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Frictional Voltammetry with Copper

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Abstract This paper presents an experimental study correlating frictional behavior with in situ voltammetry for a unidirectional sliding contact between a hemispherical tipped alumina probe and a flat rotating copper counterface (maximum Hertzian contact pressure of 68 MPa and sliding speed of 10 mm/s). The contact was immersed in an aqueous 0.1 M Na_2CO_3 solution (pH $\sim$11) where the copper counterface acted as the working electrode in a potentiostat controlled three-electrode cell; a coiled Pt wire was used as the counter electrode and a saturated calomel electrode (SCE) as the reference. Clear and reproducible trends were found between friction coefficient and published data suggesting the onset of particular redox reactions, graphically presented in a frictional voltammetry plot. At anodic potentials primarily associated with the formation of copper(I) oxide (Cu_2O) (V vs SCE ~ -0.25), the measured friction coefficient was in the range μ $\sim$0.4–0.5. At cathodic potentials primarily associated with the formation of CuO, $Cu(OH)_2$, and $CuCO_3$ (V vs SCE ~ -0.10), the friction coefficient transitions to the range μ $\sim$0.7–1.0. At sustained cathodic potentials associated with reduction of the native copper oxide, Cu_2O, (V vs SCE ~ -0.65), the friction coefficient is observed to fluctuate between μ $\sim$0.2 and 0.5, arguably a result of exposure of bare copper due to non-uniform reduction (fractional coverage) of Cu_2O.

Keywords Friction · Electrochemistry · Copper · Voltammetry

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1 Introduction

As described succinctly by Mischler in a review paper on experimental tribocorrosion [1], many interfaces exhibit a synergistic relationship between tribological and electrochemical responses defined by material composition and the environment to which they are exposed. For example, friction may provide sufficient thermal energy to not only affect the rate of oxidation but can also change the composition of the reacted species. One illustrative example is the oxidation of copper in air as a function of temperature: between room temperature and 150 °C, the primary oxidation product is the ubiquitous red hued cuprous oxide (Cu_2O), transitioning to black hued cupric oxide (CuO) above approximately 250 °C, a phenomenon experimentally verified by O'Reilly et al. [2] using X-ray diffraction (XRD). They also report a transition from a logarithmic rate of oxide formation in the lower temperature regime to a cubic rate in the higher temperature regime, measured via ellipsometry. Yet another notable example of a synergy between chemistry and tribology relating to copper is the exposure of copper to a high humidity carbon dioxide environment, a scenario typically encountered in experimental high current density sliding electrical contacts [3–6]. The pH of the condensed water films may be one of the agents aiding in the reduction of electrical contact resistance in these systems, where the partial pressure of carbon dioxide influences the pH of the water film as a result of carbon dioxide (CO_2) dissolution and its consequent reaction with water resulting in the formation of carbonic acid (H_2CO_3). A useful roadmap for understanding electrochemical oxidation/reduction was provided by Pourbaix [7] in his eponymous Pourbaix diagrams. For copper and water at room temperature, a change in pH from neutral to moderately acidic can shift the response from oxidation to reduction of Cu_2O when the surface is exposed to a driving electrochemical potential of a magnitude typically observed in high electrical current density sliding contacts, as shown by Boyer et al. [5]. Similarly, Dortwegt and Maughan [8] describe the role of pH on the corrosion rate of copper exposed to a solution of water and carbonic acid, where the continuously forming Cu_2O passivating film is dissolved as a result of the reduction of Cu_2O by hydronium ions (H_3O^+).

This article describes an experimental triboelectrochemical study of nominally pure polycrystalline copper as part of a continuing effort to understand the complex relationship between electrochemical corrosion and friction critical to the design of extreme current density copper sliding electrical contacts. The experimental procedure is similar to previous work by Mischler and Ponthiaux [9], though with some notable differences: a three-electrode cell was incorporated into a rotating pin-on-disk tribometer capable of relatively low force application and resolution (~1 N), minimizing the role of wear in the correlation of friction behavior to electrochemical oxidation/reduction of surface species by applying low contact pressures (nominally elastic contact). In an effort to broaden the impact of this study, a water-based solution of 0.1 M Na_2CO_3 (pH ~11–12) was chosen so as to parallel an experimental study of copper electrochemistry published by Pérez Sánchez et al. [10, 11] where voltammetry peak assignments were correlated to the reduction/oxidation of specific copper species. In a related experimental study by Kunze [12], they correlate potentiodynamic polarization curves to surface analysis using scanning tunneling microscopy (STM), and describe both peak assignments and the layered structure of copper oxide and copper hydroxide film growth as a function of electrical potential.

