

# TRIBOCORROSION MECHANISM STUDY OF Ni-15%Cr MODEL ALLOY IN LiOH - H<sub>3</sub>BO<sub>3</sub> SOLUTION

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## Abstract

*INCONEL 600 is one of the alloys used for the manufacture of steam generators in nuclear power plants. Due to severe environment of high temperature and high pressure, mechanical efforts and corrosion were observed. The term tribocorrosion refers to the process leading to the metallic materials surfaces damage (hardening, cracking) and wear under the combined effects of a mechanical contact (friction, impact) and corrosion by surrounding environment.*

*For studying oxide layer behavior during tribocorrosion process was chosen Ni-15%Cr model alloy. Tribocorrosion experiments were performed by using a pin-on-disc tribometer in LiOH – H<sub>3</sub>BO<sub>3</sub> solution similar to coolant water.*

*The combine corrosion – wear degradation during continuous unidirectional sliding tests was investigated by electrochemical techniques (open circuit potential measurements and electrochemical impedance spectroscopy measurements). These techniques were used to monitor and to evaluate the surface characteristics of Ni-15%Cr model alloy.*

**Keywords:** Ni-15%Cr model alloy, tribocorrosion, electrochemical measurements.

## Introduction

French nuclear fleet is composed by power plants in which INCONEL 600 alloy is used for steam generator tubes manufacturing. Steam generator tubes are designed to provide heat transfer between primary and secondary circuit of nuclear power plant through cooling water. The primary circuit water is heated to a temperature higher than 300°C and it is kept under pressure to prevent boiling. At the same time the cooling water plays the role of moderator in nuclear fission reactions. For this 1000 ppm boron is added as boron water. 2 ppm Li as LiOH is also added to maintain a neutral pH. Described conditions related to the vibrations that occur during heat transfer leads to the damaging of the steam generator tubes. INCONEL 600 has a good corrosion resistance at high temperatures, good mechanical properties and good workability. However the damage of the steam generator tubes was observed. Steam generator tube damage occurs due to corrosion and mechanical stresses encountered. In scientific literature many authors have called this loss of material due to interaction between mechanical wear and corrosion with tribocorrosion term [2-7]. In his paper, Henry [7] defined the tribocorrosion as “Phenomena involving mechanical and chemical/ electrochemical interactions between surfaces in relative motion in presence of a corrosive environment”.

INCONEL 600 alloy is a passivable material forming on its surface a protective oxide layer. Tribocorrosion process affects especially the passive materials. The protective oxide film at the material's surface can be destroyed by mechanical tensile strength. This thing can increase the corrosion and mechanical wear rate before surface's repassivation. Another particularity of the tribocorrosion phenomena is the total volume of removed material, which can exceed the sum of material separately removed by the two components of the tribocorrosion process [5-6].

This paper is part of a long-term project aimed at applying a tribocorrosion protocol for Ni-Cr model alloys.

This tribocorrosion protocol concerns the passive materials and was recently developed by Diomidis et al. The protocol extends the applicability of the ASTM G 119-04. To use the protocol was chosen a Ni-15%Cr model alloy, which in terms of Cr content is similar to that of INCONEL 600 alloy. The choice of a model alloy is determined by the fact that for this material type the alloy's protection in the passive domain it is ensured by an inner layer rich in Cr ( $\text{Cr}_2\text{O}_3$ ) [1]. From in situ analysis techniques (open circuit potential measurements and electrochemical impedance spectroscopy measurements) and ex situ analysis techniques (high resolution microtopography, scanning electron microscopy) the objective of this study is to determine the contribution of both components (corrosion and mechanical wear) involved in tribocorrosion process. The wear track is analyzed after unidirectional sliding tests realized with a pin-on-disk tribometer in  $\text{LiOH} - \text{H}_3\text{BO}_3$  solution. The purpose is to obtain information about total volume of loss material.

## Experimental details

Ni-15%Cr plates samples were used for the tribocorrosion tests in this paper. Ni-15%Cr model alloy composition is presented in Table 1 nearby INCONEL 600 composition.

