EFFECT OF NORMAL FORCE ON TRIBOCORROSION BEHAVIOUR OF Ni – 30Cr MODEL ALLOY IN LiOH – H₃BO₃ SOLUTION

Claudiu IONESCU,[a,b] Marioara ABRUDEANU,[a*] Pierre PONTHIAUX,[b]
François WENGER[b] and Vasile RIZEA[a]

[a] University of Piteşti, Faculty of Mechanics and Technology, Materials Science and Engineering Laboratory, 1 Târgul din Vale,
Piteşti 110040, Roumania
[b] École Centrale Paris, LGPM, Grande Voie des Vignes, 92295 Châtenay-Malabry, France

Tribocorrosion of Ni – 30Cr model alloy was investigated for different contact pressures in LiOH – H₃BO₃ solution at room temperature. The sliding tests were performed with a pin-on-disc tribometer designed to evaluate the synergistic effect between corrosion and wear. The combined corrosion–wear degradation during sliding tests was monitored and evaluated by open circuit potential measurements and electrochemical impedance spectroscopy measurements. The sliding track morphology was investigated by SEM and profilometric measurements after sliding tests. The total material loss generated by the deterioration of the protective oxide layer due to combined chemical / electrochemical and mechanical interactions in the sliding track area was assessed from quantitative and qualitative point of view.

INTRODUCTION

In this work, a Ni – 30Cr model alloy was used. Generally, the Ni – based alloys are commonly named super alloys due to good mechanical properties and corrosion resistance properties in higher temperature environments. These Ni – based alloys properties are determined by their ability to form on their surface a protective oxide layer. Usually, the films formed on Ni – Cr alloys consist of a nickel oxy–hydroxide layer and an inner protective barrier film mainly composed of Cr₂O₃.[1, 2] The chromium content of the Ni – 30Cr is similar with that of an industrial super alloy, INCONEL 690. The latter is used to manufacture the steam generator tubes in nuclear power plants based on pressured water reactor (PWR) technology. During their service period these tubes are subjected to the corrosion–wear degradation.[3-6]

Tribocorrosion is described as an irreversible process, which involves mechanical and chemical / electrochemical interactions between surfaces in relative motion, in the presence of a corrosive environment. Tribocorrosion process affects especially the passive materials. The protective oxide film formed on Ni – Cr alloy surface can be affected by mechanical interactions. The mechanical deterioration of the passive film on the contact surface determines a synergistic effect between corrosion and mechanical wear processes. The total material loss due to tribocorrosion process exceeds the amount of material removed as a result of the two processes acting separately. [7, 8]

The goal of this work was to evaluate from quantitative and qualitative standpoint, the total material loss of the Ni - 30Cr model alloy after tribocorrosion tests performed for different normal loads. To achieve this goal, in situ techniques as open – circuit potential measurements and electrochemical impedance spectroscopy were used.[9-11] These techniques were implemented before, during and after sliding tests, to monitor and to evaluate the surface transformation of the Ni – 30Cr model alloy. The ex situ techniques (SEM, profilometric measurements) were used to characterize the alloy surface after tribocorrosion tests.

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* Corresponding author: abrudeanu@upit.ro

EXPERIMENTAL

The Ni – 30Cr model alloy used for the tribocorrosion experiments in this work was provided by Arcelor Mittal Imphy, France. The model alloy has the following nominal composition (in wt %): 0.002% C, 0.0009% S, 0.01% N, 0.02% Mn, 69.15% Ni, 30.35% Cr and 0.25% Fe. The alloy was received in the form of sample specimens of 25 x 20 x 2 mm^3.

Prior to any test, the samples are prepared by mechanical grinding with emery paper with increasingly finer grain (down to grade 4000) and then polished with 3μm diamond paste. They are cleaned in ethanol and then in distilled water in an ultrasonic bath. After surface preparation, the sample is fixed on a metallic holder. The holder and the sample are mounted in a PVC cell. The sample area, A_0, exposed to electrolyte measures 5 cm^2. This area is isolated from the support with a silicone paste. After silicone drying, the PVC cell is mounted on a unidirectional pin-on-disc tribometer (manufactured by Falex Tribology N.V., Belgium) able to carry out tribocorrosion tests by applying sliding friction to the sample in liquid medium (electrolyte). Due to its properties (high hardness, electrochemically inert in the used electrolyte) a zirconia pin with a spherical tip having a radius of 100 mm was used as counter body. The pin was mounted vertically on the rotating head. After applying a constant contact force normal to the sample surface, the tip of the pin draws a circular sliding track (10 mm in diameter) at constant rotation rate.

