TRIBO-CORROSION OF METALLIC MATERIALS: ACTIVE WEAR TRACK CONCEPT AND ELECTROCHEMICAL TRANSIENTS FOR IN-SITU ANALYSIS OF MATERIAL DEGRADATION UNDER SLIDING

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SUMMARY
Corrosion-wear of passive materials in sliding contacts was analyzed recently based on an ‘active wear track area’ concept. In this paper, the outcome of such an approach is supported by electrochemical measurements for stainless steel sliding against corundum in a diluted sulfuric acid, under conditions where both corrosion and wear take place according the active wear track approach. Impedance and electrochemical noise in ball-on-disk sliding tests indicate the complex surface conditions of materials in sliding contacts.

Keywords: corrosion-wear, stainless steel, tribocorrosion, electrochemical measurements

1 INTRODUCTION
The upcoming limitations in the use of organic lubricants will result in a more intensive use of aqueous solutions. The presence of an electrically conductive solution in sliding contacts offers the opportunity to get in-situ information on material degradation processes through electrochemical measurements. Indeed, techniques like open circuit potential, impedance, and electrochemical noise measurements are quite sensitive to surface conditions and evolutions in surface conditions of materials immersed in electrolytes. Recent work by Mischler et al. [1], Drees et al. [2], and Ponthiaux et al. [3], has shown the possible implementation of such electrochemical measurements in wear tests.

In this paper, the corrosion-wear behavior of stainless steel disks sliding against corundum balls in sulfuric acid solutions is presented. Electrochemical measurements are reported for sliding tests performed under conditions where both corrosion and a mild oxidational wear are active as deduced from the active wear track concept developed recently by Garcia Diego et al. [4].

2 CORROSION-WEAR APPROACH BASED ON THE ACTIVE WEAR TRACK CONCEPT
The concept of active wear track area was recently proposed [4] as a way to approach corrosion-wear of passive materials under sliding contact conditions. The active wear track area is that part of the wear track that temporarily loses its passive character due to the mechanical interaction during sliding. That active wear track area was determined from repassivation kinetics measured on electrochemically activated materials by a potential pulse method, combined with anodic currents measured during sliding ball-on-disk tests.

For the case of stainless steel AISI 316 immersed in a 0.5 M H₂SO₄ solution and sliding against a corundum ball (diameter 10 mm), breakthrough of the natural oxide film (typically 2 to 5 nm thick) on stainless steel does not occur at normal loads below 2 N (Fig. 1, zone I). Material loss under such sliding conditions is mainly due to electrochemical dissolution of the native oxide film.

At normal loads between 2 and 12 N (Fig. 1, zone II), a combined corrosion-wear process takes place. The increase in material loss agrees well with Quinn’s mild oxidational wear mechanism [5]. That model states that an oxide film grows progressively in sliding contacts until it reaches a threshold thickness where the oxide film is removed mechanically from the contact area. Under such sliding conditions, the corrosion-wear of stainless steel results from a periodic delamination of the oxide film in part of the wear track, an electrochemical dissolution of active base material in the resulting active wear track area, and a progressive electrochemical repassivation of that active wear track area.

Finally, at loads above 12 N (Fig. 1, zone III), the corrosion-wear increases steeply due to additional degradation processes like abrasion and/or breakdown of more than just the oxide film.
The interesting outcome of the active wear track area concept is that ranges of normal loads were identified where different corrosion-wear processes are active. A validation of these corrosion-wear processes is presented hereafter based on electrochemical measurements for sliding contacts where the mild oxidation mechanism is active (zone II in Fig. 1).

3 OPEN CIRCUIT POTENTIAL AND IMPEDANCE MEASUREMENTS IN SLIDING CORROSION-WEAR

The open circuit potential and impedance of stainless steel were measured under unloaded and mechanically loaded conditions. Such electro-chemical data are presented here for the case of stainless steel AISI 316 (flat discs finished with emery paper #200) subjected to unidirectional sliding against corundum (balls with a diameter of 10 mm) in 0.5 M sulfuric acid. The normal load was varied between 5 N and 20 N. A three-electrode cell with a platinum counter electrode and a SCE reference electrode was used. Typical open circuit potentials recorded during corrosion-wear sliding tests are shown in Fig. 2.

Before starting the wear tests, the stainless steel disk was immersed during $10^4$ sec, until a stable passive surface state was obtained. When the corundum ball makes contact with the stainless steel disk, a rapid decrease of the open circuit potential takes place. On unloading, the open circuit potential of the stainless steel specimen increases quickly and the value of the initial open circuit potential is recovered.

Impedance spectra were recorded, in the $10^{-2}$ - $10^4$ Hz frequency range, at four different stages during this test, indicated in Fig. 2 as intervals 1 to 4. Two spectra were recorded when the material had a low open circuit potential (intervals 1 and 3), two others at high open circuit potential (intervals 2 and 4). These impedance spectra, schematically represented in Fig. 3, show large differences, not only between low and high open circuit potential, but also at a given open circuit potential value between measurements done before and after loading.

In all cases, a single semi-circle is obtained, corresponding to an equivalent circuit consisting of a parallel combination of the double layer capacity $C_{dl}$ in parallel with the transfer resistance $R_t$.

