ASPECT REGARDING MATERIAL FAILURE DUE TO TRIBOCORROSION

L. Palaghian and M. Bucsa

University “Dunărea de Jos”, Galati, Romania, liviu.palaghian@ugal.ro

ABSTRACT

This paper presents processes that appear in the superficial layer subjected to wear in corrosive environment. These processes are due to electro-chemical phenomenon and are correlated with the mechanical damage evolution. There is presented a model for wear processes prediction.

KEYWORDS: wear, corrosive environment, and prediction algorithm.

1. Introduction

Due to relative movement between two surfaces in contact, physical processes appear as well as mechanical and chemical ones in the superficial layers. As the base material has different properties the superficial layers will have a great influence on wear processes in corrosive environment.

Corrosive wear occurs when there is a combination of a wear situation (abrasive or adhesive) and a corrosive environment. The rate of material loss can be very high. Many times higher than in the situations when the individual processes of wear or corrosion are acting alone. The explanation is that corrosion products are easily removed by wear and continually reveal fresh metal beneath, which in its turn will corrode quickly. Likewise, stable oxide films that normally would limit corrosion (in the absence of wear) are instantly removed. It is not unusual to find the situation presented in Figure 1.

2. The electro-chemical mechanism of crack evolution

Knowing that, in corrosion developing period of crack, there is manifested a crack tip blunting phenomenon, due to plastic strain, and a corrosion process of the crack flanks, it is possible to establish the evolution mechanism of these processes Figure 2,[1]. The crack growth rate on Y-axis is \( v_c = \frac{\partial y}{\partial t} \) (where “t” is the time).

The crack extension rate (both senses of X-axis) due to plastic strain is \( v_p = \frac{\partial x_1}{\partial t} \) and due to crack flanks corrosion is \( v_0 = \frac{\partial x_2}{\partial t} \). Then, in corrosive damaging process, under mechanical tension action, produced by mechanical process of wear, three situations may be defined:

I. The crack is developing in depth of metal, prevalent based on the local corrosion of crack tip. In this case, the condition is:

\[
 v_c > 2(\frac{\partial x_1}{\partial t}) + 2(\frac{\partial x_2}{\partial t})
\]

\[
 \text{or}
\]

\[
 v_c > 2v_p + 2v_0
\]

Figure 1 Wear rates vs Material loss rate

Figure 2 Crack evolution mechanism
The multiplication by “2” was made because the crack is growing in both directions.

II. The crack’s evolution is slow down due to the blunting of his tip:
\[ \frac{\partial y}{\partial t} = 2\left(\frac{\partial x_1}{\partial t}\right) + 2\left(\frac{\partial x_2}{\partial t}\right) \]

\[ \text{or} \]
\[ v_e \equiv 2v_p + 2v_0 \]

This situation is possible in the case of material yield strain process intensification in the crack tip.

III. The depth crack’s evolution is practically stopped, but the rounding (the extension of his tip) is going on. This aspect can be described by the relation:
\[ \frac{\partial y}{\partial t} < 2\left(\frac{\partial x_1}{\partial t}\right) + 2\left(\frac{\partial x_2}{\partial t}\right) \]

\[ \text{or} \]
\[ v < 2v_p + v_0 \]

Knowing that the crack is a stress concentration factor then
\[ \sigma_{\text{max}} = \sigma_{\text{nom}} \left(1 + \frac{\sqrt{1/\rho}}{\rho}\right), \]
where \( \sigma_{\text{nom}} \) is the rated stress and \( \rho \) is the rounding crack tip radius. To notice that at constant \( \sigma_{\text{nom}} \) values, if \( \rho \) is growing, the \( \sigma_{\text{max}} \) value is decreasing, that leads to correspondent decrease of \( K_{\text{IC}} \) parameter.

Experimental researches (FIGURE 2), shown that on the crack’s surface, developed under mechanical solicitation action, three types of electro-corrosion currents may appear. They are generated by the electrical potentials drop between: the crack tip and the metal surface \( (E_1 = \phi_1 - \phi_2) \); the crack tip and his walls \( (E_2 = \phi_2 - \phi_3) \); the metal surface and crack walls \( (E_3 = \phi_1 - \phi_3) \). The greatest potential fall value is given by the difference between \( \phi_2 \) and \( \phi_3 \) potentials, of the crack tip and his walls.

