Electrochemical Techniques in Tribocorrosion. A New Mechano-Electrochemical Transfer Function.

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Introduction

Damages due to abrasion, wear, slurries, particles impact...in wet environment result from intricate reciprocal interactions between mechanical and electrochemical phenomena, defined as tribocorrosion. Electrochemical techniques have been applied increasingly in the last decade for understanding the mechanisms and predicting the rate of the material degradation in real-life conditions¹. That is facilitated by the improved control of the mechanical parameters, particularly by sophisticated setups known as tribometers, but is still dependent on quantitative interpretations of the so-called tribo-electrochemical data. A recent survey was published recently². This paper is aimed at presenting the background of tribo-electrochemistry and some recent developments based on a new mechano-electrochemical complex transfer function to extend the contribution of electrochemical impedances.

Mechanical Damages at the Interface and Electrochemistry: Model and Experimental

Any attempt to applying electrochemistry to tribo-corrosion studies is necessarily based on a model of the electrochemical alteration brought about to the interface by the direct interaction with a moving body. Since most practical cases are dealing with passive materials, the main available approaches focussed on the wear of the passive film and the subsequent electrochemical responses of the sample, a situation quite similar to relaxation at fresh surfaces created by particles impacts, plastic deformation (SCC)...But application of steady-state or quasi-steady state electrochemical techniques, *i.e.* the interpretation of the current response I(t) as function of electrochemical and tribological conditions requires a controlled rate and strengh of damaging as provided by various type of tribometers². The model used in this work for depicting the rubbing effect of a chemically inert abrasive counter-body on a passive surface and the subsequent electrochemical responses is shown in Figure 1. Figure 2 displays the experimental setup used in this work based on a pin-on-disc rotating tribometer.





Figure 1: Time-space representation of the surface rubbing by an abrasive body and of the components of the transient current density behind it^2 .

Figure 2 : potentiostatic control of a sample submitted to an abrasion along a circular track at a constant or time-dependant velocity v of the counterbody, under an applied normal force f_n .

For a constant velocity v of the sliding contact, the current measured at any time t=x/v is given by the integration, from the beginning of the experiment at t=0, of the current density over the track of width w:

$$I(t) = w.v.\int_{0}^{t} j(t)dt$$
 (1)

Equation 2 is of overwhelming relevance to tribo-electrochemistry since the velocity of abrasion v plays a role similar to a first-order reaction rate in the expression of the electrochemical current. Therefore a number of electrochemical techniques can be transposed by applying steady, transient or harmonic time-programs to v.

With the setup shown in figure 2, after one revolution of period T on a track of radius r, a steady-state current is obtained given by:

$$I(T) = \frac{w.2\pi r}{T} \int_{0}^{T} j(t)dt$$
(2)

Current-voltage and EIS techniques can then be applied since the components of the transient response j(t) are potential dependent. Promising results have been reported³ even though fully consistent models are not yet available. More advanced techniques such as noise analysis and local current or potential probes have also been considered². By superposing a sine wave modulation $|\Delta\Omega|e^{j\omega t}$ to the mean angular velocity $\Omega_0 = \frac{2\pi}{T}$ of the abrading body in figure 2 a sinusoidal response of the a.c. current (in potentiostatic mode) or of the a.c. potential (in galvanostatic mode) is expected. This is mathematically established as follows. In the general case where v is time-dependent Eq. (1) is recast as:

$$I(t) = w \int_0^t j(\tau) . v(t - \tau) d\tau$$
(3)

A sine wave modulation of the velocity v about its mean value v_o writes $v(t) = v_o + |\Delta v| e^{j\omega t}$ and by substitution in Eq. (3), one gets for a rotation of period T:

$$I(T,t) = w.r.(\Omega_0 \int_0^T j(\tau) d\tau + \int_0^T j(\tau) \left| \Delta \Omega \right| e^{j\omega(t-\tau)} d\tau$$
 (4)

In Eq.4 the first term is the mean current value I_o identical to Eq.2. The second term, the Fourier transform of j(t) bounded by the time window T, gives the a.c. current response to the modulation of Ω . The potentiostatic tribo-electrochemical admittance (TEA), is defined as:

$$\frac{\Delta I}{\Delta \Omega} = \frac{\int_{0}^{T} j(\tau) |\Delta \Omega| e^{j\omega(t-\tau)} d\tau}{|\Delta \Omega| e^{j\omega t}}$$
(5)

Results and Discussion

All the results given below were recorded in the following electrochemical conditions: AISI 316 L S.S., boric acid (1000 ppm of boron) and lithia (12 ppm of lithium). Passive range. +0.1V/ Ag/AgCl. A low-pass (1Hz) filtered sample of current response to the modulation of the rotation speed Ω of the abrading pin is shown in Figure 3. In spite of the large amplitude of modulation, $\Delta\Omega/\Omega$ =0.3, a fairly linear response is achieved; no harmonics of ω are detected in the FFT spectrum (Figure 4). The TEA defined in Eq. (5) is plotted in the Nyquist plane in Figure 5. A negative imaginary part is found as expected for a delayed current response to the rubbing velocity. The depressed shape is to be related to a non-exponential

shape of the current decay j(t). This agrees with the transient repassivation upon stopping the abrasion, correctly fitted by the sum of 2 exponentials as shown in Figure 6. In Figure 5, at 50RPM does correspond a modulus about twice as large as at 20RPM and an estimated apex frequency larger too in agreement with a higher mean dissolution activity of the track.



Conclusions and perspectives

Based on a widely accepted model of electrochemical response of a passivated surface to mechanical abrasion, a new mechano-electrochemical transfer function has been mathematically derived and actually measured on a passive stainless steel electrode. Preliminary results are perfectly consistent with expected behaviours in terms of amplitude and frequency distribution. Quantitative data processing of this impedance can now be implemented for gaining a deeper insight in the detailed mechanism of tribo-corrosion.

References

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