Where \( U_f \) is dissipated energy per cycle, \( F_s \) is the tangential force, \( \delta \) is the sliding displacement. This equation denotes that the work done is calculated by the addition of the energy dissipated on every small step of movement during one fretting cycle.

Based on the calculation results, there is no statistically significant variation in work done per cycle with varying frequency from 1 to 20 Hz (Fig 23).

Fig 23: The plot of average work done per cycle vs. frequency (1-20 Hz) calculated for CoCrMo/CoCrMo alloy from 3 different sample groups (Mean and SD for n=3). The applied load is 10 N and the displacement is approximately 10 \( \mu \)m.
The energy loops (Fig 24) are plotted as the tangential force vs. displacement. The height of the hysteresis loop is in accordance with the frictional force variations and the width is the effective displacement. The hysteresis area formed from the \( F_t \)-\( d \) curve is the dissipated energy per cycle.

![Energy Loops Diagram](image)

**Fig 24**: Typical energy loops for frequencies of 1-20 Hz (load: 10 N, displacement: 10 \( \mu \text{m} \)). The area of these loops represents the dissipated energy per cycle and keeps almost constant with varying frequency.
5.4 Discussion

Sliding speed plays a significant role in the fretting corrosion performance of CoCrMo-CoCrMo alloy couples. It determines how fast the metal oxide is removed from the metal surface. At low fretting speeds, oxide reformation rate is much higher than abrasion rate, so the overall rate of corrosion due to abrasion repassivation is dictated by the sliding speed. Increasing frequency can lead to a linear increase in the corrosion current since more film-based currents are generated with increased numbers of fretting cycles in a unit time. At some very high abrasion frequency when oxide abrasion rate is equal to or higher than the repassivation rate, no obvious current growth was observed and a plateau of current versus frequency was reached. The film current may not increase anymore as the maximum oxide reformation rate has been reached. An oscillating fretting current waveform can be observed within the range of low to mid frequencies, while at higher frequencies, the current values were narrowed closely to the average. The reason this occurs is that not enough time was allowed for the complete oxide reformation at very high sliding speeds. The exponential current decay during repassivation was stopped by successive fretting events which resulted in current growth once again. That is, the time constant, $\tau$, limits the ability of the current to oscillate at high frequencies. Increase in fretting frequency will make this phenomenon more obvious. And it may also lead to the decrease in wear rate as found in other literature [33-35] when there is reduced abrasion of oxide volume at high fretting speeds.
Based on the results of the one-way ANOVA tests, frequency did not significantly affect coefficient of friction (COF), tangential force or dissipated energy per cycle. The wear properties of the alloy mainly rely on the oxide film, which is influenced by contact load, potential and surface condition. All the experiments in this work were performed under the same potential, load and surface roughness. The COF is calculated from the normal load and tangential force. Under similar stress conditions, the COF will be relatively constant if tangential force is not significantly affected by frequency, or vice versa. Similarly, the work done per cycle is determined by effective displacement and tangential force. And at a fixed displacement, the energy will remain almost unchanged as well. All the elements studied in this work showed good correspondence to each other and they were all independent of the frequency variations. This phenomena indicates that the slip-stick mechanism at the contact interface wasn’t influenced or changed by increasing frequency. This may be because the fretting regime is mainly determined by contact load and surface roughness. Increase in normal load and surface roughness will magnify the friction factors which can turn the contact interface into a sticking interface.
5.5 Comparison between model and fretting current

In a paper published by Swaminathan and Dr. Gilbert in 2012 [23], another similar model was used to predict the average fretting current. The equation is presented in below form:

\[ I_{\text{film}} = \frac{\rho n F}{M_w} 2 \sqrt{\frac{F_N}{\pi H}} m(E - E_0) \frac{d\delta}{dt} \]

As stated in the previous chapter, \( \rho \) is the oxide density, \( n \) is the valence, \( M_w \) is the oxide molecular weight, \( F_N \) is the normal load, \( H \) is the hardness, \( m \) is the anodization rate, \( E \) is the potential during experiment, \( E_0 \) is the onset potential at which oxide film begins to form, \( d\delta/dt \) is the sliding speed which can be calculated as \( 2\delta v \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
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<tr>
<td>Hardness</td>
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<tr>
<td>Load</td>
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<td>10</td>
</tr>
<tr>
<td>( w )</td>
<td>cm</td>
<td>0.00798087</td>
</tr>
<tr>
<td>True contact area</td>
<td>cm²</td>
<td>0.000005</td>
</tr>
<tr>
<td>( h )</td>
<td>cm</td>
<td>0.00000018</td>
</tr>
<tr>
<td>( \Phi )</td>
<td>C/cm³</td>
<td>18477</td>
</tr>
<tr>
<td>Displacement</td>
<td>cm</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Table 3: Units and values of all the parameters used in above equation.