Cracking and restoration of oxide films (Figure 3) through an appearance and development mechanism, is evaluated by electrode potential’s evolution (Figure 4). The appearance of some new surfaces, through cracking of oxide films and re-oxidation of these ones, ascertain the evolution’s character of the electrode potential.

3. Methodology of structural changes estimation

The structural modifications in the superficial layer during the wear processes in corrosive environment may be estimated by physical and physicochemical methods. Among physical methods are mentioned: X-ray and neutrons diffractometry, electronic microscopy, visible and UV-range emission spectroscopy and ultra-sound waves attenuation.

According to the above-described mechanism, one of the methods that can estimate it is the electrode potential measurement method. For wear processes intensity evaluation the electrode potential measurement method for a roll-sabot couple tribomodel was used. The roll was made by Fc200 cast iron, the sabot was made by OL52 steel and the test environment was a 3%NaCl solution (Figure 4).

4. Experimental results

In Figure 5 and Figure 6 are presented the electrode potential evolutions for wear tests, dislocation density evolution and internal second order microstresses evolution. All measurements show that the wear damage, similar with fatigue damage, has an cumulative character. [4]. The structural modifications of superficial layer have a staged evolution, by successive strains and relaxation.
by dislocation pileup in front of obstacles and them overtaking (dislocation density).

![Graph](image1.png)

Figure 5 Electrode potential vs time

The pileup is associate with a process of extrusion or intrusion, and the number of stress cycles until a crack is initiated is take to coincide with the stored energy of the accumulated dislocations reacting a critical value. At macrostructure level, the corrosion phenomena through that the walls of the cracks which becomes anodic areas and their tips catodic areas, are manifested in three stages.

5. Results interpretation

On the basis of crack growth according to pellicular theory, on the metallic surfaces subjected to a corrosive environment appear some protective oxide films which, can slow down, more or less, the corrosive damaging of the base metal where they are formed. These films can be thin ones (up to 400 Å), medium (400 – 5000 Å) and thick (over 5000 Å).

If this fragile layer is subjected to an external mechanical stress $\sigma_i$ and admitting that the stresses intensity factor associate to each defect with $a_i$ length is $K_i$, then his value is obtained by a Griffith type relation:

$$K_i = \frac{Y \sigma_i}{\pi a_i}$$

(4)

In this formula $Y$ is a geometrical factor and $\sigma_i$ is the medium stress around the considered defect, eventually different by $\sigma_{ext}$ due to an eventually stress relaxation. A crack appear when the stresses intensity factor $K_i$ (mode I crack) due to the defect and the external stress becomes the critical value $K_{IC}$.

Over this value the crack has a quick spreading and the fragile cracking is produced. Under this value, the crack has a controlled evolution, in Paris sense [5] (Figure 7). The $K_{ISCC}$ is the smallest value. Under this value the crack doesn't develop in corrosive environment. The $K_{ISCC}$ parameter is not an intrinsic material’s characteristic, because it is dependent by metal-environment couple. This way, the density of crack appearance probability depends on diverse factors such as: tenaciousness, defect distribution, internal stresses, flaw geometry etc.

Considering the oxide layer like a covering layer, the Lawn relation, [6], can be applied to this layer, so it can be established the $K_{IC}$ value:

$$K_{IC} = 0.13 \left( \frac{E_f}{H_f} \right)^{3/2} F \cdot a^{-3/2}$$

(5)

where: $E_f$ – elasticity modulus of oxide layer; $H_f$ – oxide layer’s hardness; $F$ – normal load; $a$ – the length of the crack.

The mechanical stresses (wear) bring in the oxide superficial layer crack lattices. That’s why the phenomenon must be statistically analyzed. Following the experimental researches, dislocation density evolution and the second order internal microstresses evolution (Figure 6) is important that the process is influenced by the presence of the flaws in the crystalline lattice and by the internal stress relaxation.