The cell was filled with LiOH – H$_3$BO$_3$ solution with following composition: H$_3$BO$_3$ (5.72 g / L), LiOH (0.448 g/L). These concentrations were chosen in order to obtain at the room temperature (20 ± 5°C), the same ratio pH / pK$_e$ as in pressurized water reactor (PWR). For the electrochemical measurements a three-electrode set-up was used. In the cell, the sample surface acts as working electrode. A circular platinum grid was used as counter electrode. The reference electrode was an Ag - AgCl electrode (Ag / AgCl / saturated KCl solution). Its potential is + 200mV / SHE at room temperature). The three-electrode set-up was connected to a Solatron 1287 Potentiostat and a Solatron 1255 Frequency Response Analyzer monitored by a pc running Corrware and Zplot softwares for the electrochemical measurements.

Electrochemical measurements – namely open circuit potential and electrochemical impedance measurements – were performed before and during sliding tests. It is considered that a quasi steady-state is achieved when the evolution of the open circuit potential is smaller than 1 mV/min.[8] For electrochemical impedance spectroscopy measurements carried out at open circuit potential before and during sliding tests, a sinusoidal potential perturbation of 10 mV$_{RMS}$ amplitude was applied at frequencies ranging from 10 kHz down to 10 mHz.

Sliding tests were performed at four normal force values: 1 N, 2 N, 5 N, and 10 N. According to the Hertz's elastic theory, these loads lead to maximum contact pressures of 65 MPa, 82 MPa, 112 MPa, and 141 MPa respectively. These values of the maximum contact pressures are smaller than the yield strength of the Ni – 30Cr model alloy, in order to avoid plastic deformation under static loading conditions. The rotation speed of the pin was set at 120 rpm. The sliding tests duration is 5,000 s, corresponding to 10,000 cycles.

After sliding tests, the area of the sliding track, A_{tr}, and the wear track volume, W_{tr}, were evaluated by profilometric measurements (station Micromesure STIL, France) carried out in four areas regularly spaced along the sliding track.

From these measurements, the average track width, e, was determined and the area of the wear track was calculated:

$$A_{tr} = eL \qquad (1)$$

where, L, is the length of the sliding track.[8]

From the average area, S, of the cross-section of the wear track, and its length, L, the total wear track volume, W_{tr}, was calculated:

$$W_{tr} = SL \qquad (2)$$

The wear track morphology was analyzed with a Scanning Electron Microscope (SEM), JEOL, JSM-T220A model.

RESULTS AND DISCUSSION

Before start of sliding, the sample was immersed for three hours in the LiOH – H$_3$BO$_3$ solution. The electrochemical reactivity of the sample surface was monitored by evolution of the open circuit potential during this immersion period. At the beginning of immersion, the open circuit potential is initially around - 0.26 V / Ag - AgCl. Then, throughout the immersion period, a continuous increase of the open circuit potential is observed. This behavior suggests that the alloy is in passive state, and that the protective oxide layer formed on its surface strengthens over time (see Fig. 1).

After three hours of immersion in LiOH – H$_3$BO$_3$ solution, the open circuit potential reaches a steady state value of - 0.179 V / Ag-AgCl. At this stable value of open circuit potential, the surface state of the Ni – 30Cr model alloy was investigated by electrochemical impedance spectroscopy (see impedance plots in Fig. 2).