2 Experimental Setup—Frictional Voltammetry

A more detailed description of the force application and measurement method was provided by Argibay and Sawyer [13], including a description of the operational limits of the pin-on-disk tribometer implemented in this investigation. Figure 1 shows a photograph and corresponding line drawing of the experimental setup. The experimental setup incorporates a three-electrode cell consisting of a (1) copper disk (the working electrode), (2) coiled platinum wire (the counter electrode), and (3) saturated calomel (Hg_2Cl_2) electrode (the reference electrode). The sliding pair consisted of a non-porous high-alumina ceramic cylinder (95% alumina) with a 1.75-mm radius tip achieved by wet mechanical polishing first with increasingly finer silicon carbide paper followed by lapping with a 1 µm alumina slurry. A 20-mm diameter cylinder was machined from UNS C11000 copper. One of the flat ends of the cylinder was lapped to a mirror finish using the same procedure as described for the alumina pin, with an average roughness of Ra ~20 nm measured with a scanning white light interferometer. Both pin and disk were subsequently rinsed using acetone, methanol, and isopropyl alcohol (in that order) immediately prior to an experiment. The applied normal force was 400 µN with a sinusoidal fluctuation of ±50 µN due to runout and surface waviness of the substrate. Based on the nominal applied normal force, pin geometry, and typically reported bulk properties of sapphire and copper, the approximate value of the maximum Hertzian contact pressure (p_{max}) was calculated to be approximately 68 MPa, with a contact radius (a) 3.4 µm. A wear track radius of 7.0 mm and linear sliding speed of 10 mm/s were used (corresponding to 13.6 rpm and 4.4 s per revolution). A more detailed description of the friction testing apparatus may be

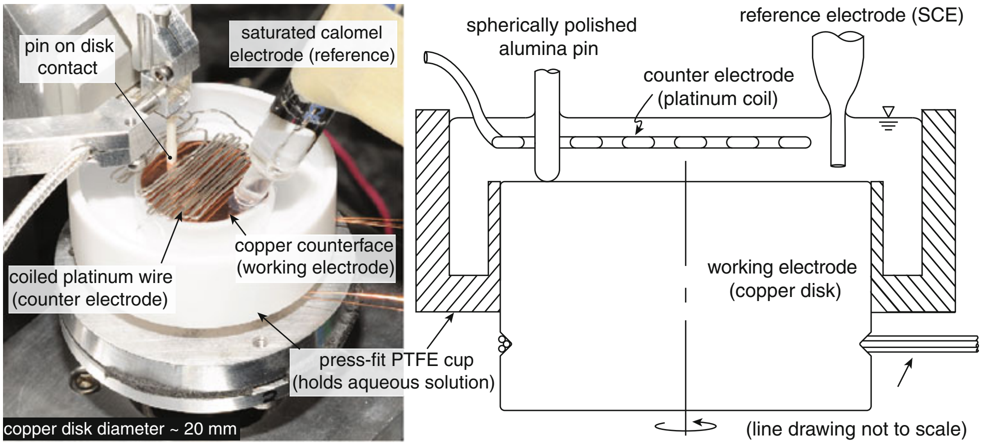

Fig. 1 (*Left*) A photographic view and (*right*) line drawing of the major components of the triboelectrochemical experimental apparatus: an alumina pin, a rotating copper disk (doubling as both countersurface and working electrode), a saturated calomel electrode (the reference electrode), a coiled platinum wire (the counter electrode), a PTFE cup press-fit onto the copper disk acting as the receptacle for the liquid medium of 0.1 M Na_2CO_3 water solution, and a three-wire copper sliding electrical contact below the polymer cup acting as an electrical connection between the working electrode and the potentiostat

