Electrochemical Behaviour of CoCrMo and CoCrMoSi5 alloys at Different Simulated Physiological Medium

MIRABELA GEORGIANA MINCIUNA*, PETRICA VIZUREANU1, DRAGOS CRISTIAN ACHITEI1, BRANDUSA GHIHAN3, ANDREI VICTOR SANDU1, DANIEL MAREC2, ADRIANA BALAN4*

1 Gheorghe Asachi Technical University from Iasi, Faculty of Materials Science and Engineering, 41 D. Mangeron Blv., 700050, Iasi, Romania
2 Gheorghe Asachi Technical University from Iasi, Faculty of Chemical Engineering and Environmental Protection 41 D. Mangeron Blv., 700050, Iasi, Romania
3 Politehnica University Bucharest, Faculty of Materials Science and Engineering, 313 Splaiul Independentei, 060042, Bucharest, Romania
4 Gr.T. Popa University of Medicine and Pharmacy, Faculty of Dental Medicine, 16 Universitatii Str., 700115, Iasi, Romania

The paper presents the study of corrosion phenomena for CoCrMo and CoCrMoSi5 alloys, in biological fluids, like citric acid (unpasteurized fresh orange juice). The study was made by electrochemical methods, using potentiodynamic method and electrochemical impedance spectroscopy. It was found that CoCrMoSi5 alloy present high properties and may be used to medical applications.

Keywords: corrosion, cyclic voltammetry, cyclic polarization, SEM, CoCrMo alloy, CoCrMoSi5 alloy

Electrochemical corrosion represents an assembly of physico-chemical processes after which the metals and their alloys go in the form of metallic compounds (oxides, hydroxides, salts) as a result of forming of micro-pores in which the metal is subject to anodic oxidation in the same time in which a component from solution, named the depolarising, undergoes the additional reduction reaction [1-3]. Between the principal causes determining the appearance of local elements may be mentioned:
- contamination with noble metals, metals oxides;
- chemical heterogeneity, for example: the existence of several phases;
- physical heterogeneity, which may appear as a result of a non-uniform mechanical or thermal treatment.

For the appearance of this type of corrosion it is necessary to exist an anode, a cathode, an electrolyte and a conductor, so a galvanic. By removing one of these conditions, the electrochemical corrosion does not occur [4-10].

The aim of the paper is to evaluate the electrochemical behavior in different physiological simulated medium, operated parameters (method, scanning speed, potential intervals, electrodes, etc.). For these studies were evaluated: corrosion time, principals parameters for corrosion process and corrosion speed.

Experimental part

Material and methods

For the study of electrochemical corrosion processes the potential-dynamic method and electrochemical impedance spectroscopy were used.

The study of corrosion phenomenon for CoCrMo and CoCrMoSi5 was made using the electrochemical methods, because the corrosion of dental alloys in biologic fluids is by electrochemical nature. To evaluate the behavior to electrochemical corrosion, in biological medium, for experimental obtained alloys, there are used the following analysis methods: cyclic voltammetry and electrochemical impedance spectroscopy.

Cyclic voltammetry is an electrochemical method with which we can study the mechanisms of electrochemical reactions. In one cyclic voltammetry experiment, it scans the potential between a positive maximum and a negative maximum tour – return, with a constant scanning speed [5]. The cyclic voltammetry is frequently used and in corrosion test to determine the localized corrosion susceptibility: in points and crevices [11-23].

Electrochemical impedance spectroscopy is a study method in alternating current of the electrode processes. Disruption of electrochemical systems is realized by applying an alternating signal, with small amplitude (5-10 m) and is observed the mode in which the electrode returns at stationary state. The advantages of this method towards that using the continuous current (linear voltammetry and cyclic voltammetry) are the following [6]:
- the method presents precision on a wide frequency spectrum;
- the possibility to correct the value of polarization resistance, for solutions which present a high electrical resistance;
- it is a nondestructive method.

The PARSTAT 4000 represents the ultimate model of potentiostat produced by Prince Applied Research. Among the characteristics of this potentiostat include the following [7-8]:
- from +/- 4 A to 10 A;
- voltage for the +/- 48 V (+/- 10 V reference voltage);
- capacity to eliminate the noise by selecting appropriate filters.

For experimental data processing, obtained with PARSTAT 4000 potentiostat, it is used VersaStudio software [9]. The analysis of cobalt based alloys corrosion was made on samples with rectangular section, with 10 mm side and 20 mm length.

* email: mirabela.minciuna@yahoo.ro; balan.gheo@yahoo.com;
Results and discussions

The characterization by electrochemical impedance spectroscopy (SIE)

The measurements were made at the potential in open circuit, in fresh orange unpasteurized juice. We chose the citric juice (fresh orange juice) for its electrochemical behaviour, because it is considered the one of 5 acids which tempts to enter in human body 5-9%.