The Nyquist plot of Fig. 2 is an arc of circle. For such an impedance plot, the electrochemical system can be represented by the so-called Randles equivalent electrical circuit. In this circuit, the resistance, R_s, of the solution between the reference electrode and the sample surface is in series with a circuit, representing the electrical properties of the metal/electrolyte interface. This circuit consists of a capacitive constant phase element, CPE, in parallel with a polarization resistance, R_p. The value of R_s and R_p are obtained by extrapolating the arc to the real axis.[14] The specific polarization resistance (value per unit of area), r_p is then:

$$r_p = R_p A_0 \qquad (3)$$

A_0 represents the area of the working surface in contact with the electrolyte. The passivation current density, i, is given by:

$$i = \frac{B}{r_p} \qquad (4)$$

In general for the metallic materials, the constant **B**, usually has a value between 13 mV and 35 mV. [8] This constant is related to a reaction mechanism, involving anodic oxidation (dissolution or passive film growth) of the material and cathodic reduction of the oxygen. The value of **B** used in this work was 26 mV. In the literature, [12] the values of specific polarization resistance are used to discriminate between passive and active metallic surfaces. For example, if the value of the specific polarization resistance is lower than 10^3 ohm cm², the oxidation current density is higher than 26 μA cm^{-2} (from equation(4)), and the metal can be considered as active. On the contrary, if the value is higher than of 100×10^3 ohm cm², the current density is lower than 0.26 μA cm^{-2}, and the metal can be considered as passive.
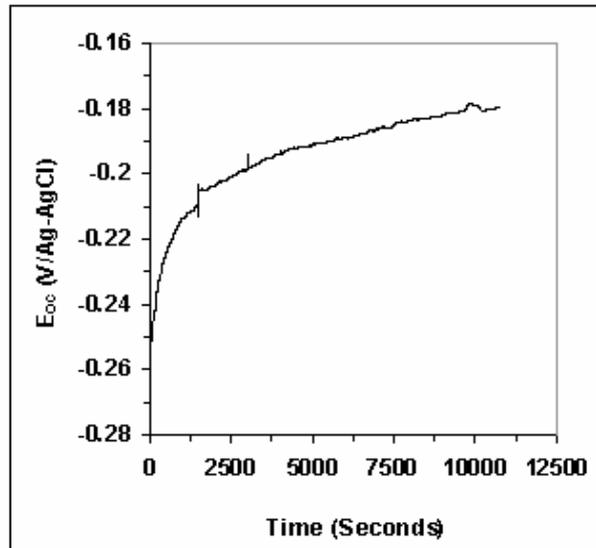

Fig. 1 – Evolution of the open circuit potential of Ni - 30Cr model alloy sample
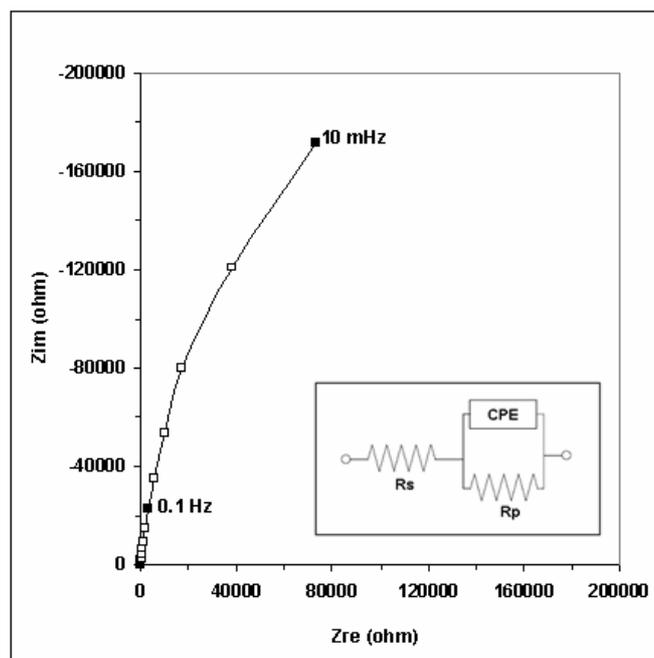in the LiOH – H_3BO_3 solution at 20 ± 0.5°C, without any mechanical solicitation.

Fig. 2 – Electrochemical impedance Nyquist plot recorded at steady state open circuit potential
in LiOH - H_3BO_3 solution at 20 ± 0.5°C.

From the value of R_p (1.64 10^5 ohm) found in our test, the following value of the current density i was calculated by equations (3) and (4):

$$i = 3.17 \ 10^{-8} \ \text{A cm}^{-2}$$

The order of magnitude of i indicates that the alloy is covered by a protective passive layer before starting of the sliding test.

