Tribo-corrosion of materials: Interplay between chemical, electrochemical, and mechanical reactivity of surfaces

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Abstract

An attempt is made to link experimental potential variations noticed during tribo-corrosion tests performed at laboratory scale, with a well known mapping tool used in corrosion, namely Pourbaix diagrams also known as *E*–pH diagrams. Backgrounds of *E*–pH diagrams and electrochemical kinetics are briefly recalled. Some explanations and/or work hypotheses concerning the effect of test parameters on the potential variation during tribo-corrosion tests are presented. The complex interplay between mechanical, chemical, and electrochemical interactions during tribo-corrosion test is discussed. It demonstrates that further research towards the development of appropriate mapping tools for tribo-corrosion is most indicated.
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1. Introduction

In 1963 Pourbaix worked out in Belgium the concept of *E*–pH diagrams in his "*Atlas d' Equilibres Electrochimiques*" [1]. That 'avant la lettre' mapping has been an important contribution to the representation of the passive, active, and immune behaviour of metallic elements in aqueous solutions. The major limitation of such *E*–pH diagrams is that they do not provide information on the corrosion rate of materials. Indeed, no kinetic aspects of corrosion processes are included in the elaboration of such diagrams fully based on thermodynamics. Another limitation of such diagrams is that they cannot be elaborated for alloys like stainless steels, brasses, or highly alloyed steels, which are, far away, the most important engineering materials. Finally, relatively few information can be derived from such maps on the possible occurrence of different corrosion mechanisms, like stress corrosion cracking, crevice corrosion, pitting corrosion, or hydrogen embrittlement.

The development of impedance measurements by Epelboin and Keddam [2] in Paris in the 1960s was an important step forward towards a better understanding of the reactivity of surfaces in electrolytes. Electrochemical equivalent reaction schemes were developed to model the interface between materials and their liquid surrounding. Unfortunately such measurements do not provide systematically quantified corrosion rate. In the case of general corrosion, the correlation between polarisation resistance and corrosion current is convincing. On the contrary, in the case of galvanic or localized corrosion, such a correlation is problematic.

In the field of wear of materials, an interesting attempt to map wear was developed by Lim and Ashby [3] based on an analysis of contact temperature in dry sliding contacts. In diagrams where a dimensionless load is plotted against a dimensionless velocity, areas were identified where different wear processes are active, mainly related to oxidation and oxide behaviour. Unfortunately no predictive wear rates could be derived directly from such maps, and the number of systems for which such maps exist, is still limited. The best that could be achieved in such graphs was the drawing of lines of constant wear rate based on laboratory wear test data. Starting from a purely mechanical approach, an interesting modelling work was done a few years ago by the research groups conducted by Dang Van [4] and Vincent and co-workers [5] in France. So, e.g. in the case of fretting wear, a crack risk analysis fitting quite well with laboratory experience was developed by Fouvry [6]. Finally, a concept of wear rate per unit of dissipated energy was proposed by the

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research group conducted by Huq and Celis [7]. That concept results in a wear rate value valid over a broad range of wear test parameters.

In the field of tribo-corrosion, most research work done up to now was related to the investigation of the effect of the main process parameters on the rate of material degradation. Assi and Böhni [8] investigated in Switzerland the corrosion-wear synergism in sliding contacts while Stack's research group [9] in Great Britain was mainly dealing with the synergism in erosion–corrosion systems. The reproducibility of tribo-corrosion tests in sliding contacts was addressed in a round robin action conducted by Mischler and Ponthiaux [10]. The presence of an electrolyte in tribo-corrosion tests allows the in situ characterisation of the surface reactivity of materials by either friction or electrochemical measurements. Potentiostatic measurements were performed by Landolt et al. [11], while impedance measurements were done by Wenger and co-workers [12], and recently the use of microelectrodes was proposed by Wu and Celis [13]. Such microelectrodes allow combined current and potential measurements at nearly open circuit potential. Recently, a model was developed by Stemp et al. [14]. Unfortunately all this development work has not yet resulted in a mapping of tribo-corrosion processes.

In this paper, experimental data on potential variations recorded during sliding tests performed in electrolytes are presented. These data are analysed in terms of possible effects of normal load and other wear test parameters, on E–pH diagrams.