In large quantity or in excess, the fresh orange juice may affect to dental enamel, thinning it and thus creating cavities.

The spectrums were recorded in 10⁻¹…10⁻²Hz frequency domain, at an alternating current potential with 10 mV amplitude, using a PARSTAT 4000. Data SIE processing was made with ZSimpWin software, 3.22 version [10].

The impedance spectrum was recorded after 750 s and respectively 3000 s from samples immersion in unpasteurized orange juice. A 3000 s time (50 min) corresponds to a bottle of juice consumption one day 28 days.

After each experiment, the impedance data have been represented as Bode diagrams (Z impedance vs. f frequency and Φ phase angle by frequency shows that may exist one or more time constants.

The impedance spectrums represented as Bode diagrams for the 2 experimental samples made from CoCrMo commercial alloy and CoCrMoSi5 alloy, immersed for 750 s, in unpasteurized fresh orange juice are presented in figures 1a,b.

In Bode representations for CoCrMo commercial alloy, as for CoCrMoSi5 alloy, it is observed the presence of one constant for relaxation time, indicated by one maximum on the variation curve of phase angle with frequency.

Electrochemical cell may be represented by an equivalent circuit (CE), consisting from different resistors combinations, capacitors and other circuit elements.

CE provides the most relevant parameters, which characterized the electrochemical process.

The correlation grade of equivalent circuit for obtained experimental data is expressed by χ² parameter, which is directly correlated with the relative error of measured current; to one χ² value of the order of 10⁻⁴ corresponded an error of measured value by 2%.

The interpretation of spectrum for all CoCrMo alloys was made by data modeling with an equivalent circuit, which is presented in figure 3. For simulation it is used ZSimpWin software.

In this equivalent circuit, R - (R Q), R -sol – represent solution resistance, and R – resistance of passive layer (resistance to polarization), and Q – capacity of passive layer.

In this case, to enlarge the scope of the model, in the place of ideal capacity of passive layer it is introduced a constant phase element Q. The impedance of this constant phase element is equal with:

\[
Q = \frac{1}{\chi_0 j \omega^n}
\]

where:

Q – is a adjustable parameter (F cm⁻² s⁻¹),
Y₀ – is a constant,
\[ j \] – is an imaginary number (j² = -1),
n – is related to the slope of the lg |Z| vs. lg frequency from Bode graphic, and \[ \omega \] is angular frequency.

When the value of n is equal with 1, the constant phase element describes an ideal capacitor (C). For 0.5<n<1, the constant phase element describes a distribution of relaxation times in the frequency spaces and when n = 0.5 the constant phase element represent a Warburg impedance with diffusion character. When n = 0 the constant phase element describes a resistor.

The χ² coefficient values are included between 2 x 10⁻⁴ and 5 x 10⁻⁴, which confirm that the chosen equivalent circuit describes well the physic model, adjustment of experimental values being placed in 2-3% error limits.

The resistance of solution does not vary in maintained time of samples in solution, the differences recorded in effectuated measurements are variable within a ± 3 Ω cm² compared to 120 Ω cm² average values. The value of electric parameters of equivalent circuit for studied CoCrMo alloys, maintained for 750 s in unpasteurized fresh orange juice, are presented in table 1.

From data presented in table 1, it is found that the passive layer resistance increase in same time with the increase of Si content. The spectra of impedance represented like Bode diagrams for the 2 experimental samples, from CoCrMo commercial alloy and CoCrMoSi5, immersed for 3000 s in unpasteurized fresh orange juice, are presented in figures 3 a,b.

From Bode spectra form for CoCrMo commercial alloy and CoCrMoSi5 it is found that these present an electrochemical behaviour similar after 3000 s from immersion in unpasteurized fresh orange juice.

As in the case of the obtained spectra for all experimental alloys, after 750 s from immersion in unpasteurized fresh orange juice, the data modeling obtained after 3000 s from
Table 1
THE ELECTRIC PARAMETERS OF EQUIVALENT CIRCUIT PRESENTED IN FIGURE 2, OBTAINED BY EXPERIMENTAL DATA ADJUSTMENT, FOR THE 2 EXPERIMENTAL DATES, IN UNPASTEURIZED FRESH ORANGE JUICE AT DIFFERENT IMMERSION TIMES

<table>
<thead>
<tr>
<th>Material</th>
<th>$10^3 R_1$ (Ω cm²)</th>
<th>$10^3 Q_1$ (S/cm² s)</th>
<th>$n_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>After 750 s from the immersion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoCrMo</td>
<td>32</td>
<td>3.7</td>
<td>0.79</td>
</tr>
<tr>
<td>CoCrMoSi5</td>
<td>295</td>
<td>1.9</td>
<td>0.83</td>
</tr>
<tr>
<td>After 3000 s from the immersion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoCrMo</td>
<td>38</td>
<td>3.7</td>
<td>0.79</td>
</tr>
<tr>
<td>CoCrMoSi5</td>
<td>435</td>
<td>1.6</td>
<td>0.83</td>
</tr>
</tbody>
</table>

![Bode diagrams](image1)

![Linear polarization curves](image2)

Immersion in unpasteurized fresh orange juice, were realized with same equivalent circuit, present in figure 2.

