A Comparative Study on Tribocorrosion of Two Ni-Cr Model Alloys in Solution of Boric Acid and Lithium Hydroxide

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Tribocorrosion of two Ni –Cr model alloys was investigated for different contact pressures in a solution of boric acid and lithium hydroxide 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 and compared from quantitative and qualitative point of view for these two Ni –Cr model alloys.

Key words: tribocorrosion, wear, Ni – Cr model alloys

In this work, two Ni – Cr alloys were used, namely Ni - 15Cr model alloy and Ni – 30Cr model alloy. 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 – 15Cr model alloy is similar with that of an industrial super alloy, INCONEL 600. The Ni – 30Cr model alloy has almost the same chromium content as another industrial super alloy, INCONEL 690. In nuclear power plants based on pressurized water reactor (PWR) technology, the steam generator tubes are made from these two industrial super alloys. During their service period these tubes are subject to 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 aim of this work was to compare from quantitative and qualitative standpoint, the total material loss of two Ni - Cr model alloys 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 – Cr model alloys. The ex situ techniques (SEM, profilometric measurements) were used to characterize the alloys surfaces after tribocorrosion tests.

Experimental part

The Ni – Cr model alloys used for the tribocorrosion experiments in this work were provided by France. The chemical composition of the two model alloys is listed in table 1.

The alloys were received in the form of sample specimens of 25 x 20 x 2 mm3.

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, A0, exposed to electrolyte measures 5cm2. 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 (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...

**Table 1**

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Ni</th>
<th>Cr</th>
<th>C</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>Mo</th>
<th>Cu</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni - 15Cr</td>
<td>84.84</td>
<td>14.82</td>
<td>0.012</td>
<td>0.09</td>
<td>0.005</td>
<td>0.084</td>
<td>0.0043</td>
<td>0.001</td>
<td>0.099</td>
<td>-</td>
</tr>
<tr>
<td>Ni - 30Cr</td>
<td>69.15</td>
<td>30.35</td>
<td>0.002</td>
<td>0.25</td>
<td>0.02</td>
<td>0.1</td>
<td>0.0009</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
</tr>
</tbody>
</table>

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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 a boric acid and lithium hydroxide solution with following composition: boric acid (5.72 g / L), lithium hydroxide (0.448 g / L). These concentrations were chosen in order to obtain at the room temperature (20 ± 5°C), the same ratio pH/pKa 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 + 200 mV / SHE at room temperature. The three-electrode set-up was connected to a Solartron 1287 Potentiostat and a Solartron 1255 Frequency Response Analyzer monitored by a pc running Corrware and Zplot softwares for the electrochemical measurements (fig. 1).

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 amplitude was applied at frequencies ranging from 10 kHz down to 10 mHz.

Fig. 1. Mounting scheme of the electrochemical cell on the pin – on – disc tribometer type.

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 66 MPa, 83 MPa, 113 MPa, and 142 MPa for the Ni – 15Cr model alloy, respectively 65 MPa, 82 MPa, 112 MPa, and 140 MPa for the Ni – 30Cr model alloy. Making the hypothesis that the yield strength of INCONEL 600 is the same for the Ni -15Cr model alloy and the yield strength of INCONEL 690 is the same for the Ni -30Cr model alloy, the values of the maximum contact pressures presented above are smaller than the yield strength of the Ni - Cr model alloys, 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 5000 s, corresponding to 10000 cycles.

After sliding tests, the area of the sliding track, \( A_t \), and the wear track volume, \( W_w \), 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:

\[
A_t = eL
\]

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, \( W_w \), was calculated:

\[
W_w = SL
\]

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

**Results and discussions**

Figures 2 shows the evolution of open – circuit potential for two Ni – Cr model alloys, during three hours of immersion in the boric acid and lithium hydroxide solution. This technique was used to monitor electrochemical reactivity of the samples surface before start of sliding. Immediately after immersion, the open – circuit potential value for the Ni -15 Cr model alloy is - 0.267 V / Ag – AgCl, respectively - 0.256 V / Ag - AgCl for the Ni - 30Cr model alloy. Then, throughout the immersion period, a continuous increase of the open circuit potential is observed, for the both alloys. However, a slightly faster increase of the open circuit potential can be observed for Ni -30Cr model. This behaviour suggests that the alloys are in passive state, and that protective oxide layer formed on their surface strengthens over time.

At the end of the immersion period, the open – circuit potential stabilizes at - 0.183 V / Ag – AgCl for Ni – 15Cr model alloy and at - 0.179 V / Ag – AgCl for Ni – 30Cr model alloy. At these values of open circuit potential, electrochemical impedance measurements were done for both alloys. The aim was to gather more information about the mechanism and kinetics of electrochemical reactions occurred at the surface of the Ni – Cr model alloys.