2. Experimental

The experimental data reported are related to sliding tests performed in water-based electrolytes, namely artificial seawater, 0.02 M Na_3PO_4 or 0.5 M H_2SO_4. Two types of sliding tests were performed, namely uni-directional pin-on-flat tests and bi-directional ball-on-flat tests. The main test parameters are mentioned in the captions of the figures. Materials used as disk material are stainless steel 304L, 316L, and 321, as well as Stellite 6. The pin and ball counter bodies were made out of corundum. All materials were degreased before starting up sliding tests. Details on the experimental test set ups used for uni-directional sliding can be found in [15], for bi-directional ones in [16].

3. Effect of load and sliding speed on E–pH diagrams

On immersion of a sliding contact in an electrolyte, the potential of electrical conductive materials constituting that sliding contact can be measured. A lowering of the open circuit potential is frequently experienced during sliding, mainly on passivating materials. That effect is illustrated in Fig. 1 for the case of stainless steel immersed in seawater and slit against corundum. During such uni-directional sliding tests, the normal load was increased stepwise as well as the sliding speed. A lowering of the open circuit potential at increasing normal load and/or sliding velocity is evident. On performing similar experiments on non-passivating materials like copper, the variation of the amplitude
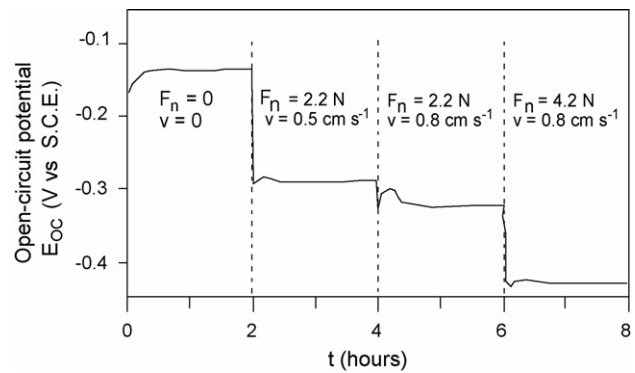

Fig. 1. Dependence of the open circuit potential of stainless steel 316L tested in a pin-on-disk uni-directional sliding set up immersed in seawater. Diameter of the stainless steel disk 2.5 cm, diameter of the spherical end of the corundum pin 1.6 cm. Normal load and sliding speed of the pin are indicated in the figure.

of the open circuit potential is in that case much more limited. This indicates that the potential drop may not be attributed solely to a mechanical degradation of the passive surface layer. Other possible interfering factors can be varying hydrodynamics and material transformations due to elastic or plastic deformation. Backgrounds on the open circuit potential of metals can provide a first explanation for the potential variations noticed on materials in sliding contacts operated under increasing loads and immersed in electrolytes.

An E–pH diagram for a metal is schematically represented in Fig. 2. Areas of immunity where the metal cannot corrode, of corrosion where the metal dissolves, and of passivation where metal oxides or hydroxides are the stable compounds, can be distinguished. Lines separating these areas are calculated from thermodynamic data. These lines represent the potential–pH conditions where equilibrium exists between two given species. The mathematical expression of such lines is known as Nernst equations:

$$E = E^0 + \left(\frac{RT}{nF} \right) \ln([Ox]/[Red]) \tag{1}$$
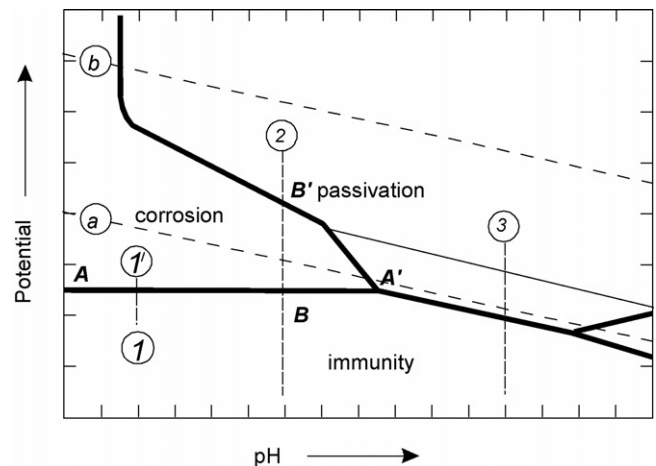

Fig. 2. Schematic E–pH diagram for iron. Lines 'a' and 'b' indicate the boundary of the stability of water. Dotted lines 1–3 are discussed in the text.