Fig. 3 presents the evolution of the open circuit potential during sliding test performed at four different values of the normal force. A passive film was formed on the Ni – 30Cr model alloy after three hours of immersion in LiOH – H$_3$BO$_3$ solution at $20 \pm 0.5°C$, before starting the sliding tests. At the start of sliding, a deterioration of the passive film was produced for all values of the normal force.

This passive film degradation is reflected by the sharp drop of the open circuit potential (from -0.179 V / Ag – AgCl to around -0.4 or -0.5 V / Ag - AgCl) when the sliding tests started. The open circuit potential drop indicates depassivation of the metal in the sliding track on areas in contact with the pin and the occurrence of a dissolution process, inside the sliding track area. The increase of the open circuit potential for all four normal forces after the initial potential drop is related to changes of contact conditions, resulting from straining generated by friction. Inside the

sliding track, a hardened layer was formed with microstructural properties, mechanical properties and electrochemical reactivity very different from those of the unaffected surface.

The sliding track area, A_{tr}, obtained after applying the four normal forces represents only about between 3-6% of the sample area, A_0, exposed to the electrolyte. The open circuit potential value recorded during sliding tests is a mixed potential, resulting from the galvanic coupling between the bare material, inside the sliding track and the rest of the sample surface, which is not subjected to rubbing and remains in a passivated state.

The whole sliding track area can be considered to be in an active electrochemical state (corrosion) during sliding tests, because the rotation rate of the pin, 120 rpm, can be considered high enough to prevent the restoration of the passive film everywhere in the sliding track. For this reason, in the case of continuous sliding tests, it is considered that the whole area of the sliding track is in an active state $A_{tr} = A_{act}$, where A_{act} is defined as the active area in the sliding track. [13]

During sliding tests, the active area in the sliding track, A_{act}, increases with the normal force, as presented in Fig. 4.
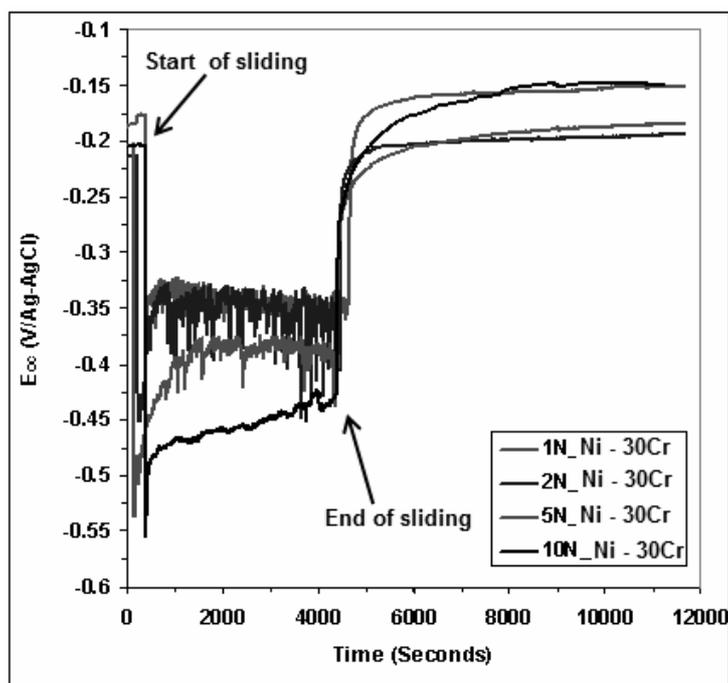