found in Argibay and Sawyer [13]. A polytetrafluoroethylene (PTFE) liquid retention cup was press-fit onto the copper cylinder with a volume capacity for electrolyte of 12.5 mL. The electrolyte consisted of a 0.1 M solution of Na_2CO_3 (sodium carbonate) with a measured pH ~11–12. The electrical connection between the potentiostat and working electrode was achieved using a multi-copper wire bundle sliding on a V-notch groove machined onto the copper cylinder. The submerged portion of the platinum wire acting as counter electrode had a 0.50 mm diameter, 400 mm length, and an approximate nominal surface area of 628 mm^2. The nominal surface area of the platinum counter electrode was two times greater than that of the copper working electrode. A potentiostat (Gamry Instruments, Reference 600 model) was used to control the three-electrode cell. The potentiostat acquired data at a constant rate of 100 Hz and was used to apply both constant and cyclic voltages (saw tooth wave output varying at a rate of 10 mV/s).

3 Results and Discussion

Figure 2a presents a plot of friction coefficient (the leftmost ordinate) and electric potential between the copper disk and reference electrode (the rightmost ordinate) as a function of sliding distance/time (the abscissa). Figure 2b shows a plot of current density as a function of voltage (versus a saturated calomel electrode, SCE) corresponding to the period of cyclic voltammetry shown in Fig. 2a beginning at approximately 1,075 s and ending at 1,600 s. Current density is proportional to the chemical reaction rate at the interface, where each electron supplied to (or received from) the working electrode by the potentiostat represents the reduction (or oxidation) of a surface species. An example of a reaction taking place at a reducing potential is given in Eq. 1,

$$Cu_2O(s) + 2e^- + 2H^+ \longrightarrow 2Cu(s) + H_2O(aq) \qquad (1)$$

Here, two electrons are supplied by the potentiostat to the copper working electrode in the process of reducing copper(I) oxide. The driving electrochemical potential was initially set to −0.75 V to promote electrochemical reduction of copper(I) oxide, exposing bare copper. The reduction of the native copper oxide does not guarantee the continued exposure of bare copper as oxygen in the aqueous solution will continue to react with the bare copper to generate more copper oxide which can then be reduced in a continuing cyclic process. This behavior is manifested

