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## CORROSION ASSESSMENT OF NICKEL – BASE – DENTAL ALLOYS IN RINGER BIOLOGICAL SOLUTION STUDIED BY ELECTROCHEMICAL TECHNIQUES

The aim of this paper was to study the corrosion behavior of Nickel – Base – Dental Alloys in Ringer biological fluid. The Nickel base alloys are widely used for medical purposes, especially for prosthetic works in the field of dentistry. The applied electrochemical methods used for corrosion investigations are Open Circuit Potential, Linear Polarization during time of immersion in order to calculate the polarization resistance and corrosion rate. Potentiodynamic Polarization diagrams was performed to appreciate the passive domain. Ni-Cr Ugirex alloy show a better corrosion resistance in Ringer solution which will be reflected in a longer life of the dental structures made with this alloy as compared to the Ni-Cr Ducinox alloy, which will result in dental structures with a shorter lifespan.

The electrochemical studies has shown that the alloy have a corrosion behavior similar to a passivating alloy, displaying an extensive passivity area due to formation of an oxide film.

*Keyword:* Corrosion; Biocompatibility; Dental alloys; Ringer fluid; Dental bridge; Electrochemical methods

## 1. Introduction

Dental alloys are widely used in dentistry. They are exposed to the oral tissues for long periods of time, which shows how important it is to study and deepen research in this field. The interaction between alloys and oral tissues can take place through various mechanisms that can lead to various toxic effects or even allergies [1-2].

Some researchers have shown that the metal alloys introduced into the oral cavity for long periods can lead to various corrosion processes [1-10].

Moslehifard et al. [11] studied the corrosion behavior of Ni-Cr alloy in artificial saliva with different pHs using methods such as weight loss described by corrosion rate and potentiodynamic polarization concluded that in more acidic saliva, the corrosion rate of Ni-Cr alloy is greater.

Porojan et al. [12] studied by electrochemical methods different commercial Ni-Cr dental alloys in modified Fusayama saliva and shown that the alloys with Cr and Mo in composition revealed a high corrosion resistance. Kassab et al. [13] corrosion of NiCr-based casting alloys in oral environments. The results showed that the chemical composition of the source material was the determining factor for corrosion resistance, while the casting route and environment modification with fluoride addition did not affect the corrosion behavior of NiCr alloys.

Dental biomaterials must fulfill various characteristics such as the defined composition, the corrosion resistance in contact with body fluids and last but not least biocompatibility [2].

There are many cobalt base or nickel base alloys with different chromium content used in structural dentistry. Regarding the study of these biomaterials, it is imperative to know if certain changes can occur over time on the respective materials in contact with both dental tissues and saliva [1,2,4,6-8].

Studying the corrosion of metal alloys based on Ni-Cr in the oral environment is important because this process can negatively affect the mechanical integrity of dental prosthetic works and at the same time, this can eventually lead to treatment failure [9,10].

Therefore, it is very important to study the corrosion resistance of nickel-based dental alloys for a better understanding of their behavior in the biological environment and finally yet importantly to be able to observe whether they suffer a corrosion degradation process over time [2].

The research work presents the results of corrosion resistance tests applied to study two-nickel base alloys (Ni-Cr)

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widely used in dentistry having the commercial name Ducinox and Ugirex III. The electrochemical studies has shown that the studied alloys behave differently to corrosion tests but similar to passivating alloys.

## 2. Experiment

In order to evaluate the corrosion behavior of nickel-based dental alloys (Ni-Cr) there were taken for study two commercial types of dental alloys frequently used for making fixed metal-ceramic prosthetic restorations with the name Ducinox and Ugirex III. The alloys were purchased from the manufacturer Ugin Dentaire. The chemical composition of Ni-Cr-based alloys is shown in TABLE 1.

TABLE 1

Chemical composition of Ni-Cr alloys

| Type samples Ni-Cr | Ni | Cr | Fe | Mo | Si | Cu | Mo |
|---|---|---|---|---|---|---|---|
| Ducinox | 28.0% | 22.0% | 42.0% | 3.0% | 4.0% | <1% | — |
| Ugirex III | 62% | 26.2% | — | — | 2.4% | — | 9.4%. |