Fig. 3 – Evolution of the open circuit potential of Ni – 30Cr model alloy in LiOH – H$_3$BO$_3$ solution at $20 \pm 0.5°C$, before, during and after continuous unidirectional sliding tests performed at 120 rpm, 10,000 cycles, for four values of the normal force: 1 N, 2 N, 5 N and 10 N.
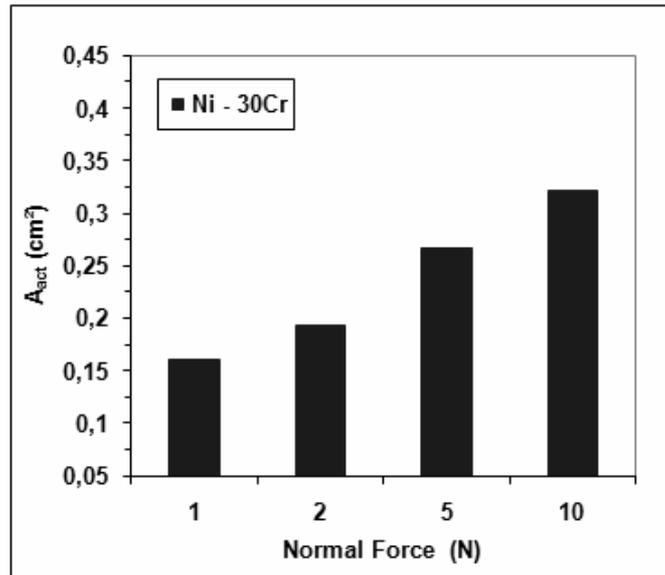
Fig. 4 – Increase of the active area in the sliding track with the normal force during tribocorrosion tests performed on the Ni – 30Cr model alloy in LiOH – H$_3$BO$_3$ solution at 20 ± 0.5°C, 120 rpm and 10000 cycles.
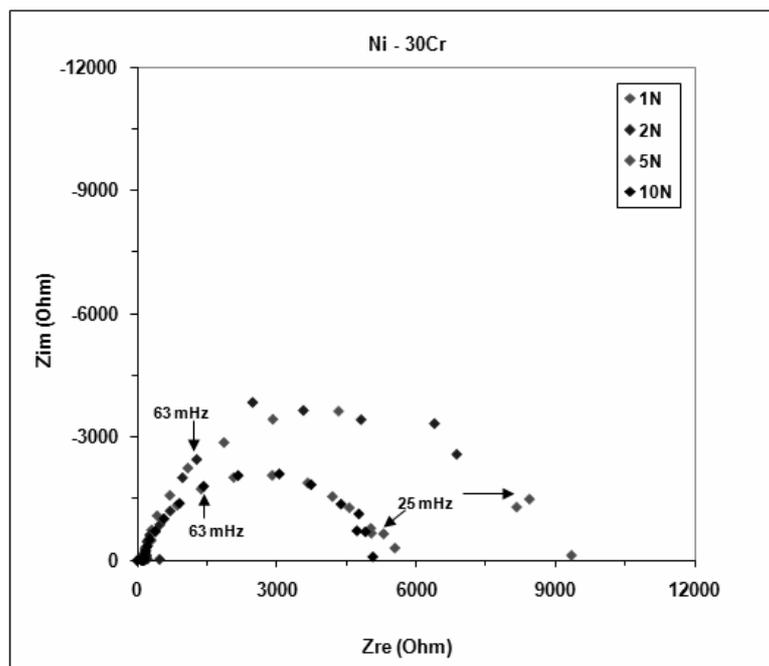

Fig. 5 – Electrochemical impedance Nyquist plots of the Ni – 30Cr model alloy immersed in LiOH – H$_3$BO$_3$ solution, recorded under sliding at the open circuit potential. Sliding tests performed at 120 rpm, 10000 cycles, for four normal forces: 1 N, 2 N, 5 N and 10 N.

The increase of the open circuit potential drop with the normal force, as was already shown in Fig. 3, can be explained by the increase of the active/passive areas ratio.

Impedance measurements were carried out at the open circuit potential during the second part of the continuous unidirectional sliding tests, for the four values of the normal force. The obtained impedance plots are presented in Fig. 5. By electrochemical impedance spectroscopy measurements during sliding tests, the electrochemical activity of the wear track can be assessed quantitatively. The polarization resistances during sliding, R_{ps}, were calculated using the same Randles equivalent electrical circuit. The polarization resistance obtained during a sliding test, R_{ps}, is in fact the combination of two

polarization resistances connected in parallel. The first one, R_{act}, is related to the active sliding track area ($A_{act} = A_{tr}$) and the second one, R_{pass}, to the area outside of the sliding track ($A_0 - A_{act}$). Consequently, R_p is given by the following expression:

$$\frac{1}{R_{ps}} = \frac{1}{R_{act}} + \frac{1}{R_{pass}} \qquad (5)$$

In the tribocorrosion protocol developed by Diomidis *et al*,[14] R_{pass}, is calculated from the specific polarization resistance r_p, for the passive material at open circuit potential before sliding, as:

