Application of the voltammetry of microparticles for characterizing wear debris produced in the sliding wear regimes of steels

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Abstract. Electrochemical characterization of wear metallic particles produced during pin-on-disc sliding tests is not conventionally carried out, possibly because of their small grain size, irregular shape and heterogeneous composition. The characterization of its reactivity can be important in the study of the relationship between oxidative and mechanical processes occurring at the sliding interfaces. Towards this goal, here we report the application of voltammetry of microparticles methodology to investigate the reactivity of sliding wear debris from steels. Low alloy (AISI 4140) and tool (AISI H13) steels were used as pin and disc materials, respectively, during the sliding wear tests. The variations of hardness of both sliding bodies resulted in the operation of mild and severe wear regimes. The worn surfaces were examined by stereoscopic and scanning electron microscopes. The wear particles were mechanically immobilized on the surface of a paraffin-impregnated graphite rod electrode and characterized by voltammetry in 0.1M HClO$_4$. The voltammograms reveal important information on oxidation stability of worn surfaces. Results were confirmed by electrochemical impedance spectroscopy measurements of both pin and disc surfaces for the mild and severe wear.

1. Introduction
The tribochemical reaction products of worn surfaces have been extensively investigated [1], but there are many unexplored aspects involved in the reactivity of wear debris surfaces. Indeed, it is claimed that the wear debris properties provide powerful information for mechanical diagnosis [2]. During the sliding wear of steels is widely recognized the action of two main wear regimes: mild and severe [3]. These wear regimes produce well-defined features in worn surfaces as much as in wear debris characteristics [3]. An understanding about the cause of the wear regimes operation is necessary, since many mechanisms have been proposed and there is no agreement about what the cause of wear regimes action [4]. Owing the mild wear regime involves generation of oxidized wear debris, its electrochemical characterization appears as a suitable tool to face new issues related to the mechanisms promoting mild and severe wear.
Voltammetry of microparticles (VMP) offers a powerful technique that can be applied to analysis of powdered solids [5]. The methodology is simple, easy, rapid and do not require sample preparation. It has been used for identification of iron oxide nanoparticle surfaces [6], determination of reactivity of sulfide minerals [7], analysis of metal alloys [8], among others [5]. Taking advantage of the fact that the surface compositions of the debris obtained in the mild and severe wear regimes are different, herein, VMP is applied to assess the reactivity and susceptibility to oxidation of wear debris surfaces.

2. Experimental

2.1. Sliding wear tests

The tested materials were AISI 4140 and AISI H13 steels, whose chemical compositions are given in Table 1. The pins were obtained from AISI 4140 steel screws of different mechanical strength levels. On the other hand, AISI H13 discs were thermal treated with quenching and tempering processes. Different discs hardness was obtained by varying the tempering temperature. Different conditions of hardness were used for both sliding bodies.

Table 1. Chemical composition of steels used in this study.

| Steel | Element %a |
|-------|------------|
|       | C  | Mn | P  | S  | Si | Cr | Mo | V  |
| 4140  | 0.35 | 0.91 | 0.010 | 0.007 | 0.150 | 0.25 | 0.069 | 0.002 |
| H13   | 0.51 | 0.55 | 0.017 | 0.005 | 0.976 | 4.98 | 1.210 | 0.900 |

a Determined by spark emission spectroscopy.

Sliding wear tests were performed in a pin-on-disc machine, where the pin was loaded with a normal load of 49N and under a sliding velocity of 0.1ms⁻¹. Two combinations of pin and disc hardness were analyzed. In the first one, a pin of 39 HRC and a disc of 35 HRC were used, which produced a severe wear regime. On the other hand, a disc of 50 HRC was used and the pin hardness was kept in 39 HRC, for which a mild wear regime was observed. Worn surfaces and wear debris produced with these conditions were selected to perform the electrochemical measurements. The characterization of worn surfaces was made by camera, stereoscopy and scanning electron microscopy (SEM) techniques.