Based on the known parameters of CoCrMo alloys and experimental conditions (listed in Table 3), a plot of model film current versus sliding speed was generated and compared with experimental result as shown in figure 25. Note that the above current equation does not incorporate the effects of the time constant for current decay, which may lead to a slight
overestimate of the high speed current, as seen in Fig 25.

Fig 25: The data points with error bars are average fretting currents obtained from three different experimental groups. The solid linear line is based on model calculations. There is a strong correlation between experimental data and theory model data ($R^2 = 0.889$).
5.6 Conclusions

For CoCrMo/CoCrMo fretting interfaces in PBS solution at room temperature, the following conclusions can be drawn:

1. Increasing sliding speed leads to a linear increase in fretting corrosion currents up to an upper limit sliding speed.

2. The fretting current deviates from linearity at the point where the sliding speed equals the limiting oxide reformation rate at 400 μm/s.

3. The shape of the current versus time response is dependent on frequency. Complete current waveforms were observed at the low to mid frequency range, while at high frequencies the RMS current was diminished.

4. The variation in frequency does not significantly affect tangential force, coefficient of friction or dissipated energy per cycle, which indicates that frequency has a limited influence on changing the stick-slip contact behavior of the fretting interfaces.
6 Work Summary and future works

Mechanically assisted crevice corrosion continues to be the major problem leading to the corrosion of modular implants. It is a relative cyclic micro-motion process between two contact metal surfaces that involves both mechanical and electrochemical events.

This study set up the data collection system of the 2-D fretting test device which is an integration of the displacement sensors, National Instrument DAQ board and LabVIEW™ program. All of the important factors related to fretting system can be captured and saved using computer based data acquisition methods. A theoretical model to predict and simulate the fretting corrosion current behavior was established and verified. This model built up correlations between the instantaneous fretting currents with the normal load, material properties, relaxation time and sliding speed. The calculations of the model based on known parameters showed a good match with the experimental current. In this thesis, the current variations with increasing frequency/sliding speed of CoCrMo/CoCrMo alloy couples was explored systematically as well. Tests were carried out with varying frequency during fretting at a fixed potential, normal load and displacement. It was found that there is an upper limit point where fretting current stops linear growth. The abrasion speed at this point is considered as the maximum oxide reformation rate for CoCrMo alloys in PBS solution at room temperature. The current data from the frequency tests were also compared with another model proposed by our group in 2012 and the results showed a strong correlation.
Future work might investigate several aspects: The first one is the geometry. In this work the pin was perpendicular to the sample surface that leads to the simple tangential fretting. But in vivo the contact mechanism between real hip joints is different (e.g. rotational fretting and torsional fretting) which could change the corrosion behavior. Second, the potential drop was not considered because all the samples were potentiostatically held during the fretting tests, which is not true for metallic biomaterials that are freely corroded in human body. The cathodic shift is mainly affected by cathodic area, frequency and material properties. In the third place, the single asperity model was assumed and applied for the hard-on-hard contact situation. In fact, the true contact area could be larger than the model prediction as stated in section 2. To explore this problem. One can start fretting tests at a pin area smaller than \( \frac{F}{H} \). Then keep other conditions the same and observe the current behavior with the gradually increasing pin area. Based on the current prediction model and known parameters, one will be able to deduce a relationship between pin area and true contact area. Besides, the contact mechanisms between hard-on-soft and soft-on-soft materials need to be studied as well. The fourth is about the dissolution current. From Ambrose model the total current is consisted of the film current and the dissolution current. The model in this study mainly predicted the film current and the computations had strong correlations with the experimental results. And this is evidence that the film current is the dominant percentage of the total current. However, to estimate the dissolution current, we need to detect the amount of Co\(^{2+}\) and Cr\(^{3+}\) ions in solution after specific fretting cycles at different frequencies.
7 Appendix

Fig 1: The pin-on-disk testing device.

Fig 2: The 2-D fretting device
Fig 3: The LabVIEW program (DAQ and averaging)
Fig 4: The wire connections between displacement sensors and DAQ board.

Fig 5: Post-fretting impedance testing results at different potentials for CoCrMo alloy couples.
Fig 6: The raw average current collected during fretting tests.

