



## Modeling tribocorrosion of passive metals – A review

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### ABSTRACT

Tribocorrosion is a material degradation phenomenon resulting from interactive effects between wear and corrosion. It is commonly found in engineering applications (e.g. biomedical implants and marine equipment) which involve relative motion of contacting metals in a corrosive environment. In this study, models describing tribocorrosion of passive metals in sliding contacts were reviewed. Different categories of models (two-body or three-body contact models, lubricated tribocorrosion model, empirical models, multi-degradation models) were found in the literature. Through the identification of relevant chemo-mechanical degradation mechanisms, robust analytical expressions accurately predicting the overall material loss in tribocorrosion have been developed. Numerical methods have been used to describe time dependent transitions in tribocorrosion. Possibilities and limits of the proposed models in the literature as well as future trends are discussed in this review.

### 1. Introduction

Nearly all metals react chemically with the environment. In contact with air or water, passive metals form a thin surface oxide film (passivation) which protects the underneath metal from further corrosion. Most of the alloys used in marine, biomedical devices and chemical reactors owe their good corrosion resistance to passivity [1–5]. On the other hand, these metals are usually under mechanical loading which can deteriorate these protective films. Despite the thinness of these films (in the range from nm to  $\mu\text{m}$ ), it has been found that they do not only affect the corrosion behavior but also the mechanical wear properties [6–10]. Tribocorrosion studies the overall material loss which encompasses not only the conventional detachment of metallic particles as found in wear but also the detachment of metal oxide films and the accelerated emission of metal ions as the consequence of oxide film abrasion.

The complexity of tribocorrosion of passive metals arises from the interaction between base metal deterioration and the oxidation of the metal. The total degradation due to the tribocorrosion of passive metals was found to be not simply the sum of corrosion of the metal without rubbing and wear in absence of corrosion [1]. Indeed, the continuous cycle of passive film removal followed by the spontaneous re-growth of the film usually accelerates significantly corrosion. On the other hand, surface chemical reactions can influence tribological phenomena such as work hardening and/or metallurgical transformations in the near contact surface zone [6,7,11–13] and thus wear. Adsorbed layers can act as boundary lubricants and therefore modify the stress field acting

on the wearing material [10,14–16]. In lubricated condition, hydrodynamic lubricating films formed by the corrosive fluid can provide a load bearing effect to reduce the actual load transmitted through the contacting asperities and consequently wear [17,18]. Detached particles may remain trapped in the contact (forming the so-called third bodies) where they modify the stress field by enhancing the local contact pressure in the case of loose particles or distributing more uniformly the load in the case of particles agglomerating in form of films [1,10,19].

Due to the high complexity of the tribocorrosion system of passive metals, tribocorrosion modeling taking into account all the affecting factors is elusive. However, great progress has been made in the last decades in better understanding the tribocorrosion mechanisms and integrating different factors into basic tribocorrosion models. The achievement of the progress is largely ascribed to the novel experimental methods integrating electrochemical techniques into conventional tribological measurements [1,6–10,20,21]. These methods allow one to precisely control the electrochemical condition (e.g. potential) and to distinguish chemical wear (the amount of metal released during rubbing in oxidized form) and mechanical wear (the amount of released metallic particles) in the total material degradation. As an example, Guadalupe Maldonado et al. [8] used this method to systematically study the effect of electrode potential (driving force for metal corrosion) on the tribocorrosion of a CoCrMo alloy in 0.5 M sulfuric acid solution. As shown in Fig. 1, the applied potential clearly influenced the chemical wear in the passive domain. More interestingly, the mechanical wear was significantly promoted when moving from a cathodic

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## Nomenclature

$A_a$	anodic surface area (mm <sup>2</sup> )
$A_{average}$	average area of the asperity contacts (mm <sup>2</sup> )
$A_c$	cathodic surface area (mm <sup>2</sup> )
$a_c$	constant
$A_p$	arrhenius constant for parabolic oxidation
$A_{real}$	real contact area (mm <sup>2</sup> )
$b$	proportionality factor
$b_c$	constant
BEM	boundary element method
$C$	number of cycles
$d$	diameter of asperities (mm)
$E'$	effective Young's modulus (GPa)
$E_0$	electric field in the film
$E_{applied}$	applied potential (V)
$E_c$	actual electrode potential in galvanic coupling (V)
$E_{corr}$	corrosion potential (V)
$F$	Faraday's constant (C/mol)
$f$	cycle frequency (1/s)
FEM	finite element method
$F_n$	normal force (N)
$F_{eff}$	effect normal force carried by asperities (N)
$f_{ox}$	fraction of oxygen in the oxide film
$g^+$	generalized charge transfer coefficient
$H$	surface hardness (HV)
$h_{min}$	minimum film thickness (nm)
$I$	excess current (mA)
$i_a$	anodic current density (mA/cm <sup>2</sup> )
$i_c$	cathodic current density (mA/mm <sup>2</sup> )
$i_{growth}$	film growth current density (mA/mm <sup>2</sup> )
$i_{growth}^0$	long term film growth current density (mA/mm <sup>2</sup> )
$k_1$ to $k_{11}$	proportionality factors or constants
$k_m$	proportionality factor for mechanical wear
$k_c$	proportionality factor for chemical wear
$k_{mech}$	proportionality factor for mechanical wear
$k_{chem}$	proportionality factor for chemical wear
$k_{wt}$	constant
$L$	stroke length (mm)