$$R_{pass} = \frac{r_p}{(A_0 - A_{act})} \qquad (6)$$

Using the value of, R_{act}, determined from equation 5, the specific polarization resistance of the active sliding track can be calculated as:

$$r_{act} = R_{act} A_{act} \qquad (7)$$

During continuous sliding tests, A_{tr}, is considered to be equal with A_{act}. The values of A_{tr} are measured at the end of the sliding tests for each normal force. As was already shown in Fig. 4, the increasing of the normal force leads to an enlargement of the sliding track area. From the value of r_{act} calculated by equation (7), the value of the current density i_{act} due to corrosion of the active area was calculated using equation (4) by replacing r_p with r_{act}. Comparing the values found for i_{act}, at the different normal forces with the current density value measured before sliding ($i = 3.17 \ 10^{-8}$ A cm^{-2}), it can be concluded that a significant degradation of the protective oxide layer occurs during sliding tests performed on the Ni – 30Cr model alloy. A slight increase of i_{act} with the normal force was observed. This result shows that the damaging of the passive film increases with the increasing of the normal force.

In Fig. 3, at the moment when the sliding test is ended, it can be observed that, for all four normal forces, the value of the open circuit potential increases once again, suggesting a restoration of the passive film in the sliding track. At the end of the sliding tests, the open circuit potential was recorded for two hours. After this period, steady state open circuit potential conditions were obtained, and impedance measurements were carried out. The specific polarization resistance values calculated (by equation 3) from these impedance data are found higher than 10^6 ohm

cm², independent of the applied normal force. This order of magnitude of r_p, confirms repassivation of the sample surface.

The result of the damaging of the passive film on the total wear is quantitatively evaluated in Fig. 6. To describe the total material loss in the sliding track, W_{tr}, was used. The total material loss, W_{tr}, was determined from profilometric surveys of the wear track.

W_{tr} can be expressed as the sum of two components (equation 8):

$$W_{tr} = W_{act}^c + W_{act}^m \qquad (8)$$

W_{act}^c represents the material loss due to corrosion of active area in the sliding track and W_{act}^m is defined as the material loss due to mechanical wear of active material.[14]

To calculate the material loss due to corrosion of active area in the sliding track, Faraday's law was used:

$$W_{act}^c = \frac{1}{Fd} \left(\frac{X_{Ni} n_{Ni}}{M_{Ni}} + \frac{X_{Cr} n_{Cr}}{M_{Cr}} \right)^{-1} i_{act} A_{act} t_{lat} \qquad (9)$$

In equation (9), F is Faraday's constant (96458 C mol^{-1}), d, is the density of the Ni – 30Cr model alloy, X the mass fraction of the component (Ni, Cr) of the alloy, M the atomic mass, and n the number of electrons involved in the oxidation of the component. The latency time, t_{lat}, is the period between two successive contacts at a given location in the sliding track with the zirconia pin. In this work, $t_{lat} = 0.5$ s.

The material loss due to mechanical wear of active material in the wear track, W_{act}^m, was calculated from equation (8) as the difference between the total material loss in the sliding track and the material loss due to corrosion of active area in the sliding track.