The alloys were machined into cylindrical bars with a diameter of 8.2 mm. To make the working electrodes, Figure 1, smaller cylindrical samples were cut from the initial bars in the form of pellets, which were connected to a 2.5 mm thick copper electric wire, which is attached to the samples. After making the electrical contact, the samples were embedded in VersoCit-2 Acrylic resin Kit to assure the insulation effect of unnecessary areas. In this way, the area of the active surfaces is maintained at 0.53 cm$^2$ for all samples.
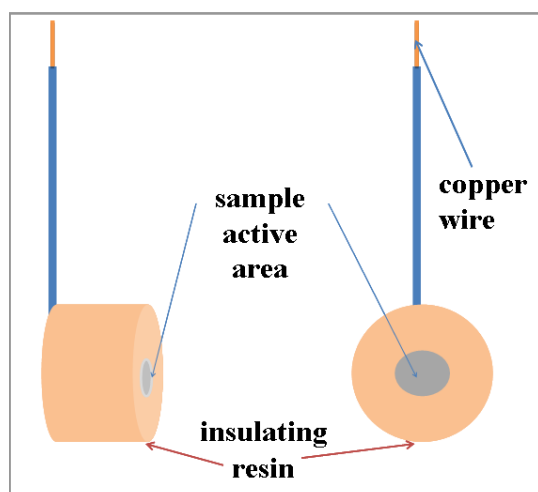


Fig. 1. Schematic representation of Ni-Cr biomedical alloy samples used as working electrode after preparation before exposure to electrochemical corrosion tests

For testing, it was used as an electrolyte in the form of the biological solution Ringer whose composition is given in TABLE 2.

TABLE 2

Chemical composition of biological Ringer solution

| Compound ( g / L) | Ringer's saliva |
|---|---|
| Natrium chloride, NaCl | 8.402 |
| Kalium chloride, KCl | 0.302 |
| Calcium chloride, CaCl$_2$ | 0.298 |
| pH | 6.4 |

To test the corrosion behavior of Ni-Cr-based alloy samples, a three-electrode cell is used, consisting of a borosilicate glass container to which 200 ml of electrolyte is added and in which the working electrode is immersed (WE), the auxiliary electrode in the form of a metal network Pt-Rh and finally the reference electrode Ag/AgCl (saturated KCl, +199 mV vs NHE). The electrochemical cell is connected to the computer-assisted electrochemical workstation. Using Voltamaster 4.0 software data acquisition was made.

The electrochemical measurements are:
–  Open circuit potential (OCP1) during 6 hours;
–  100 linear polarization curves at ±50 mV around the free potential with a scan rate of 1 mV/s.
–  Open circuit potential (OCP2) during 6 hours;
–  100 linear polarization curves at ±50 mV around the free potential with a scan rate of 1 mV/s.
–  Open circuit potential (OCP3) during 6 hours;
–  One Linear polarization curves at ±50 mV around the free potential with a scan rate of 1 mV/s.
–  Potentiodynamic diagram (PD) from – 1500 mV vs Ag/AgCl to 1500 mV vs Ag/AgCl, with a scan rate of 5 mV/s.

## 3. Results and Discussion

### 3.1. Monitoring of open circuit potential (OCP)

The evolution of the open circuit potential of the two Ni-Cr – based biomedical materials was monitored for three times of 6 hours. Between time 1 and time 2 and between time 2 and time 3 the measurement of the free potential was interrupted to measure the 100 linear polarization curves that were used to evaluate the polarization resistance. The results of monitored open circuit potential are shown in Fig. 2.

As it can be seen from Figure 2, the Ni-Cr alloy (Ugirex III) has a nobler value from the beginning of immersion starting at $E = –253$ mV vs Ag/AgCl, curve (2). Further, the open circuit potential for this alloy show a slight tendency to move towards more positive (noble) values. At second period of measurement the open circuit potential of Ugirex III alloy is about constant during the 6 hours having the value of $E = –157$ mV vs Ag/AgCl.