$l$	distance of a wearing contact (mm)
$M$	molecular mass (g/mol)
MSE	mercury/mercurous sulfate electrode
$n$	number of asperities
OCP	open circuit potential (V)
$P_m$	yield pressure (MPa)
$Q$	activation energy for parabolic oxidation (kJ/mol)
$Q_p$	passivation charge density (mC/cm <sup>2</sup> )
$R$	gas constant
$R'$	effective radius of curvature (mm)
$R_g$	growth fraction
$R_\Omega$	ohmic resistance in the electrolyte ( $\Omega$ )
$S$	total wear–corrosion synergy
$s$	distance between two successive asperities (mm)
$S'$	increase of wear due to corrosion (mm <sup>3</sup> )
SHE	standard hydrogen electrode
$S''$	increase of corrosion due to wear (mm <sup>3</sup> )
$T$	temperature in the contact ( $^{\circ}$ C)
$t$	sliding time (s)
$u$	entraining velocity (mm/s)
$V$	wear volume (mm <sup>3</sup> )
$V_{chem}$	chemical wear rate (mm <sup>3</sup> /s)
$V_{mech}$	mechanical wear rate (mm <sup>3</sup> /s)
$v_s$	sliding velocity (mm/s)
$V_{tot}$	total wear rate (mm <sup>3</sup> /s)
$W_c$	corrosion in absence of wear (mm <sup>3</sup> or g)
$W_{cfw}$	fatigue wear due to corrosion (mm <sup>3</sup> or g)
$W_{chem}$	chemical wear (mm <sup>3</sup> or g)
$W_{fw}$	fatigue wear in absence of corrosion (mm <sup>3</sup> or g)
$W_{mech}$	mechanical wear (mm <sup>3</sup> or g)
$W_{running-in}$	running-in wear (mm <sup>3</sup> or g)
$W_{tot}$	total wear (mm <sup>3</sup> or g)
$W_w$	wear in absence of corrosion (mm <sup>3</sup> or g)
$W_{wc}$	wear accelerated corrosion (mm <sup>3</sup> or g)
$z$	oxidation valence
$\xi$	oxide film thickness (nm)
$\eta$	viscosity of solution (Pa·s)
$\rho$	density (g/cm <sup>3</sup> )
$\rho_{ox}$	oxide density (g/cm <sup>3</sup> )

potential to a passive one. Without such an experimental method, this phenomenon could hardly be illustrated.

The aim of this study is to review the tribocorrosion models of passive metals so far published in the literature. The main focus is on sliding conditions where metals slide against a solid counter body. Erosion-corrosion situations, where fluid or solid particles suspended in

the fluid hit the metallic sample are not considered here as they imply different mechanisms and parameters. This review of the tribocorrosion models starts from a simpler two-body contact situation in which many models have been developed (Section 2) based on plastic deformation (Section 2.1–2.4) or fatigue failure mechanism (Section 2.5) mediated wear. Two body numerical models are discussed in Section 2.6. Then, a more complicated model is reviewed which integrates lubrication effect into two-body contact based models (Section 3). Models considering third body contact are reviewed in Section 4. An empirical approach from the literature is described in Section 5. Finally, a multi-degradation tribocorrosion model is presented (Section 6). The reviewed models are critically assessed in their possibilities and limitations and ways for further improvement are explored.

## 2. Two-body contact based models

In 1954, Uhlig [22] postulated that a chemical factor and a mechanical factor were involved in the mechanism of fretting corrosion. Based on this hypothesis, two fundamental mechanisms contribute to material removal from rubbing surfaces: emission of base material particles detached by mechanical action (mechanical wear) and emission of chemically reacted base material (chemical wear). As shown in Fig. 2, rubbing can remove the passive film and thus induce much higher corrosion by exposing the bare metal to the corrosive medium.

In the case of metals, particle detachment results from material

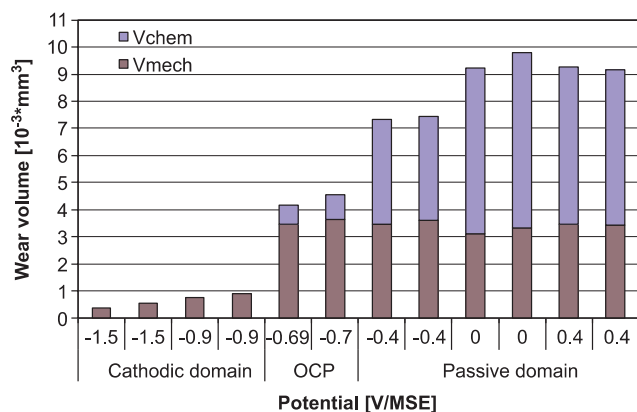


Fig. 1. Variation of chemical and mechanical wear of a CoCrMo alloy in 0.5 M H<sub>2</sub>SO<sub>4</sub> with increasing applied potential (Figure reprinted from [8] with permission from Elsevier 2013).

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