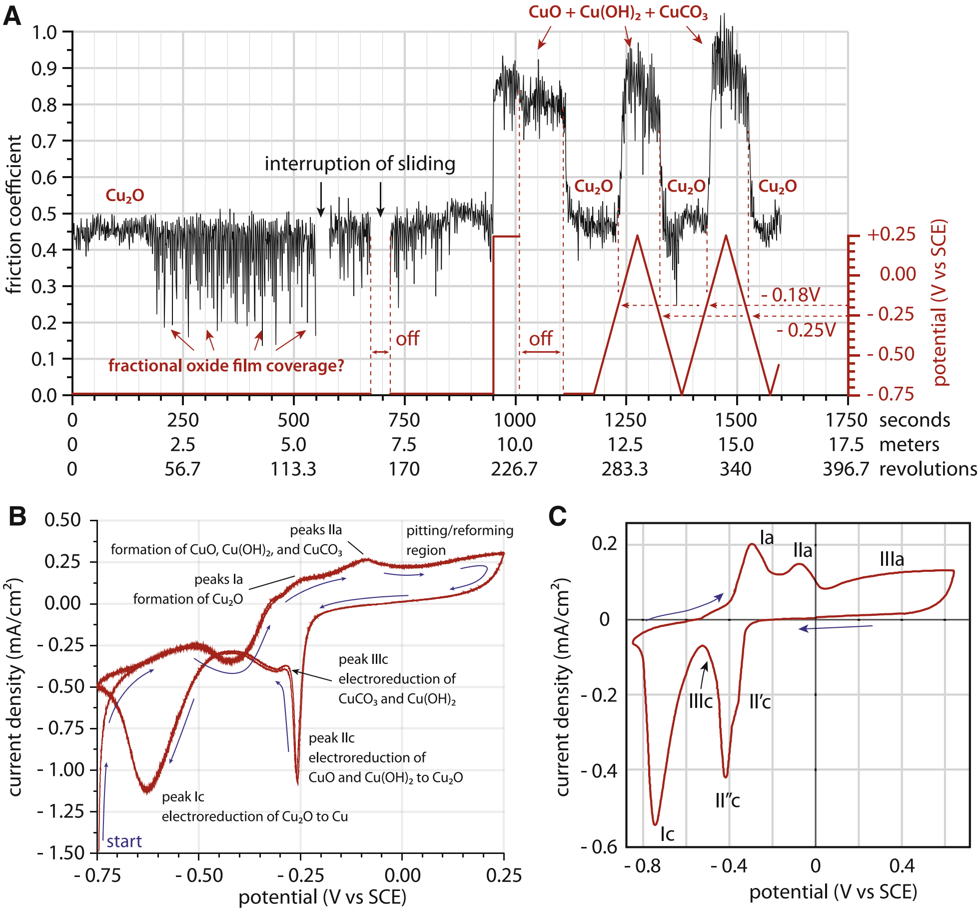

Fig. 2 Friction and voltammetry data from alumina on copper sliding experiments with in situ voltammetry. **a** Plot of friction coefficient vs sliding distance/time/revolutions, and an overlaid plot of the applied voltage (vs SCE) showing the friction response to the electrical potential driving electroformation/reduction of copper oxide and hydroxide species; **b** plot of cyclic voltammetry corresponding to the time interval between 1,175 and 1,600 s in (**a**); **c** plot of cyclic voltammetry data for a rotating copper disk electrode submerged in a 0.1 M sodium carbonate solution (pH 11.1 at 25 °C) adapted from Pérez Sánchez et al. [11]; peak assignments are based on *ex situ* electron microprobe spectroscopy

in the voltammetry measurements as a non-zero steady-state current density at a low enough constant reducing potential. In addition, the fraction of the copper electrode surface that constitutes the wear track is approximately 1% (assuming a nominal wear track width of 100 m) of the total area, so it is reasonable to assume that as a result of non-uniform reduction of the copper oxide film the effect will not cause an immediate change in friction behavior. During the period of constant reducing electrical potential (−0.75 V) with sliding the friction coefficient was in the range of 0.4–0.5. At a sliding distance of 2 m (approx. 34 revolutions or 150 s), the friction coefficient began to vary between 0.2 and 0.5. It is postulated that this behavior is the result of intermittent exposure of nascent copper along the wear track as the process of copper(I) oxide reduction begins to affect the area encompassing the wear track. When a positive potential of +0.25 V was applied the friction coefficient sharply increased to the range 0.7–0.9. After each change in prescribed steady-state potential from electroreducing to electroforming and from electroforming to electroreducing extremes there was a transient in current density lasting approximately 55 s (12 revolutions), after which current density was constant with no apparent fluctuation in current density with continued sliding (±0.01mA/cm^2). The current density (mA/cm^2) reached steady-state values of −0.40 and +0.02 mA/cm^2 at sustained potentials of 0.75 and +0.25 V, respectively. The period of cyclic voltammetry revealed a transition in friction from $\mu \sim 0.4$–0.5 to $\mu \sim 0.7$–1.0 that occurred at the onset of electroformation and electroreduction of the species CuO, Cu(OH)$_2$, and CuCO$_3$. Voltage was varied linearly and cyclically from −0.75 V, low enough to reduce the native copper oxide Cu$_2$O, to strongly electroforming (passivating) +0.25 V potentials at a constant rate of 10 mV/s. Figure 2c presents a reproduction of cyclic voltammetry data for copper in an equivalent electrochemical environment (0.1 M Na$_2$CO$_3$ at room temperature and a pH ∼11.1) published by Pérez Sánchez et al. [11]; these authors provide peak which are reproduced in this study, facilitating a comparison between friction response and the principal electrochemical oxidation/reduction products.