At the end of the measurement of the free potential, at the third sequence of 6 hours, its value has a slight tendency to move towards more negative (active) values, reaching at the end the value of $E = –175$ mv vs. Ag/AgCl.
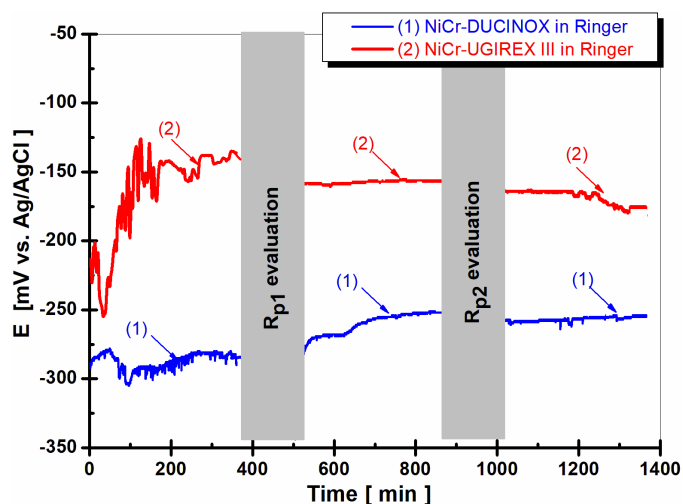
Fig. 2. Evolution of the open circuit potential (OCP) for the investigated samples: (1) Ni-Cr alloy Ducinox; (2) Ni-Cr alloy Ugirex III
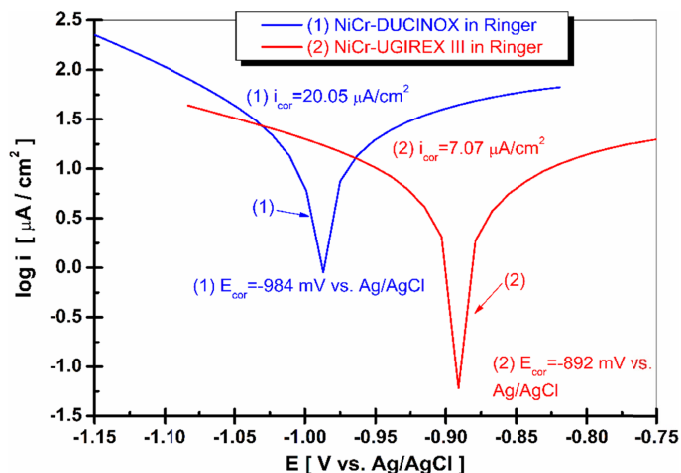


Fig. 3. Linear polarization diagrams recorded in Ringer solution with a scan rate of 1 mV/s for Ni-Cr alloy: (1) Ni-Cr alloy Ducinox; (2) Ni-Cr alloy Ugirex III

The free potential of the Ni-Cr Ducinox alloy, Fig. 2, curve (1) is from the beginning of immersion in Ringer's solution to more negative (active) values, starting from the value of $E = -286$ mV vs Ag / AgCl. At the second measurement period of 6 hours, the free potential of this alloy shows a slight tendency to move towards more positive (noble) values, $E = -253$ mV vs Ag / AgCl. At the end of free potential measurement the value of open circuit potential for this alloy is stabilized at, $E = -253$ mV vs Ag/AgCl.

From the evolution of the free potential of the two alloys immersed in the Ringer, biological solution results in a nobler behavior for the Ni-Cr Ugirex III alloy explained by its higher chromium content, 26.2%, which gives it a higher state of passivity through the formation of chromium oxide on its surface.

### 3.2. Polarization resistance resulting from linear polarization curves ($R_p$)

As mentioned in the literature, polarization resistance is the only method of corrosion monitoring that makes it possible to measure corrosion rates (expressed as thickness loss over time) directly, in real time. The corrosion current determined by this method represents the current that occurs at the metal / corrosive environment interface when the metal is immersed in the solution.

Polarization resistance and corrosion rate are evaluated by the linear polarization method by plotting 100 linear polarization curves for each alloy and for each step, 1 and 2 as shown in Figure 2.

The linear polarization curves was plotted by sweeping the potential around the free potential with a small amplitude of ±50 mV. Figure 3 shows only two of these linear polarization curves for both alloy presented in the form of log (i) versus potential.

Using the 100 polarization curves by plotting the Tafel slopes and using the Stern Geary equation. Equations (1) and (2),

100 values of polarization resistances and 100 values of corrosion rate was calculated for each alloy on each measurement step.

$$R_p = \frac{B}{i_{corr}} = \frac{(\Delta E)}{(\Delta i)_{\Delta E \mapsto 0}} \tag{1}$$

$$B = \frac{b_a \cdot b_c}{2.3(b_a + b_c)} \tag{2}$$

where: $R_p$ is the polarization resistance; $i_{corr}$ the corrosion current density;

The proportionality constant, $B$, for a particular system can he determined as it is shown by Stern and Geary, calculated from $b_a$ and $b_c$, the slopes of the anodic and cathodic Tafel, Equation (2).

The evolution of the polarization resistance for the two alloys immersed in the Ringer biological solution is shown in Fig. 4. in layer (a) for the first measurement period and in layer (b) for the second measurement period, when the time starts from 860 minutes.

Analyzing Figure 4, on curve (2) it is observed that the polarization resistance of Ni-Cr alloy Ugirex III has a higher value than that of Ni-Cr alloy Ducinox throughout the measurements, having a slight decrease and then an increase and stabilizing during the first measurement period at the value of $R_p = 240$ k$\Omega \cdot$cm$^2$.