The electric parameters values of equivalent circuit for CoCrMo commercial alloy and CoCrMoSi5 alloy, maintained 3000 s in unpasteurized fresh orange juice, are also presented in table 1.

We have to note that in the figures 1 and 3, the experimental data are presented like individual points, and by continuous line is presented the theoretic spectrum obtained after the simulation, using the equivalent circuit presented in figure 2.

The resistance of passive layer increase in same time with the increase of Si content and reaches a maximum value in the case of 5%Si sample, which means that do not catalyse the oxidation process at the superficial layer.

Also, it was find that for the 2 alloy, the resistance of passive layer increased in same time with the immersion time in unpasteurized fresh orange juice.

**Cyclic polarization curves**

Linear polarization curves were drawn in potential domain: -0.8...+1 V, using a 1 mV/s scanning speed.

The representation of linear polarization curves in coordinates: current density (j) / potential (E) (fig. 4 a,b), allows highlighting of corrosion potential ($E_{corr}$) and corrosion currents ($j_{corr}$).

The main parameters for corrosion process ($E_{corr}$ and $j_{corr}$), obtained by linear polarization curves processing for the 2 experimental alloys are centralized in table 2.

The corrosion potentials ($E_{corr}$) present positive value for CoCrMoSi5 experimental samples comparative with the value for CoCrMo commercial alloy. The corrosion current ($j_{corr}$) is representative for the damage degree of material.

It is noted that the corrosion current density, a representative size for the level of sample damage, is in range of tens of μA/cm² in the case of CoCrMo commercial alloy and CoCrMoSi5 alloy.

The corrosion current value decrease in same time with the increase of Si content up to 5%. The same trend is noted also in the case of passivity current density ($j_{pas}$). It is known that the polarization resistance ($R_p$) is inversely proportional with corrosion current density ($j_{corr}$), according Stern-Geary equation [12]:

$$i_{corr} = B/R_1$$

where:

B – is a constant which depends on material nature.

From this reason it is noted a good concordance between the results obtained from electrochemical impedance spectroscopy tests and those of linear polarization.

![Cyclic polarization curves](image3)
Table 2

THE MAIN PARAMETERS FOR CORROSION PROCESS FOR COBALT BASED ALLOYS, IN UNPASTEURIZED FRESH ORANGE JUICE.

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_{pitting}$ (mV)</th>
<th>$j_{corr}$ ($\mu$A/cm$^2$)</th>
<th>$j_{corr}$ ($\mu$A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCrMo</td>
<td>-245</td>
<td>755</td>
<td>39.1</td>
</tr>
<tr>
<td>CoCrMoSi5</td>
<td>-217</td>
<td>290</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Surface analysis for CoCrMo commercial alloy and CoCrMoSi5 alloy, after corrosion testing by electronic microscopy method

The SEM micrographs for CoCrMo commercial alloy and CoCrMoSi5, after corrosion testing, at different magnifications of 500x and 2000x, are presented in the figures below.

In the figures 5 and 6 is presented the surface morphology for the 2 samples: CoCrMo commercial alloy and CoCrMoSi5 alloy, at different magnitudes, where the impedance spectra after 750 s and respectively 3000 s from sample immersion in unpasteurized fresh orange juice.

The scanning electronic microscopy, after corrosion study, is shown the surface morphologies which result after chemical attack.

The SEM micrographic of CoCrMo commercial alloy and CoCrMoSi5 alloy indicates that the samples are uniformly corroded, and the attack is poorly visible, because the sample have a high corrosion resistance.

The CoCrMo commercial alloy presents a good corrosion behaviour, on the surface presents some oxide points. Comparative with the control sample, the CoCrMoSi5 alloy has a visible better behaviour, with less oxide points on surface.

Conclusions

The characterization of corrosion resistance was made using the linear potenio-dynamic polarization and electrochemical impedance spectroscopy, where it is noted that the passive layer resistance increases in the same time with Si content and reached a maximum value in the case of sample with 5%Si, which means that the oxidation process does not catalysis at the superficial layer.

Also, it was found that for the second alloy, the resistance of passive layer increases in same time with the immersion time in unpasteurized fresh orange juice.

The SEM micrographic of CoCrMo commercial alloy and CoCrMoSi5 alloy indicates that the samples are uniformly corroded, and the attack is poorly visible, because the sample have a high corrosion resistance.

Behind this study it follows that CoCrMoSi5 alloy present high properties and it may be used with success in medical applications.

References

23. CROITORU, G., Urbanism Arhitecturã. Construcþii, 4, no. 2, 2013, p. 75

Manuscript received: 5.06.2014