2.2. Chemical, solutions and preparation of electrode

Reagents were of analytical grade and were used as received without further purification. All solutions were prepared with deionized water (18.2MΩcm). To prepare the paraffin impregnated graphite electrode (PIGE), a spectroscopic graphite rod was submerged in melted paraffin wax (mp 55°C) under negative atmospheric pressure for 2h to fill all the pores. The bar was removed from the melt chamber and the excess of paraffin was removed.

2.3. Electrochemical characterization of worn surfaces and wear debris

Electrochemistry was performed in a three-electrode electrochemical cell with an Ag|AgCl|3M KCl reference electrode, and a graphite rod auxiliary electrode using an Autolab PGSTAT302N potentiostat. The dissolved oxygen was removed from the electrolyte solutions prior to the measurements by bubbling nitrogen for 20min. In order to characterize the steel surfaces, the side of pin and part of the front side of disc were covered with a non-conductive coating, leaving uncovered a circular area (0.196cm²). Wear debris of steels were immobilized on the surface of the PIGE. Linear sweep voltammetry was conducted in 0.1M HClO₄ at a scan rate of 10mVs⁻¹. Potential sweeps were initiated in positive-going direction. Electrochemical impedance spectroscopy (EIS) measurements were performed potentiostatically at open-circuit potential using an ac amplitude of 10 mV in the frequency range 100kHz to 10mHz. EIS were performed for pin and disc surfaces in 3% NaCl. All experiments were done in triplicate.
3. Results and discussion

3.1. Sliding wear tests

As mentioned before, mild and severe wear regimes were obtained with the variation of the hardness of discs. Mild wear exhibits low wear rate and produce small, low quantity and oxidized wear debris, together with smooth, dark and oxidized worn surfaces. On the other hand, severe wear regime promotes bigger, high quantity and metallic wear debris and rougher, brighter and worn surfaces with plastic deformation traces.

Figure 1 shows the representative camera images of the discs which exhibited severe (figure 1(a)) and mild (figure 1(b)) wear regimes. There, it can be observed the wear tracks of the discs with a high and a low quantity of wear debris obtained in severe and mild wear condition, respectively. The corresponding stereoscopic images are shown in figure 2. In figure 2(a) is presented the worn surface image of a 39 HRC pin, which slid against the 35 HRC disc and evidenced the action of a severe wear regime. Meanwhile, a mild wear regime can be observed in the worn surface of 39 HRC pin (figure 2(b)) which slid against the 50 HRC disc. The mild wear regime is characterized by worn surfaces oxidation.

![Figure 1](image1.png)

**Figure 1.** Camera images of the 35 HRC disc with severe wear (a) and of the 50 HRC disc with mild wear (b). Wear debris is shown as bright coarse (a) and dark fine (b) powder.

![Figure 2](image2.png)

**Figure 2.** Stereoscope images of 39 HRC pin surfaces with severe (a) and mild (b) wear regimes.

The SEM images of worn surface for the pin exhibiting mild wear regime are shown in figure 3. A scratch texture is observed, with cracks and fissures parallel to the sliding direction. Backscattering electron image shows that iron oxides are uniformly cover the surface (bright contrast), which was confirmed by the EDS analysis (not shown).
Figure 3. SEM images of worn surface of 39 HRC pin with mild wear regime in both secondary (a) and backscattered (b) modes.

3.2. Electrochemical characterization of wear particles

Cyclic voltammetry of the pin and disc in pristine condition as well as wear debris particles is shown in figure 4. Both, pin and disc, show the typical behavior of the AISI 4140 and H13 steels, which are characterized by iron dissolution. High Cr-content in H13 steel (Table 1) cause a sudden drop in the anodic current at 0.07 V, which is ascribed to the passivation layer formed by chromium-bearing oxides and oxyhydroxides (figure 4(b)), as has been reported previously for stainless steel [9,10].

Figure 4. Linear sweep voltammetry (v=0.10Vs⁻¹) of pristine AISI a) 4140 pin and b) H13 disc, as well as c) mild and d) severe wear debris immobilized at the PIGE surface. Supporting electrolyte: 0.1MHClO₄.