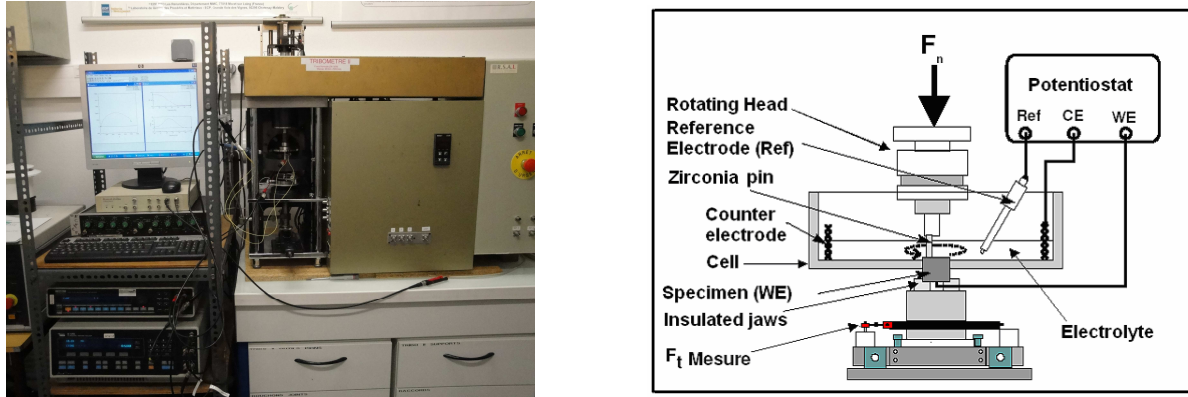
**Table 1. Composition of the INCONEL 600 and Ni-15%Cr alloys**

Alloys	Composition (wt.%)							
	C	Ni	Cr	Fe	Si	Mn	S	Cu
INCONEL 600	0.10	72	17	10	0.50	1	0.015	0.50
Ni-15%Cr	-	84.65	15.35	-	-	-	-	-

Prior to any test, the samples are prepared by mechanical grinding with emery paper (grade 4000) and polished with  $3\mu\text{m}$  diamond paste. They are cleaned in ethanol and then in distilled water in an ultrasonic bath. After surface's preparing the sample is fixed on a metallic support. The support is mounted in a PVC cell. Sample area  $A_0$  measuring  $4.3\text{ cm}^2$  exposed to electrolyte is isolated from support with a silicone. After silicone drying PVC cell is mounted on a unidirectional pin-on-disc tribometer (Falex Tribology) able to tests carried out in liquid medium. Due to his properties (hardness, electrochemically inert) it was used a zirconia pin with a spherical tip having a radius of 100  $\mu\text{m}$ . The pin was mounted vertically on the rotating head. After applying a constant contact force the end of the pin draws during rotation a circular wear track (10 mm in diameter) on the sample surface.

Cell was filled with  $\text{LiOH} - \text{H}_3\text{BO}_3$  solution with following composition:  $\text{H}_3\text{BO}_3$  (5.72 g/L),  $\text{LiOH}$  (0.448 g/L). These concentrations were chosen in order to obtain at the room temperature ( $20 \pm 5^\circ\text{C}$ ), the same ratio  $\text{pH}/\text{pK}_e$  as in pressurized water reactor (PWR). Pin-on-disc tribometer was connected to a Solatron 1287 Potentiostat and a Solatron 1255 Frequency Response Analyzer controlled by a pc running Corrware and Zplot software for the electrochemical measurements. For the electrochemical measurements it was used a three-electrode set-up. Sample surface acts as working electrode, a circular platinum grid as counter electrode. Reference electrode was  $\text{Ag}-\text{AgCl}$  electrode ( $\text{Ag}/\text{AgCl}/$  saturated  $\text{KCl}$  solution,  $+200\text{mV}/\text{NHE}$  at room temperature), Fig. 1. Electrochemical measurements namely open circuit potential and electrochemical impedance spectroscopy were performed before, during and after sliding tests. A quasi steady-state is attained when the variation of the open circuit potential in time is smaller than 60 mV/h. Before and during sliding tests for the electrochemical impedance spectroscopy measurements a

sinusoidal potential variation of 10mV was superimposed at frequencies of 10kHz down to 1mHz, on the  $E_{oc}$ .