In tribocorrosion conditions, interactions between mechanical and electrochemical processes are responsible for the so-called synergy effect on wear. This effect usually results in an increase of the total wear with respect to the wear calculated by summing the mechanical wear in non corrosive conditions and the electrochemical wear measured when the metal is in contact with the solution, without applied friction. In the case of passivating materials like the Ni – 30Cr alloy, depassivation by friction is the process which has the prevailing contribution in this synergy effect and in the corresponding increase of total wear.
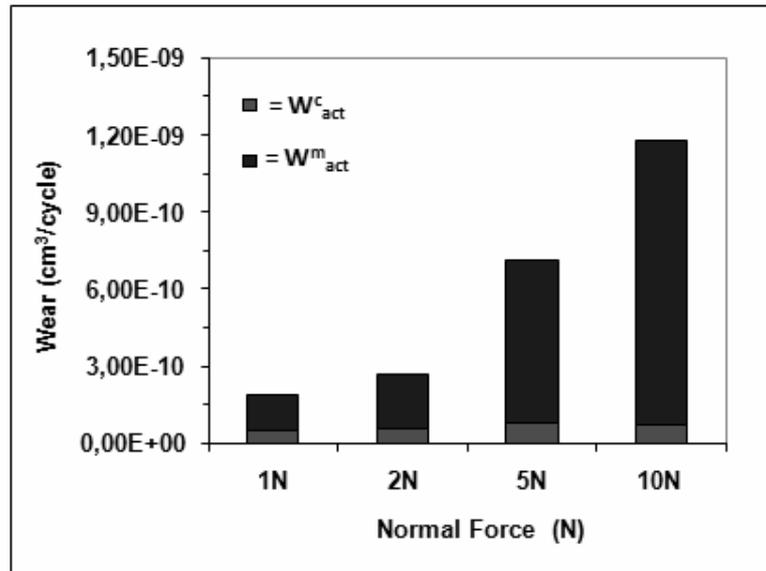
Fig. 6 – Contribution of the two tribocorrosion components to total volumetric material loss in the sliding track for the Ni - 30Cr model alloy immersed in LiOH – H_3BO_3 solution at 20 ± 0.5°C. Sliding tests performed at 120 rpm, 10000 cycles, for four normal forces: 1 N, 2 N, 5 N and 10 N.

Analyzing the results synthesized in Fig. 6, an increase of the total wear is observed when the normal force increases.

The increase of the material loss due to corrosion of active area in the sliding track with the normal force can be mainly related to the increase of the active area in the sliding track, as was already shown in Fig. 4. Moreover, Fig. 6 shows that the main component of the total volumetric material loss in the sliding track is the mechanical wear of the active material, for all four normal forces.

Micrographs presented in Fig. 7 were obtained by SEM in the middle of the sliding tracks, after the sliding tests. Based on these images, a qualitative assessment of the surface morphology can be proposed. The morphology of the wear tracks on Ni – 30Cr model alloy exhibits grooves parallel to the sliding direction for all four normal forces. In their work Julián and Muñoz[15,16] identified the grooves parallel to the sliding direction as a mark for the abrasive wear mechanism produced by micro-ploughing. The micro-ploughing wear leads to the formation of lateral ribs. In Fig. 7, it can be observed that these grooves widen if the normal force increases. The grooves are probably produced by hard abrasive particles originating from the alloy. Some of these particles were found stuck in the grooves. No zirconia particles coming from the pin were found. A local analysis of the particles by EDS revealed chromium, oxygen and carbon contents higher than in the surrounding matrix. Abrasive particles could consist in chromium oxides or/and chromium carbides. Chromium oxide particles could be identified by SEM – EDS analysis on the surface of the alloy samples after polishing.

The morphology of wear revealed by micrographs of Fig. 7 is consistent with the fact that, at applied normal forces from 1 to 10 N, the prevailing component in the total wear is the mechanical wear component. The influence of corrosion on the morphology of the wear track is not clearly visible on the micrographs, even at the lowest normal force. Despite the very low value of the contact pressure at a normal force of 1 N, mechanical wear by abrasion is the process having the largest contribution in total wear.

CONCLUSIONS

The effect of the normal force on the tribocorrosion behavior of a Ni – 30Cr model alloy was investigated by unidirectional continuous sliding tests against a zirconia pin in LiOH – H_3BO_3 solution at 20 ± 0.5°C. The open circuit potential measurements and electrochemical impedance measurements were used to evaluate the electrochemical reactivity of the Ni – 30Cr model alloy surface before, during and after sliding tests. Before starting the sliding tests, a protective

oxide layer formed at the surface of the alloy, after three hours of immersion in the electrolyte. When the sliding started, a degradation of the passive film was observed. This deterioration of the passive film and the resulting electrochemical wear component were quantitatively evaluated.