From the Nyquist plots of figure 3 are two arcs of circle. For such an impedance plots, the electrochemical system can be represented by the so – called Randles equivalent electrical circuit, shown in figure 4.

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
The specific polarization resistance is lower than \(10^2\) ohm cm\(^2\), the oxidation current density is lower than 0.26 \(\mu\)A cm\(^{-2}\), and the metal can be considered as passive.

In table 2 the values of \(r_p\) and \(f\) for the Ni – Cr model alloys at steady state open circuit potential are presented. The values obtained for \(r_p\) and \(f\) indicate that both alloys are covered by a protective passive layer before starting of the sliding test. A very small difference can be observed between the values of \(r_p\) and \(f\) obtained for the two Ni – Cr model alloys. This variation can be related to the chromium content.

In the second part of this study, sliding tests were performed at four different values of the normal force. A passive film was formed on the Ni – Cr model alloys after three hours of immersion in a solution of boric acid and lithium hydroxide at 20 ± 0.5°C, before starting the sliding tests. For both alloys, at the start of sliding, a deterioration of the passive film was produced for all values of the normal force.

The passive film degradation is reflected by the sharp drop of the open circuit potential 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 main difference between the two alloys is the amplitude of the initial drop at the beginning of sliding and can be explained by the higher chromium content of the Ni – 30Cr model alloy. The standard potential of chromium (-0.71 / SHE) is significantly lower than that of nickel (-0.23 / SHE). During sliding tests a galvanic coupling appears between bare material inside the sliding track and the rest of the sample surface, which is not subject to rubbing and remains in a passivated state. As a consequence, the potential value of the galvanic coupling will be lower for the Ni –Cr model alloy with the higher chromium content.

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 micro structural 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, \(A_s\), 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 subject 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 \(A_{act} = A_{act}\), where \(A_{act}\) is defined as the active area in the sliding track [13].

### Table 2

<table>
<thead>
<tr>
<th>Alloys</th>
<th>(A_s (cm^2))</th>
<th>(R_p (ohm))</th>
<th>(r_p (ohmmcm^{-2}))</th>
<th>(i (Acm^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni – 15Cr</td>
<td>5</td>
<td>1.50 x 10(^5)</td>
<td>0.75 x 10(^6)</td>
<td>3.47 x 10(^{-8})</td>
</tr>
<tr>
<td>Ni – 30Cr</td>
<td>1.64 x 10(^5)</td>
<td>0.82 x 10(^6)</td>
<td>3.17 x 10(^{-8})</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 3.** Electrochemical impedance Nyquist plots recorded at steady - state open circuit potential in a solution of boric acid and lithium hydroxide at 20 ± 0.5°C

**Fig. 4.** Electrical equivalent circuit of an electrochemical system with one capacitive loop impedance plot.
During sliding tests, the active area in the sliding track, $A_{\text{act}}$, increases with the normal force, as presented in figure 6. This increase is more accentuated for the Ni – 30Cr model alloy.

The increase of the open circuit potential drop with the normal force, as was already shown in figure 5, can be explained by the increase of the active / passive areas ratio. Due to higher active / passive areas ratio for all normal forces, Ni – 30Cr model alloy exhibits more cathodic values of the open circuit potential than Ni – 15Cr model alloy.

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 figure 7.

By electrochemical impedance spectroscopy measurements during sliding tests, the electrochemical activity of the wear track can be assessed quantitatively. The polarization resistances during sliding, $R_{p_{sliding}}$, were calculated using the same Randles equivalent electrical circuit, shown in figure 4. 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:

\[
\frac{1}{R_p} = \frac{1}{R_{act}} - \frac{1}{R_{pass}}
\]  

(5)

In the tribocorrosion protocol developed by [14], \( R_{pass} \), is calculated from the specific polarization resistance \( r_p \), for the passive material at open circuit potential before sliding, given in table 2 as:

\[
R_{pass} = \frac{r_p}{(A_0 - A_{act})}
\]  

(6)

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

\[
r_{act} = R_{act} A_{act}
\]  

(7)

The results presented in tables 3 and 4 show a decrease of the specific polarization resistance resulting in a slight increase of the current density with the applied normal force. Comparing these results with those presented in table 2, it can be concluded that a significant degradation of the protective oxide layer occurs during continuous unidirectional sliding tests performed on the Ni – Cr model alloys. This deterioration of the passive film increases with the increasing of the normal force in tribocorrosion tests. Comparing the values of the current density presented in tables 3 and 4, it can be observed that the degradation of the passive layer formed on Ni -30Cr model alloy is lower than the deterioration of passive film formed on Ni – 15Cr, for all four normal forces. This effect may be related to the difference in chromium content between the two model alloys.

In figure 5, at the moment when the sliding test is ended, it can be observed that, for all four normal forces and both alloys, 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 eq. 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 the repassivation of the sample surface.