**Figure 1. Pin-on-disc tribometer**

Unidirectional continuous friction tests were performed. These tests were done at a normal force of 5N, which according to Hertz theory leads to a maximum contact pressure  $P_{max} = (117 \pm 5)$  Mpa, smaller than yield strength of the Ni-15%Cr model alloy in order to avoid plastic deformation. The speed of rotation of the pin was set at 120rpm. The friction test duration corresponds to 10000 laps, whether 5000 s or 315 m traveled. The tangential force due to friction was measured with a strain gauge during sliding, Fig. 1.

After friction tests, the area of the sliding track,  $A_{tr}$ , and the wear track volume,  $W_{tr}$  were derived from profilometric measurements (station Micromesure STIL, France) done at eight locations uniformly distributed along the sliding track. From these data, the average track width,  $e$ , was calculated (eq 1),

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

with  $L$  the length of the sliding track. From the average area,  $S$ , of the cross-section of the wear track, and its length,  $L$ , the wear track volume was calculated (eq 2),

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

Wear track morphology was analyzed with Scanning Electronic Microscopy (SEM) (JEOL, JSM-T220A model).

## Results and discussions

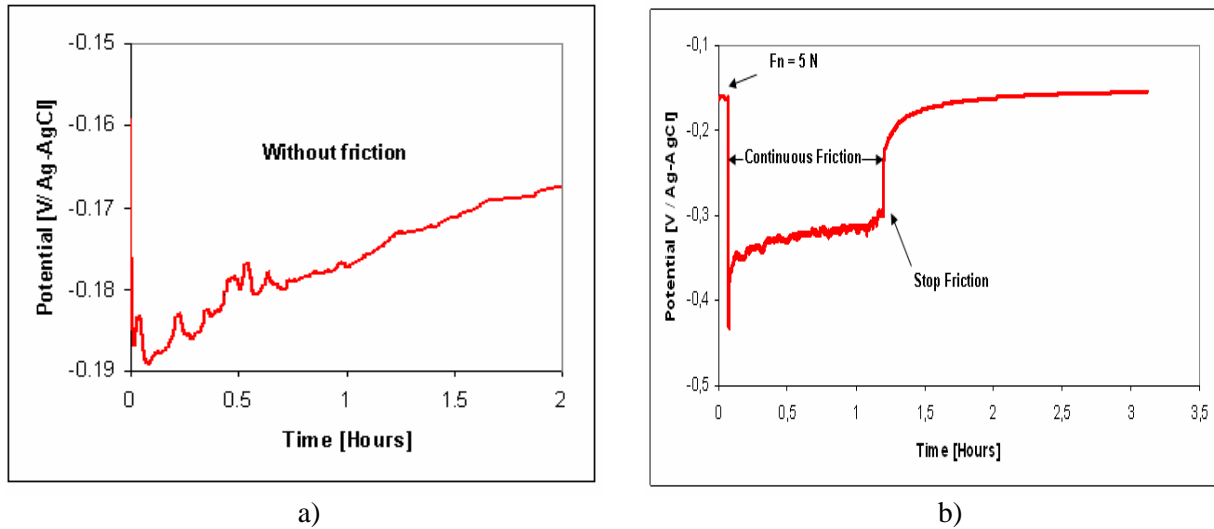
### Open circuit potential measurements

Before unidirectional sliding test the sample surface mounted in PVC cell is maintained in  $\text{LiOH} - \text{H}_3\text{BO}_3$  solution, until the evolution of the free potential reaches the quasi-stationary condition (free potential fluctuations are below 1 mV / min) [8]. After this quasi-stationary condition is reached the zirconia pin is put in contact with sample surface and unidirectional sliding test is performed. The normal force is applied (pin rotation speed 120 rpm). During the term of friction (10000 tours, or 5000s) the evolution of free potential and a diagram electrochemical impedance are recorded.