Two characteristics can appreciate the damage intensity: the density of cracking probability of the oxide layer and the relaxation of the stresses around the crack (Figure 8).
Considering an oxide layer element with an infinitesimal length \(dx\) and the thickness \(h\), the function \(f(\varepsilon)\) is the probability of a crack appearance due to an elementary growth of the deformation, from \(\varepsilon\) value to \(\varepsilon + d\varepsilon\) value. The function \(f(\varepsilon)\) is the elementary probability of cracking density. The probability for an \(dx\) length element to crack, if the deformation’s value is \(\varepsilon\), will be \(F(\varepsilon)dx\), where:

\[
F(\varepsilon) = \int_{0}^{\varepsilon} f(\varepsilon) \, d\varepsilon \tag{6}
\]

\(F(\varepsilon)\) is the probability density of integral braking and is represented, generally, by a Weibull function. The number of cracks within the oxide layer will grow, the density of them is:

\[
D(\varepsilon) = \frac{N(\varepsilon)}{L} \tag{7}
\]

Where: \(N(\varepsilon)\) is the number of cracks detected on measurement length \(L\). The growing rate of the crack density can be established knowing that the growth of the crack’s number is equal with the number of intercrack distances, Figure 8, [7].

Thus:

\[
\frac{dD(\varepsilon)}{d\varepsilon} = \frac{1}{L} \left[ \int_{0}^{\varepsilon} n(\varepsilon, u) + f(\varepsilon, u) \, du \right] \, d\varepsilon \tag{8}
\]

Where: \(n(\varepsilon, u)\) - the elementary density of probability; \(n(\varepsilon, x)dx\) – the number of intercrack distances, with \(dx\) length; \(\varepsilon(\varepsilon, u)\) – the local deformation along the x-length inter-cracks area. Following this is obvious that the electrode potential and the anodic current can be considered like a measure method for damaging processes of the superficial layers, linked with the stress intensity factor. The anodic current is proportional to the newly created surface area at the crack tip, which in its turn is proportional to the crack opening displacement and hence proportional to the square of the stress intensity factor or the square of applied stress \(\sigma_0.2 \approx \sigma^2\) [8].

The crack opening displacement can be calculated with the following relation

\[
\delta = \frac{\pi \sigma_0.2^2 a_k}{E f_0} \tag{9}
\]

where \(\sigma_0.2\) is the yield limit of material. Then the next relation can be written:

\[
i = C \Delta K_{eff}^2 \tag{10}
\]

where \(C\) is the proportionality coefficient and \(\Delta K_{eff}\) is the effective stress intensity range.

6. Prediction possibilities

On the basis of the repassivisation model, it is possible to calculate the anodic current. The length of the wear track was divided into \(N\) segments of equal length. Each segment has a surface \(a_k\). This surface is activated each time the pin moves over the segment \(k\). The total repassivisation current in the wear track is the sum of the current flowing into activated segments.

The seeming profile of the dry surfaces due to wear in corrosive environment is very complex (Figure 9) [9].

\[i_1, i_2, i_3, ..., i_n\]

... These currents have different measures and depend of the local resistance values \(r_1, r_2, r_3, ..., r_n\) and of the local electrical tensions potential drop \(\varphi_1, \varphi_2, \varphi_3, ..., \varphi_4\) (between the anodic surfaces and the catodic ones)

\[
i_1 = \frac{\varphi_1}{r_1}; i_2 = \frac{\varphi_2}{r_2}; ..., i_n = \frac{\varphi_n}{r_n} \tag{11}
\]

That means there will be a system of elementary currents (Figure 10). Their vectors will form a complex surface that will determine a mean current with.

Based on the previous schemes it has to be
determined the mean repartition current \( i_m(t) \) if the values in time for the elementary currents are known. In order to solve the problem it can be presumed that each and every one of these elementary currents changes in time after a cubic function

\[
i(t) = \frac{t}{D t^2 + N t + M} \tag{12}\]

Where \( D, N, M \) - coefficients.

The interpretation of this law for the \( n \) elementary currents is shown in Figure 11.

The mean value for the current can be calculate with

\[
i_m(t) = \frac{1}{n} \left[ i_1(t) + i_2(t) + \ldots + i_n(t) \right] \tag{13}\]

The mean value of the current can be determined at different periods of time \( (t_1, t_2, t_3, \ldots, t_n) \). They can be founded in the schema in the sections 1-1', 2-2', 3-3', ..., n-n'. Thus:

\[
i_m(t) = \frac{1}{n} \left[ i_1(t_1) + i_2(t_1) + \ldots + i_n(t_1) \right] \tag{14}\]

\[
i_m(t) = \frac{1}{n} \left[ i_1(t_2) + i_2(t_2) + \ldots + i_n(t_2) \right]
\]

\[
i_m(t) = \frac{1}{n} \left[ i_1(t_n) + i_2(t_n) + \ldots + i_n(t_n) \right]
\]

In the case when a rough rigid body press against a ductile metal, the asperities of the rigid body cause a plastic stain until the contact pressure correspond to the metal hardness.

\[
p = \frac{F}{\sum A_i} H \tag{15}\]

Where \( p \) - contact pressure;

\( F \) - the applied load;

\( A_i \) - asperity contact area;

\( H \) - metal hardness.