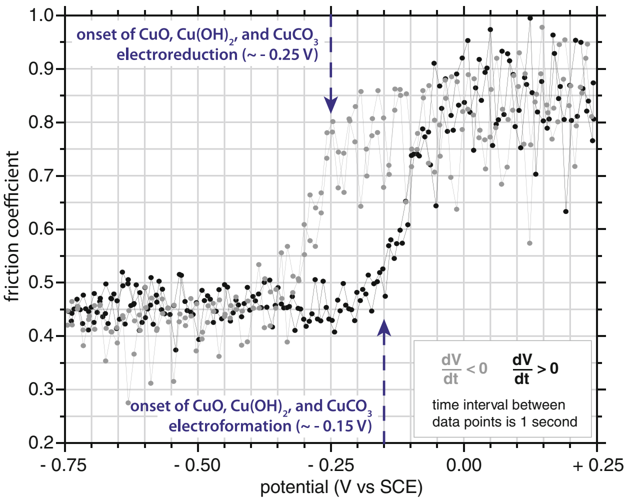

Fig. 3 Plot of friction coefficient as a function of prescribed potential (versus SCE); the temporal spacing between data points is approximately 1 s (approximately a 1/4 revolution of the rotating copper substrate) and the rate of change of voltage was 10 mV/s. Note the transition to relatively high friction coefficient at the onset of electroformation of cupric oxide (CuO), copper hydroxide (Cu(OH)$_2$), and copper carbonate (CuCO$_3$) [10, 11], in contrast to a transition to relatively lower friction at the onset of electroreduction of the same species; based on measured steady-state friction coefficients in the range of 0.4–0.5 and the relatively weak Ia peak it is possible that the complete reduction of cuprous oxide was not achieved

Figures 3 and 4, respectively, present plots of the friction coefficient response as a function of varying electrochemical potential and friction coefficient and current density as a function of time for the period of cyclic voltammetry. The data in Fig. 3 are temporally correlated; the spacing between data points corresponds to a 1 s time interval. The plots illustrate the friction response of the alumina/copper pair as a result of changing surface composition (analogous to the measured current density response). Along with the peak assignments from Figs. 2b, c, Fig. 3 highlights the transition from relatively high to low and low to high friction coefficient occurring at what is correlated primarily to the onset of electroformation or electroreduction of the copper species CuO, Cu(OH)$_2$ and CuCO$_3$. Lower friction corresponds to what was likely a predominately Cu$_2$O covered surface, while higher friction corresponds to a regime resulting in the electroformation of the species CuO, Cu(OH)$_2$, and CuCO$_3$. The plot of friction coefficient as a function of applied electric potential (voltage with respect to a reference electrode) is a useful and elegantly simple method of correlating frictional and electrochemical data. It should be possible to establish a correlation between the wear rate and oxidation/reduction rate of a prevalent species by establishing a steady-state current density at a given anodic potential and comparing to the measured current density with the addition of sliding contact. As the period of applied cathodic potential below about −0.6 V during cyclic voltammetry lasts less than about 60 s, it is reasonable to expect that the reduction of Cu$_2$O within the wear track area is not likely to dominate the friction response, as is evidenced by a lack of friction coefficient values below about 0.3–0.4, with the exception of the period coinciding with a spike in current density near the cathodic potential associated with electroreduction of Cu$_2$O at approx. 1,360 s (presented in Fig. 4). Previous work by the authors [13] suggests that a self-mated copper contact in a nominally non-oxidative environment exhibits friction coefficients on the order of $\mu \sim 0.3$, while the same contact in a highly oxidizing environment produces friction coefficients in the range of $\mu \sim 0.4$–0.8.