Under unload conditions, in first half hour of sample surface immersion in  $\text{LiOH}-\text{H}_3\text{BO}_3$  solution; we observe a free potential perturbation. After that the variations are quite small and reach stable passive value (Fig. 2a).

In Fig. 2b., at the moment when the friction begins to be applied we observe a sudden drop of the free potential about 0.35 V. A value of -0.4 V / Ag-AgCl about is reached within seconds. This value characterizes a state of galvanic coupling between the surface areas located in the trace undergoing the

friction and unsolicited areas outside the track. The potential drop at the beginning of friction can be interpreted by the alloy's depassivation in the trace of friction.



**Figure 2. a) Evolution of the open circuit potential of Ni-15%Cr model alloy in LiOH – H<sub>3</sub>BO<sub>3</sub> solution. Variation of free potential after immersion in the solution without friction. b) Variation of the free potential before loading, during continuous friction, and after stopping the friction.**

After the initial potential's drop, an evolution of the latter is observed. A rapid increase of free potential (0.05 V in one minute) which corresponds to the "accommodation" of the surfaces in contact. The zirconia pin does not undergo deformations but the sample surface is deformed and is formed in the friction trace a hardened layer whose structural characteristics, mechanical and electrochemical reactivity is very different from the material present on the rest of the surface.

A steady and slow increase of free potential can be seen beyond the first minute of friction. This increase is probably related to changing contact conditions during the test. During friction, wear causes increasing the width of the track and therefore its surface, due to the geometry sphere - plane contact.

Increasing the area of the track has two consequences:

- 1) A changing in terms of galvanic coupling between the depassivated track (anode area) and the rest of the passive state surface. Increasing the anodic area should, however cause a decrease in potential. It's not that effect is predominant in this case.
- 2) A continuous decrease of the contact pressure since the test is performed at a constant normal force. This could result in a decrease in the area of contact, sufficiently large to offset the influence of increasing the track area.

Once sliding was ended, the open circuit potential rises suggesting that the sliding track is repassivating.

### Electrochemical impedance spectroscopy measurements

To verify if an electrochemical stable passive state was reached after the 2 hours of immersion, electrochemical impedance measurement was performed, Fig 3a.