The result of the damaging of the passive film on the total wear is quantitatively evaluated in figure 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 (eq. 8):

\[
W_{tr} = W_{act}^* + W_{act}^{mech}
\]  

(8)

\( W_{act}^* \) represents the material loss due to corrosion of active area in the sliding track and \( W_{act}^{mech} \) 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:

\[
W_{act}^* = \frac{F d}{M_n} \left( X_{Ni} n_{Ni} + X_{Cr} n_{Cr} \right) t_{lat} A_{act} f_{lat}
\]  

(9)

In equation (9), \( F \) is Faraday’s constant (96458 C mol⁻¹), \( d \) is the density of the Ni – Cr model alloys, \( X \) the mass fraction of the component (Ni, Cr) of the alloys, \( M \) 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, $W_{\text{act}, \text{mech}}$, 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 – Cr alloys, depassivation by friction is the process which has the prevailing contribution in this synergy effect and in the corresponding increase of total wear.

Analyzing the results synthesized in figure 8, increases of the total wear, of the material loss due to corrosion of the active area in the sliding track and of the material loss due to mechanical wear of active material in the wear track are observed when the normal force increases, for both Ni – Cr model alloys. We note also that for all four normal forces, the total wear and mechanical wear of active material in the sliding track are higher for the Ni – 30Cr model alloy than for Ni – 15Cr model alloy. This observation is confirmed by figure 6. In this figure the active area in the sliding track is higher for the Ni – 30Cr model alloy than for the Ni – 15Cr model alloy, for all four normal forces. However, the material loss due to corrosion of the active area in the sliding track is superior for the Ni – 15Cr model alloy. In tables 3 and 4 were already shown that the values of the corrosion current density of the Ni – 30Cr model alloy are inferior to those of the Ni – 15Cr model alloy. The increase of the chromium content leads to a strengthening of the passive film properties formed on the surface of the Ni - 30Cr model alloy and therefore to a lower material loss due to corrosion of the active area in the sliding track.

Micrographs presented in figures 9 and 10 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 – Cr model alloys exhibits scratches and grooves parallel to the sliding track.

![Fig. 8. Contribution of the two tribocorrosion components to total volumetric material loss in the sliding track for the Ni - Cr model alloys immersed in a solution of boric acid and lithium hydroxide 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.](image-url)

![Fig. 9. Scanning electron micrographs of the Ni – 15Cr model alloy after sliding tests performed at 120 rpm, 10000 cycles, for four normal forces: a) 1 N, b) 2 N, c) 5 N, d) 10 N, in a solution of boric acid and lithium hydroxide at 20 ± 0.5°C](image-url)
direction for all four normal forces. In their work Julián and Muñoz [15, 16] identified the scratches and the grooves parallel to the sliding direction as a mark for the abrasive wear mechanism produced by micro-cutting and micro-ploughing. Analyzing figures 9 and 10, it can be stated that the scratches observed in the middle of the sliding tracks, for the Ni – 15Cr model alloy have transformed into real grooves for the Ni – 30Cr model alloy, for all four normal forces. Hence, a more aggressive deterioration is produced by the abrasive wear mechanism, for the Ni – 30Cr model alloy. This observation is confirmed by the results showed in figure 8.

The micro-ploughing wear leads to the formation of lateral ribs. In figure 10, 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 and/or chromium carbides. Chromium oxide particles could be identified by SEM – EDX analysis on the surface of the alloys samples after polishing.

The morphology of wear revealed by micrographs of figures 9 and 10 are 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

A comparative study on tribocorrosion of two Ni - Cr model alloys was done. Ni – 15Cr model alloy and Ni – 30Cr model alloy were investigated by unidirectional continuous sliding tests against a zirconia pin in a solution of boric acid and lithium hydroxide at 20 ± 0.5°C, using four normal forces. The open circuit potential measurements and electrochemical impedance measurements were used to evaluate the electrochemical reactivity of the Ni - Cr model alloys 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. This passive film has better protective properties for the Ni – 30Cr model alloy than for the Ni – 15Cr alloy, due to higher chromium content. 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. For both Ni – Cr model alloys the total wear increases with the normal force. The corrosive (electrochemical) wear slightly increases as a result of the increase of the active area. The material loss due to corrosion of the active area in the sliding track is lower for the Ni - 30Cr model alloy, because of higher chromium content. 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. The main difference between the two model alloys is given by this component of the total wear. The mechanical wear of the active material in the sliding track is higher for Ni – 30Cr model alloy than for Ni – 15Cr model alloy, for all four normal forces.

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. Consistent with the quantitative assessment, the abrasive wear revealed by SEM micrographs is more accentuated in the sliding tracks of the Ni-30Cr model alloy than in the sliding tracks of the Ni-15Cr model alloy.

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References

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