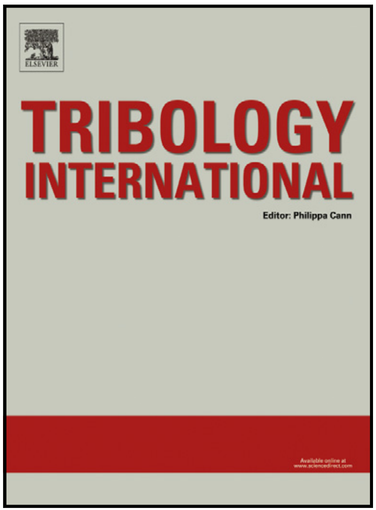

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The relevance of Cathode kinetics to the interpretation of Triboelectrochemical corrosion.

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keywords: tribocorrosion, triboelectrochemistry, dynamic modeling, corrosive wear, wear accelerated corrosion, galvanic coupling, electrochemical techniques, CoCrMo, titanium, zirconium

Abstract

Cathode properties were shown to indirectly impact the magnitude of the anodic current density, i_a, of the wear track under reciprocating wear. The direct measurement of i_a for CoCrMo, Zircaloy and Ti tribocorrosion was conducted on surface insulated samples by using novel techniques such as hetero-cathode tribocorrosion (HCT) and insulated electrode triboelectrochemistry (IET) under applied potential. The i_a measured for the above systems exhibited a strong correlation with potential, which was different in each system. The variation of i_a with time during sliding experiments at OCP, understood to affect the wear rates (i.e. Wear Accelerated Corrosion) observed under tribocorrosion, was experimentally quantified and proven to be linked to the cathode properties. Marked deviations in OCP behavior were recorded by changing the cathodes utilized and the subsequent cathode effect on the wear mechanism was demonstrated via HCT experiments by substituting different size hetero-cathodes. Data derived from IET and HCT also resulted in the predictive numerical modeling of several tribocorrosion experiments performed on CoCrMo and Zircaloy, by accurately accounting for the interdependencies between cathode kinetics, i_a and the OCP.

1. Introduction

Passive metals owe their corrosion resistance to a dense oxide film of a few nanometers on their surface **[1].** Engineering materials such as stainless steels, Ti alloys, CoCr alloys, NiCr alloys, etc., are passive in a wide range of electrolytes under equilibrium conditions. These materials are usually applied in corrosive environments and their corrosion resistance is an important parameter for their successful operation. When mechanical loading can act simultaneously to corrosion, this degradation process is known as tribocorrosion and its extent generally depends on the prevailing electrochemical conditions **[1,2].** Tribocorrosion is a material deterioration or transformation resulting from simultaneous action of wear and corrosion. The consequences of coupling wear and corrosion are complex. The knowledge of the tribological behaviour in the absence of corrosive medium and that of the electrochemical behavior in absence of wear is not sufficient to predict the tribocorrosion behaviour. There is synergy between wear and corrosion. Reviews are available on these different tribocorrosion situations **[3–7].**

When passive materials are subjected to sliding in equilibrium conditions, worn areas are formed where the passive layer is removed and leaving the unworn areas passive. The interaction between mechanical and chemical factors governing tribocorrosion is still little understood and there is a need for more insight into the mechanisms in order to identify critical mechanical, material and chemical factors which contribute to this degradation. Prerequisite for tribocorrosion experiments is therefore the possibility to control not only the mechanical but also the chemical test conditions. In aqueous ionic electrolytes, electrochemical techniques offer the possibility to control in-situ and in real time the surface reactivity of metals and other electronically conductive materials. However, the interpretation of electrochemical results obtained in tribocorrosion tests is much more delicate than in the case of pure corrosion. A tribological experiment carried out in an ionic conductor under controlled electrochemical conditions is defined as a triboelectrochemical experiment **[1]**

2. Fundamental background

An effort to emulate practical tribocorrosion processes in the laboratory is done by rubbing the passive metal against an inert counterpiece while simultaneously measuring electrochemical potential or current parameters. Tribocorrosion testing at open circuit potential (OCP) of passive metals results in a shift of the potential from an initial equilibrium to lower values (cathodic shift). This drop in potential is a result of the galvanic coupling established between the active worn area and the often much larger passive unworn area **[1]**, since the wear track is in an active state. In current literature, OCP during tribocorrosion is mainly measured over the whole surface and consists of the mixed potential of both worn (active) and unworn (passive) areas. Therefore, the measured potential is considered neither that of the worn nor of the unworn area, but a coupling potential between these areas **[8-10].** However, this aspect has been clarified in recent publications **[11,12]** via a galvanic coupling model, where the OCP experimental value was shown to coincide with the potential established on the cathode of the sample subjected to tribocorrosion. The measured potential continuously adapts to changing active-to-passive surface area ratios during tribocorrosion and evaluation of the corrosion kinetics or mechanisms of the process hence becomes extremely complex, especially in view of the fact that the equilibrium potential changes during the experiment, which can influence the wear accelerated corrosion in the worn regions or be a source of experimental ambiguity if the passive cathode area is chemically unstable during tribocorrosion.

The drop in potential during sliding in tribocorrosion tests has been extensively reported for different electrolyte-passive material systems **[1, 10-12, 13].** Since the system experiences a total net current of zero under tribcorrosion, the internal galvanic current is not accessible experimentally through the conventional triboelectrochemical set-up, thus inhibiting the direct quantification of the wear accelerated corrosion expected