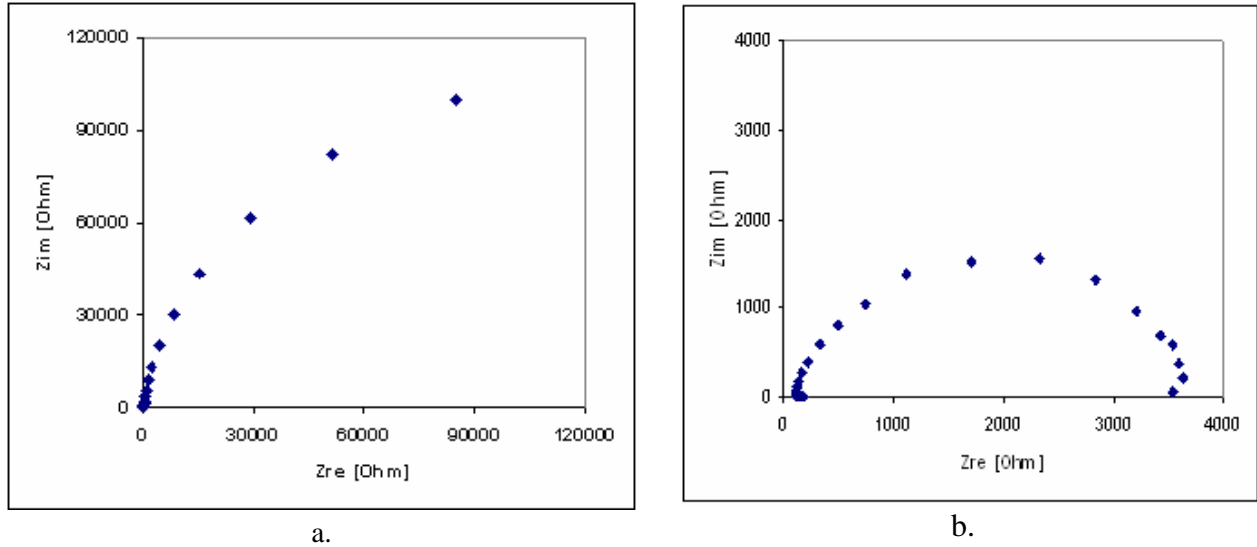


Figure 3. a) Electrochemical impedance Nyquist plot recorded at the open circuit potential after stabilization in LiOH – H<sub>3</sub>BO<sub>3</sub> solution at 25°C. b) Electrochemical impedance Nyquist plot recorded at the open circuit potential value during continuous unidirectional sliding tests performed at 5N and 120 rpm on Ni-15%Cr model alloy immersed in LiOH – H<sub>3</sub>BO<sub>3</sub> solution at 25°C.

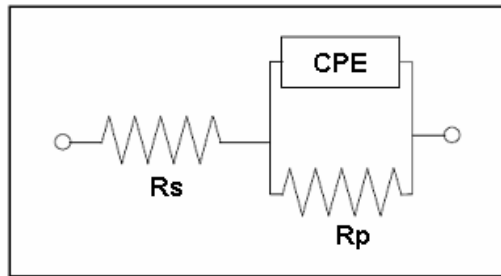


Figure 4. Electrical equivalent circuit for a material – electrolyte interface with one capacitive loop.

Such an impedance plot corresponds to the electrical circuit shown in Fig 4. in which solution resistance,  $R_s$ , is in series with a circuit consisting of a constant phase element CPE, in parallel with a polarization resistance,  $R_p$ . [6]. From the Nyquist plot is obtained the polarization resistance. The specific polarization resistance (value per unit of area),  $r_p$  is then:

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

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

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

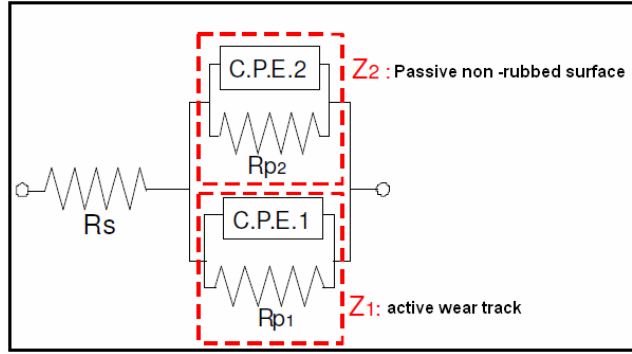
$B = 24$  mV, a value corresponding to a reaction mechanism involving a reaction of anodic dissolution and cathodic reduction of oxygen, passivation current density,  $i$  we obtain the value of passivation current density.

**Table 2. Specific polarization resistance and passivation current density of Ni-15%Cr model alloy immersed in LiOH – H<sub>3</sub>BO<sub>3</sub> and measured at its stable open circuit potential at 25<sup>0</sup>C under mechanically unloaded conditions.**

$A_0 (cm^2)$	$R_p [\Omega]$	$r_p [\Omega cm^2]$	$i [A cm^{-2}]$
4.3	$3.46 \times 10^5$	$1.42 \times 10^6$	$1,69 \times 10^{-8}$

Specific polarization resistance values for metallic materials in the range of  $10^3 \Omega cm^2$  (or lower) indicate the presence of an active sample surface, while values around  $100 \times 10^3 \Omega cm^2$  (or higher) indicate a passive state. [6] From the table 2, we observe that in this case we are in second hypothesis.

Impedance measurements were carried out during continuous unidirectional sliding test. By electrochemical impedance spectroscopy can be assessed quantitatively the electrochemical activity of the wear track. The obtained impedance plot is presented in Fig 3b. Nyquist plot from Fig. 3b can be interpreted using the equivalent circuit shown in Fig. 5.