For the second period of measurements the polarization resistance of this alloy shows a very slight decreasing tendency, still remaining always higher than the polarization resistance of the Ni-Cr Ducinox alloy, $R_p = 143$ k$\Omega \cdot$cm$^2$.

The value of the polarization resistance for the Ni-Cr Ducinox alloy, immersed in the Ringer biological solution, is much smaller but also more constant in time during the two measurement stages. Thus, in the first measurement stage, the value of the polarization resistance of the Ducinox Ni-Cr alloy remains practically constant at $R_p = 26$ k$\Omega \cdot$cm$^2$, decreasing only very little at $R_p = 21$ k$\Omega \cdot$cm$^2$ and remaining constant for the second measurement period.
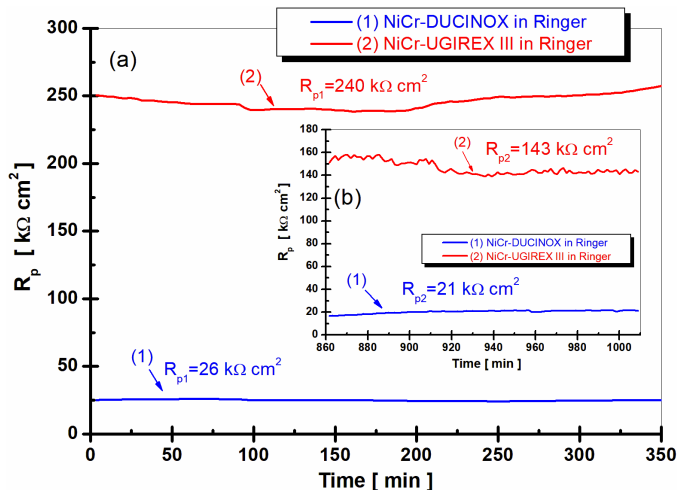
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Fig. 4. Evolution of the polarization resistance of the two alloys immersed in the Ringer biological solution for the first measurement period (layer a) and for the second measurement period (layer b): (1) Ni-Cr alloy Ducinox; (2) Ni-Cr alloy Ugirex III
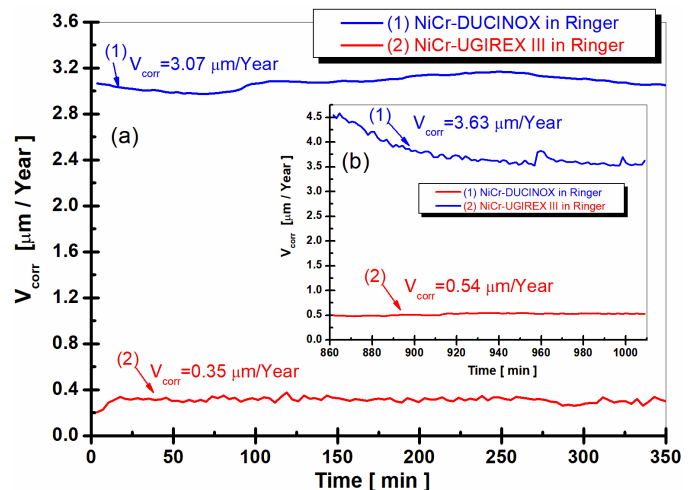


Fig. 5. Evolution of the corrosion rate expressed as penetration index calculated for the two measurement stages (a and b) during the immersion of the alloys in Ringer's solution for: (1) Ni-Cr alloy Ducinox; (2) Ni-Cr alloy Ugirex III

The maximum value of the polarization resistance, $R_p$, is reached by the Ni-Cr alloy Ugirex III, being about 10 times higher as compared with the value of polarization resistance of the Ni-Cr alloy Ducinex. The higher the polarization resistance, the lower the corrosion rate [2].

### 3.3. Evolution of corrosion rate during immersion in Ringer solution ($V_{corr}$)

The variation of the corrosion rate expressed as penetration index is presented in Figure 5.

The corrosion current density calculated from the linear polarization curves shown in Figure 3, $i_{corr} = I_{corr} / S$, is important, and can be directly correlated with the corrosion rate, $V_{corr}$ [2].

The corrosion currents estimated using linear polarization curves and the equations (1) and (2) can be converted into corrosion rate expressed as penetration rates using *Faraday's* law.

It can be seen from Figure 5 that the highest corrosion rate expressed as loss of thickness over time (μm/an) is recorded on the Ducinox Ni-Cr alloy sample reaching a value of $V_{corr} = 3.07$ μm/year, Figure 5, layer (a) curve (1), during the first measurement step. In the second stage of measurement, the value of the corrosion rate of this alloy increases slightly, stabilizing at a constant value of 3.63 μm/yea, Fig 5 layer (b), curve (1).