The total area of the depassivated surface on the track of wear length can be written as

\[
S = (1 - P)n \cdot 2 \cdot z \cdot L \frac{A_{i,a}}{\pi} \tag{16}\]

Where \( z \) - the function of the wear track area becoming effectively depassivated;

\( P \) - the probability that an asperity contact takes place on an area already depassivated by another asperity;

\( n \) - number of asperity contacts;

\( l \) - the truck length;

\( A_{i,a} \) - the average contact area, each of the asperity contact assumed having a circular shape.

Finally the anodic current will have the value [11]:

\[
I = 2\pi^{-0.5} z (1 - P)n^{0.5} L \cdot f \cdot F^{0.5} H^{-0.5} \int_0^{1/f} i_p dt \tag{17}\]

Where: \( i_p \) - the repassivating current density;

\( f \) - the frequency at which surface is depassivated

This equation allows to predict the effect of rubbing on the dissolution rate in the passive potential region as a function of the hardness of the metal at the measured passivation charge on of the applied parameters (frequency, load and wear track length). The proportionality factors \( P, z, \) and \( n \) are usually not known apriori and for this reason the equation cannot be used for predicting absolute values at wear accelerated corrosion but it allows the rationalization of the influence of material and at the operating parameters.

A prediction of corrosion current value \( I \) in the crack tip as function of the crack geometry parameters and environmental concentration of \( Fe^{2+} \) ions [12] can be written as following:

\[
I = k_0 \cdot C_{Fe^{2+}} \cdot \delta^m \left[ \frac{a(h + 0.35a)}{(h - a)^m} \right] \tag{18}\]

Where: \( txh \) - thickness x height of the specimen

\( \delta \) - the crack opening displacement;

\( C_{Fe^{2+}} \) - concentration of \( Fe^{2+} \) ions;

\( k_0 \) - experimental constant;

\( m \) - material constant;
\(a\) - crack length.

The discrete nature of the wear process may be considered as determined by the effect of wear mass losses, losses that have an inhomogeneous character. The mass loss can be determined by [13]:

\[ G = G_{\text{mech}} + G_{\text{cor}} + G_{\text{acc}} \]  

(19)

Where:
- \(G_{\text{mech}}\) - mass loss due to mechanic factor;
- \(G_{\text{cor}}\) - mass loss due to chemical reactions;
- \(G_{\text{acc}}\) - acceleration factor due to oxide layer removal.

The mass loss, \(G\), can be considered as a result of local mass loss during the time \(t\) (Figure 12).

![Figure 12 Statistical distribution in time of local mass losses](image)

The mean values will be:

\[ G_{(t_1)} = \frac{1}{n} \left[ G_1(t_1) + G_2(t_1) + G_3(t_1) + ... + G_n(t_1) \right] \]

\[ G_{(t_2)} = \frac{1}{n} \left[ G_1(t_2) + G_2(t_2) + G_3(t_2) + ... + G_n(t_2) \right] \]

(20)

On the other hand the mass loss can be expressed by:

\[ G = G_{\text{mech}} + G_{\text{cor}} + \Delta G \]

where:

\[ \Delta G = \Delta G_w + \Delta G_{\text{cor}} \]

\(\Delta G\) is a synergetic component between corrosion and wear, determined by the wear determined corrosion, \(\Delta G_w\) and corrosion determined wear \(\Delta G_{\text{cor}}\).

### 7. Conclusions

In the wear process in corrosive environment the mechanical and electrochemical parameters play an important role and interfere. The evolution of the failure can be determined by physical and electrochemical methods.

There is the possibility of prediction of the tribo-corrosion process based on a model that combines mechanical parameters of braking in the superficial layer and the electrochemical parameters.

### REFERENCES

10. Assi, F. Tribo-electrochemistry of Micrometer – Scale Dissertation submitted to the Swiss Federal Institute of Technology, Diss ETN no 13715.