The oxidation of wear debris exhibits two anodic peaks, $A_1$ peak is ascribed to reactivity of 4140 steel, while $A_2$ peak to H13 steel. The anodic $A_1$ peak of severe wear debris sample is more than twice of the current response of the mild wear debris, while the differences in intensity for the $A_2$ peak are much greater. The high reactivity of the severe wear debris is due to the fact that a new surface without passive layer is exposed as a result of plastic deformation. Besides, residual stress can facilitate surface oxidation where occurred microstructural changes by the plastic deformation such as strain-hardening. Hence, severe wear debris is more prone to oxidation. As voltammetry curve in figure 4(c) shows, mild wear debris rendered less susceptible to oxidation after oxidation wear, because the sliding induced the formation of iron oxides (figures 1 and 2), which confers greater stability.
The impedance behavior of worn disc surfaces for the severe and mild conditions is given in figure 5. Nyquist plots consist of a depressed semicircle (capacitive loop) followed by a small inductive loop at low frequencies. The frequency dispersion in the capacitive loop is associated to roughness and other inhomogeneities of the worn surfaces. Whereas the inductive loop is related to mechanism of iron dissolution, which involves two consecutive steps coupled by an adsorbed intermediate [11]. Larger capacitive loop is observed for the mild worn surface compared to the severe worn surface. This indicates a high charge transfer resistance of the former and hence greater stability. Thus, in spite of the composition of the particle debris could be slightly different respect to the worn surfaces, these results confirm those obtained by VMP.

Figure 5. Nyquist plots of impedance data measured on worn surfaces of AISI H13 disc, as indicated in the figure legends. Supporting electrolyte: 3% NaCl.

4. Conclusions
The possibility for reactivity characterization of wear debris on the paraffin-impregnated graphite electrode surface by voltammetry of microparticles is exploited. AISI 4140 and H13 steels were used to illustrate the methodology. Electrochemical behavior of wear debris determined during the voltammetry studies was confirmed by impedance spectroscopy measurements of worn disc surfaces. Our results are consistent with the type of operating wear mechanism. The use of this method can contribute to a better understanding of the wear mechanisms through access to reactivity of wear debris. Specifically, VMP together impedance measurements allowed confirming the effect of strain-hardening of steels on the oxidational wear mechanism, as previously suggested in literature [4]. Indeed, this type of information is not available by current methods.

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References
[1] Zum Gahr K-H 1987 Microstructure and wear of materials vol 10 (North Holland: Elsevier) p 378
[2] Hong W, Cai W, Wang S, Tomovic M M 2018 Chinese J. Aeronaut. 31 867
[3] Viafara C, Sinatora A 2009 Wear 267 425
[4] Viafara C, Sinatora A 2011 Wear 271 1689
[5] Grygar T, Marken F, Schröder U and Scholz F 2002 Collect. Czech. Chem. Commun. 67 163
[6] Gualdrón-Reyes A F, Meléndez A M, González I, Lartundo-Rojas L and Niño-Gómez M E 2018 J. Phys. Chem. C 122 297
[7] Meléndez A M, Arroyo R and González I 2010 Chem. Phys. Chem. 11 2879
[8] Scholz F, Müller W-D, Nitschke L, Rabi F, Livanova L, Fleischfresser C, Thierfelder Ch 1990 Fresen. J. Anal Chem. 338 37
[9] Olefjord I, Brox B and Jelvestam U 1985 J. Electrochem. Soc. 132 2854
[10] Zhang B, Wang J, Wu B, Guo X W, Wang Y J, Chen D, Zhang Y C, Du K, Oguzie E E, Ma X L 2018 Nat. Commun. 9 2559
[11] Keddam M 2012 Anodic dissolution. In: Corrosion mechanisms in theory and practice, 3rd ed. Marcus P (Ed.) (United States: CRC Press), chapter 3, p. 164.