In comparison, the Ni-Cr alloy Ugirex III shows a much lower $V_{corr}$ value having, in the first measurement stage, the value of $E = 0.35$ μm/yea, Fig 5 layer (a), curve (2), which increases slightly in the second measuring stage at the value of $E = 0.54$ μm/yea.

Monitoring the polarization resistance and the corrosion rate during the immersion of the two alloys in Ringer biological solution concludes the better resistance of the Ni-Cr Ugirex III alloy which will be reflected in a longer life of the dental struc-

tures made with this alloy compared to the Ducinox Ni-Cr alloy, which will result in dental structures with a shorter lifespan.

### 3.4. Potentiodynamic polarization curves

Additional information about the behavior of the two dental alloys immersed in the Ringer biological solution can be obtained by studying the potentiodynamic polarization curves, shown in Figure 6. Usually, the passive state was studied in terms of protection against corrosion. If the passive state covers a larger potential range and this passivation current is lower, then the metal or other has a higher corrosion resistance [2].

Figure 6, layer (a) shows the current density variation over the entire scanned potential range to achieve potentiodynamic polarization curves while layer (b) shows a zoom in the passive region to better observe the difference between the passivation
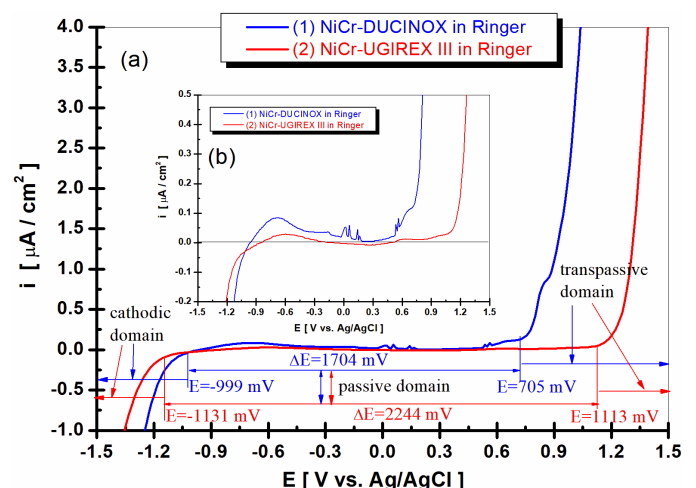


Fig. 6. Potentiodynamic polarization diagrams recorded in Ringer biological solution recorded at a scan rate of 5 mV/s for: (1) Ni-Cr alloy Ducinox; (2) Ni-Cr alloy Ugirex III

of the two dental alloys when are immersed in Ringer biological solution.

From Fig 6 can be observed that there is a difference between the two-potentiodynamic polarization curves especially in terms of passive and transpassive domains.

Thus, the passive range of the Ni-Cr Ugirex III alloy extends over a higher potential range, respectively 2244 mV from $E = -1.131$ V vs Ag/AgCl to $E = 1.113$ V vs Ag/AgCl.

At the same time, the passive range of the Ducinox Ni-Cr alloy is narrower, being only 1704 mV stretching from $E = -0.999$ V vs Ag/AgCl to $E = 0.705$ V vs Ag/AgCl.

The passivation current denity is higher for Ni-Cr Ducinox alloy showing also in the passive domain some fluctuations of current due to the localized corrosion perhaps due to the onset of localized corrosion.

In the transpassive anodic region the current density increases faster for the Ni-Cr Ducinox alloy than that for Ni-Cr Ugirex alloy.

Potentiodynamic polarization curves also show a better behavior of the Ni-Cr Ugirex alloy compared to the Ni-Cr Ducinox alloy.

## 4. Conclusions

The corrosion resistance of the two dental alloys Ni-Cr Ducinox and Ni-Cr Ugirex III is evaluated comparatively for corrosion resistance in the biological Ringer's solution by electrochemical methods as a preclinical study.

Thus, from the point of view of the value of the open circuit potential, it is considered a better behavior of the Ni-Cr Ugirex III alloy, due to its more positive or noble value throughout the experiment.

From the evaluation of the polarization resistance, the results show its highest value as being reached by the Ugirex Ni-Cr alloy, being ten orders of magnitude larger than the polarization resisance recorded for Ducinox Ni-Cr alloy.

The lowest corrosion rate was also recorded by Ugirex III alloy, with a value ten times lower compared to the corrosion rate for Ni-Cr Ducinox biomedical alloy.

Potentiodynamic polarization curves also show a better behavior of the Ni-Cr Ugirex alloy compared to the Ni-Cr Ducinox alloy.

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