![Fig. 3: Impedance spectra recorded on stainless steel immersed in 0.5 M H$_2$SO$_4$ and rotated at 400 rpm. The corresponding time intervals where the spectra were recorded, are indicated in Fig. 2: (a): intervals 1 and 3. (b): intervals 2 and 4.](image)

The values of the transfer resistance are given in Table 1, together with the corresponding values of the active and passive areas of the disk, and values of specific transfer resistances (in $10^3$ ohms cm$^2$), calculated by considering the following assumptions:

- Before applying friction, the surface state is uniform, active (interval 1 in Fig. 2) or passive (interval 2).
- Under friction (interval 3), only area $S_a$ of the wear track is active. $S_a$ is calculated as explained in [4].
- The equivalent circuit is assumed to be a parallel
combination of two circuits ($C_{da} // R_{ta}$ and $C_{dp} // R_{tp}$), corresponding respectively to the impedance of the active wear track, and of the rest of the disk surface, in a passive state, as shown in Fig. 4. Hence, the overall transfer resistance $R_{t3}$ is given by the following expression:

$$\frac{1}{R_{t3}} = \frac{1}{R_{ta}} + \frac{1}{R_{tp}}$$

**Fig. 4: Equivalent circuit of the disk under friction**

- By the time sliding is interrupted and unloading took place (interval 4), the whole surface gets re-passivated.

<table>
<thead>
<tr>
<th>Interval</th>
<th>$R_t$ ($10^3$ ohms)</th>
<th>$S_a$ (cm$^2$)</th>
<th>$S - S_a$ (cm$^2$)</th>
<th>$R_{ta}$ ($10^3$ ohms cm$^2$)</th>
<th>$R_{tp}$ ($10^3$ ohms cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.17</td>
<td>28</td>
<td>0</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>290</td>
<td>0</td>
<td>28</td>
<td>8.1 x 10$^3$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.92</td>
<td>0.4</td>
<td>27.6</td>
<td>0.37</td>
<td>?</td>
</tr>
<tr>
<td>4</td>
<td>49</td>
<td>0</td>
<td>28</td>
<td>1.4 x 10$^3$</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Transfer resistance values and areas of active and passive surfaces on the disk, in intervals 1 to 4 of Fig. 2.

Under sliding conditions, the value of $R_{t3}$ is much smaller than the value $R_{t2}$, measured before loading, when the steel was passive. This can be explained by the fact that the transfer resistance of the active wear track, $R_{ta}$, is much smaller than $R_{tp}$, relative to the rest of the disk. In such conditions, $R_{ta}$ acts as a short-circuit and the measured transfer resistance $R_t$ is virtually equal to $R_{ta}$.

It must be noticed that, in spite of very close values of the open circuit potential in intervals 1 and 3, the transfer resistances $R_{ta}$ are different. Before passivation and loading (interval 1), the electrochemical state of the disk is assumed as uniform, and the open circuit potential is then the corrosion potential of active material. During sliding (interval 3), a non-uniform state is obtained, with galvanic coupling between the active wear track area and the rest of the disk surface that is in the passive state. As a result, the active wear track area is under anodic polarization, the dissolution rate is higher than at the corrosion potential, and the specific transfer resistance is smaller.

Finally, impedance spectra shown in Fig. 3b, indicate that the passive state after unloading (interval 4), is not restored to the level before loading (interval 2), since a smaller transfer resistance is obtained.

### 4 ELECTROCHEMICAL NOISE IN CORROSION-WEAR SLIDING TESTS

A modified tribo-electrochemical noise technique using only one working electrode and a microcathode [6] was used to measure simultaneously potential and current variations in the time domain on AISI 304 stainless steel immersed in 0.02 M Na$_3$PO$_4$ (pH 12.0). A bi-directional sliding test (fretting) was used with a corundum ball as counterbody. Tests were performed at a normal load of 5 N, corresponding to contact conditions in zone II in Fig. 1. At the start of fretting tests, a significant shift of the open circuit potential of stainless steel towards negative potentials was noticed, accompanied by a pronounced positive increase of the current (Fig. 5a). At the end of the fretting tests when the corundum counterbody is lifted away from the stainless steel surface, the potential of the working electrode returns very quickly to potential values noticed before the start of the fretting test, as does the current. This indicates that the passive film, which is removed from stainless steel during fretting test, is reformed once the mechanical interaction is interrupted. When zooming in on the potential and current values recorded during sliding, periodic variations of both current and potential were noticed (Fig. 5b).

![Fig. 5: Potential and current variations on AISI 304 sliding against corundum ball (diameter 10 mm) in 0.02 M Na$_3$PO$_4$. Fretting at 5 N normal load, 10 Hz, 200 µm displacement amplitude.](image-url)

These fluctuations of current and potential during the fretting tests consist of current increases accompanied by potential decreases. Experimental data reveals that processes of repassivation (= potential increases) and removal of the passive film (= current increases) on stainless steel continuously take place during the whole
fretting test. This indicates that the active wear track area is a quite dynamic concept and has to be considered as a dynamic state rather than a static one. Finally on unloading, the stainless steel quickly repassivates, and the original open circuit potential is restored.

5 CONCLUSIONS
Electrochemical measurements in sliding tests performed in an electrolyte offers the opportunity to gather in-situ information on the surface conditions of materials in sliding contacts. Tribo-electrochemical noise measurements and impedance clearly indicate that processes of passivation and depassivation take place in the wear track on stainless steel immersed in dilute sulfuric acid or sodium phosphate solutions, and sliding against corundum. The surface conditions evolve with time and the rate at which transitions from a more active to a more passive state occur, is not directly related to the frequency at which sliding contact events take place. Tribo-electrochemical noise measurements in combination with impedance measurements are thus most appropriate to investigate the surface conditions of materials in corrosion-wear sliding tests. The active wear track area in such tests must be considered as a dynamic concept evolving continuously or in a cyclic way.

6 ACKNOWLEDGMENTS
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7 REFERENCES