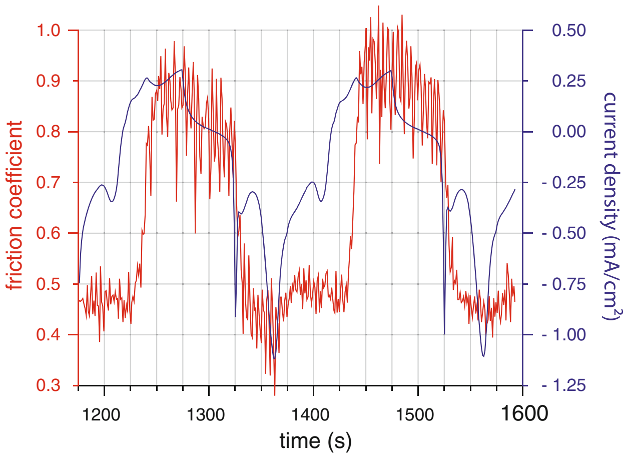

Fig. 4 A plot of friction coefficient (*left* ordinate) and current density (*right* ordinate) corresponding to the period of cyclic voltammetry presented in Fig. 2a. This plot illustrates the temporal lag between friction coefficient and current density, attributed to the time required for the redox reaction(s) on the copper disk surface to occur along the wear track. The current density is a measure of the average reaction rate taking place on the entire disk surface, so that the lag between friction coefficient and current density after an effectively instantaneous change in the electric field across the copper disk surface is indicative of a non-uniform redox reaction

It is important to note that surface reaction rates are dependent on the surface area of the working electrode. The surface area of the counter electrode should be greater than the area of the working electrode (typically double, as a conservative estimate) as it is undesirable for the counter electrode to be the limiting factor in an oxidation/reduction experiment. A second geometry effect to consider is the placement of the counter electrode. Charge transport through an electrolyte is effectively the result of diffusion of dissolved ionic species. A useful approximation is to consider the electrolyte as a homogeneously conductive medium in the bulk, so that ion diffusion will follow the shortest geometrical path when a DC voltage is used as the driving potential. The diffusion path of ions will coincide with the electric field lines through the electrolyte, from the counter electrode to the working electrode. If it is desirable for a reaction to take place symmetrically along, in this case, the surface of a copper disk then it is necessary to have the counter electrode evenly distributed and nominally equidistant from the working electrode. As an example of an asymmetric reaction, the authors attempted rapid oxidation of a copper disk where the platinum counter electrode was coiled along the perimeter of a copper disk and a gradual darkening of the disk from the periphery of the disk toward the center was observed. Similarly, the area of the disk being worn by the sliding contact is a small fraction of the total surface of the working electrode, complicating an in situ comparison between wear rate and reaction rates. In many instances, reaction products as a result of oxidation will be partially soluble (with the dissolution rate varying over time as the electrolyte becomes saturated), making it difficult or impractical to experimentally achieve a steady-state condition. Likewise, during a reduction experiment it is possible that continued redox of the nominally bare metal surface will continue as a result of dissolved oxygen in the electrolyte, observed as a non-zero steady-state current density. It may be possible to perform in situ quantitative comparisons of wear rate and redox rates if these complexities are taken into account.

4 Conclusions

Triboelectrochemical experiments were performed using a pin-on-disk tribometer with an alumina ceramic pin sliding against a copper substrate, where the contact was immersed in a potentiostat controlled three-electrode electrolytic cell. A correlation was found between friction response and the applied electrical potential. At electrical potentials primarily associated with the formation of copper(I) oxide (Cu_2O) (V vs SCE ~ -0.25), the measured friction coefficient was in the range $\mu \sim 0.4$–0.5. At electrical potentials primarily associated with the formation of CuO, $Cu(OH)_2$, and $CuCO_3$ (V vs SCE ~ -0.10), the friction coefficient transitions to the range $\mu \sim 0.7$–1.0. At sustained electrical potentials associated with reduction of the native copper oxide (Cu_2O, at V vs SCE ~ -0.65) ,the friction coefficient is observed to fluctuate between $\mu \sim 0.2$ and 0.5, arguably a result of partial exposure of bare copper due primarily to the non-uniform reduction (fractional coverage) of Cu_2O. The transition in friction behavior correlates well with potentiodynamic peak assignments identifying the onset of electroformation/electroreduction of various copper species. Plots of temporally synchronized measurements of friction coefficient, current density, and applied electrical potential were presented. Graphical presentation of frictional voltammetry data provides an insightful analytical tool for correlating transitions in tribological behavior regimes to redox products.

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