**Figure 5. Electrical circuit equivalent of a sample under constant friction.**

That polarization resistance obtained during sliding,  $R_{ps}$ , is in fact the combination of two polarization resistances connected in parallel. The first one is related to the sliding track area,  $R_{p1}$  and the second one to the area,  $R_{p2}$ , outside the sliding track [6]. Consequently,  $R_p$  is given by the following expression:

$$\frac{1}{R_{ps}} = \frac{1}{R_{p1}} + \frac{1}{R_{p2}} \quad (5)$$

If we consider that the surface is not rubbed in the passive state, and its area is not very different from that of the sample (the area of the trace represents less than 5% of the sample) we can take as magnitude of  $R_{p2}$ , that one found for passive samples.

It is found that  $R_p \ll R_{p2}$ . This means that  $R_p \approx R_{p1}$ . Resistance  $R_p$  measured on diagrams can be considered characteristic of the wear track.

$$I_{corr} = \frac{B}{R_{ps}} \quad (6)$$

Applying the relationship (6) by taking From the area of the sliding track,  $A_{tr}$ , and from  $I_{corr}$ , we can calculate the corrosion current density of the alloy in the active state in the sliding track, which we note  $i_{act}$ :

$$i_{act} = \frac{I_{corr}}{A_{tr}} \quad (7)$$

Then calculated:

$$r_{act} = R_{p1} A_{tr} \quad (8)$$

**Table 3. The sliding track area, specific polarization resistance, and corrosion current density, of Ni-15%Cr model alloy in LiOH – H<sub>3</sub>BO<sub>3</sub> solution at open circuit potential under continuous unidirectional sliding at 5N, 120 rpm, and 25°C.**

$A_{tr} (cm^2)$	$r_{act} (\Omega cm^2)$	$i_{act} (A cm^{-2})$
0,202	803.09	$2.99 \times 10^{-5}$

### 3.3 Wear measurements

The global material loss in the wear track,  $W_{tr}$ , is the sum of two components.

$$W_{tr} = W_{act}^c + W_{act}^m \quad (9)$$

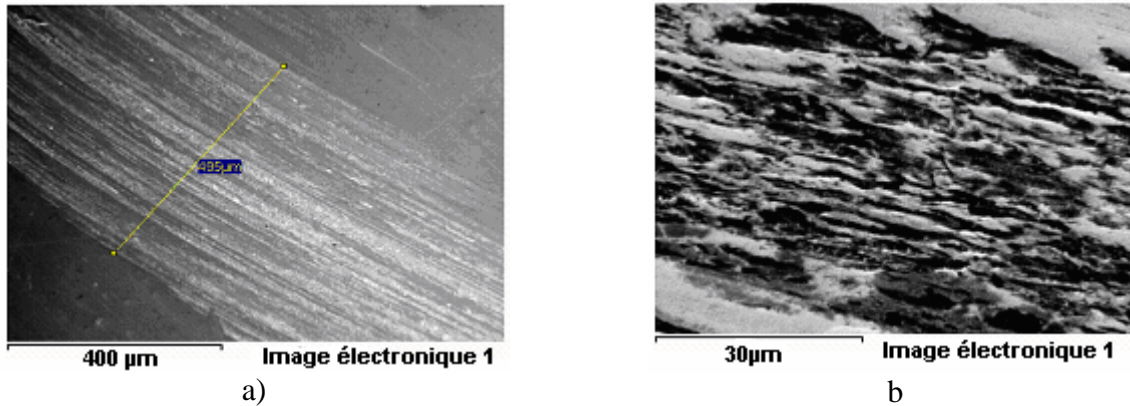
With:

$W_{tr}$  - the global material loss in the sliding track,

$W_{act}^c$  - the material loss due to corrosion of active material in the sliding track,

$W_{act}^m$  - the material loss due to mechanical wear of active material in the sliding track.

Total local wear  $W_{tr}$  on the wear track was measured by an optical high resolution microtopograph (station Micromesure STIL, France).