<table>
<thead>
<tr>
<th>Material</th>
<th>CoCrMo alloy</th>
<th>Ti4Al6V alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main oxide constituents</td>
<td>CoO, Cr₂O₃, Mo₃</td>
<td>TiO₂</td>
</tr>
<tr>
<td>Ratio</td>
<td>65.8%:31.19%:3.01%</td>
<td>≥90%</td>
</tr>
<tr>
<td>Onset potential (E_{onset}, V)</td>
<td>-0.5</td>
<td>-1</td>
</tr>
<tr>
<td>Break down potential (E_{break down}, V)</td>
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<td>1</td>
</tr>
<tr>
<td>Charge per oxide volume (Φ, C/cm³)</td>
<td>18477</td>
<td>21498</td>
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<tr>
<td>Anodization rate (m, nm/V)</td>
<td>1.8-2</td>
<td>2</td>
</tr>
<tr>
<td>Hardness (H, GPa)</td>
<td>1.5-2</td>
<td>0.8-1</td>
</tr>
</tbody>
</table>

Table 1: The related parameters for the heredity model in this work.
8 Bibliography


9 Vita

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Education

Master of Science in Biomedical Engineering (August 2013-May 2016)
Syracuse University, College of Engineering and Computer Science, Syracuse, NY
GPA: 3.2

Bachelor of Science in Bioengineering (September 2009-June 2013)
China Pharmaceutical University, College of Life Science and Technology, Nanjing, China
GPA: 3.1

Summary of Skills

- Solid research background in metallic biomaterials, protein chemistry, and pharmacy
- Superior knowledge in National Instruments LabVIEW and related applications (Certified LabVIEW Associate Developer, 2-year experience)
- Well-versed with programming, machine designing, mechanical testing for different experiment aims.
- Good proficiency with AutoCAD (1-year experience), SolidWorks (1-year experience), SPSS and Microsoft Office Suite (Word, Excel, PowerPoint)
- Having good working knowledge with different sensors, and instrumentations
- Extensive experimental skills: SEM, electro-microscope, HPLC, microbial inspection, cell cultivation, patch clamp technique, protein purification, DNA extraction
- Highly skilled in data analysis and math computations
- Proved ability to work in a team environment and independently
- Excellent communication and writing skills
Professional Experience

Graduate Research Assistant
September 2014-present (1 year 7 months), Syracuse University Biomaterial Institute, Syracuse, NY
M.S. Thesis: Fretting corrosion of CoCrMo alloy biomaterials: Instrumentation development, heredity integral modeling and the effect of frequency
Research Advisor: Dr. Jeremy L. Gilbert

- Designed and built a novel mechanical testing device for exploring fretting corrosion behavior of metallic biomaterials through collaboration with colleagues
- Established data acquisition system of the device with NI-DAQ boards and sensors
- Wrote LabVIEW program to monitor, analyze, and collect important mechanical and electrochemical data associated with mechanically assisted corrosion through computer user interface
- Presented and validated a new theoretical model for corrosion current prediction during fretting with a mathematical method of Duhamel heredity integral
- Evaluated sliding speed/frequency effect on CoCrMo/CoCrMo alloy couples
- Designed experimental protocols to assess impedance behavior of CoCrMo and Ti6Al4V alloys under different potential conditions

Other Lab Internships
June 2014- August 2014 (3 months), Fudan University Medical Neurobiology Laboratory, Shanghai, China
- Explored the mechanism and effects of morphine on Hippocampal Neuron synaptic transmission
- Attached microelectrode to an intact cell and performed whole cell patch clamp to observe cell voltage changes

February 2013-May 2013 (3 months), Chinese Medicine Recourses Com. Ltd., Inner Mongolia, China
B.S. Thesis: Extraction and analysis of effective components contained in Chinese traditional medicine ‘nutrition for liver and kidney’
- Classified and purified traditional Chinese medicine
- Prepared staphylococcus aureus, escherichia coli and bacillus subtilis bacteria suspension for medicine bacteriological examination
- Analyzed effective components of traditional Chinese medicine with a method of HPLC.

April 2012-December 2012 (8 months), China Pharmaceutical University Biomedical Engineering Laboratory, Nanjing, China
- Prepared culture medium composed of DEME and 10% FBS, and cultured HepG2 tumor cells
- Analyzed the causes of bacteria pollution and explored methods for prevention and
improvement

- Synthesized and further characterized MPA-ICG-Der-02 probe and MPA-PEG-ICG-Der-02 probe
- Applied cell uptake study to test targeting-ability to MUC1 of the two probes
- Analyzed intracorporeal processes and tissued distribution of the two probes and performed tumor imaging by near infrared CCD imaging system

July 2011-September 2011 (2 month), China Pharmaceutical University Biochemistry Laboratory, Nanjing, China

- Maintained accurate records of chemical consumptions
- Learned various lab safety policies and requirements

Language

English
Chinese