The total volumetric material loss in the sliding track was measured. The total wear increases with the normal force. The corrosion current density does not change when the normal force increases, but the corrosive (electrochemical) wear slightly increases as a result of the increase of the active area. Nevertheless, even at the lowest contact pressure, the prevailing contribution in the total volumetric material loss is the material loss due to mechanical wear of active material in the sliding track.

a)   b)

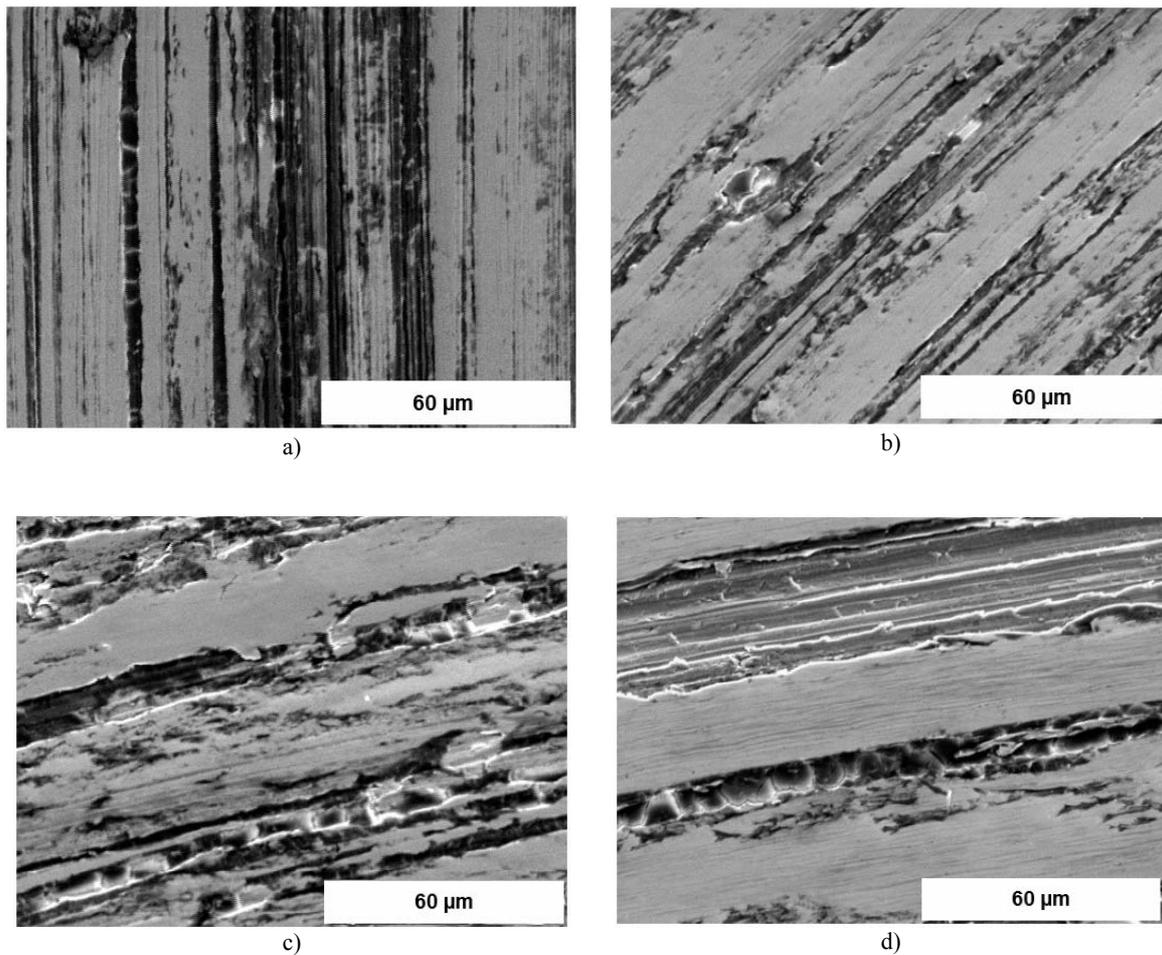c)   d)

Fig. 7 – Scanning electron micrographs of the Ni – 30Cr model alloy after sliding tests performed at 120 rpm, 10,000 cycles, for four normal forces: a) 1 N, b) 2 N c) 5N, d) 10 N, in LiOH – H_3BO_3 solution at 20 ± 0.5°C.

From qualitative viewpoint, a mechanism of abrasive wear by micro-ploughing was revealed in the sliding tracks by SEM micrographs, probably generated by abrasive particles pulled out of the metal matrix.

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