**Figure 6. SEM images of wear track on Ni-15%Cr model alloy (5N and 120 tours/min, 10000 tours of friction)**

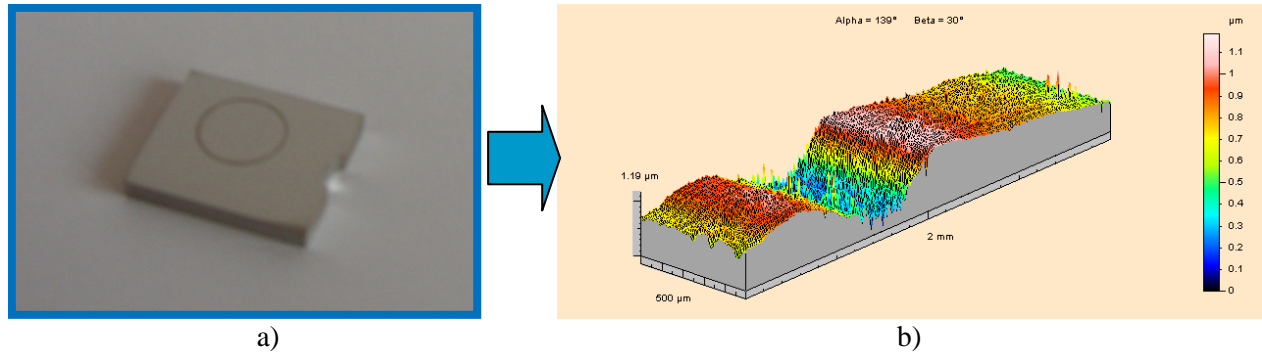


Figure 7. a) Optic image of wear track, b) 3D microtopograph image of wear track area after continuous sliding of Ni-15Cr model alloy ( $F_n = 5\text{N}$ , 120 rpm, 10000 tours)

In Fig.6a, it is presented the morphology of wear track and how it is measured the wear track width.

The material loss due to the corrosion of the active material can be calculated for a given test as:

$$W_{act}^c = i_{act} A_{tr} \frac{M}{nFd} N \Delta t \quad (10)$$

with M the molecular weight, n the number of electrons involved in the anodic process, d the density,  $\Delta t$  sliding time and F the Faraday constant. In the case of alloys, the molecular weight and the number of electrons are calculated as weighted averages of the atomic weights and the number of exchanged electrons of the alloying elements.

The material loss due to the mechanical wear of the active material,  $W_{act}^m$ , can be calculated based on the wear track volume,  $W_{tr}$  measured after the continuous sliding test:

$$W_{act}^m = W_{tr} - W_{act}^c \quad (11)$$

Table 4. Ni-15%Cr model alloy component wear caused by tribocorrosion in continuous unidirectional sliding (5N, 120 rpm, 10000 tours).

Wear	$W_{tr}$ [ $\text{mm}^3/\text{cycle}$ ]	$W_{act}^c$ [ $\text{mm}^3/\text{cycle}$ ]	$W_{act}^m$ [ $\text{mm}^3/\text{cycle}$ ]
Ni-15%Cr	$2.57 \times 10^{-7}$	$9.69 \times 10^{-8}$	$1,60 \times 10^{-7}$

## Conclusions

The tribocorrosion behavior of Ni-15%Cr model alloy in unidirectional sliding test conditions in LiOH – H<sub>3</sub>BO<sub>3</sub> solution was investigated in pin – on – disk contact configuration combined with in situ electrochemical measurements (open circuit potential measurements and electrochemical impedance spectroscopy measurements) and ex situ SEM and micro topographic surveys.

The evolution of the open circuit potential allowed a monitoring of the passive/active surface state of the Ni-15%Cr model alloy sample on immersion, and of the sliding track, revealing the removal and re-growth of the passive surface film. Electrochemical impedance measurements allowed the determination of the oxidation rate of the Ni-15%Cr model alloy material in areas covered with a passive surface film, or from which the passive film was removed mechanically.

The experimental results showed that the global wear,  $W_{tr}$ , track is mainly the material loss due to mechanical wear of active material in the sliding track during unidirectional continuous sliding tests.



This result is obtained under conditions of normal force, which, seem less severe as the maximum contact pressure. In the initial conditions of Hertzian contact the maximum contact pressure does not exceed 120 MPa, a value which can be assumed that it probably corresponds to the material at elastic deformation conditions.

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