The advanced characterization of a new alloy by Co-Cr-Mo system

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The paper presents some aspects regarding the structural, mechanical and electrochemical characterization for CoCrMo and CoCrMoSi4 alloys, by identifying of structural constituents, hardness determination, and experimental researches for determination of corrosion resistance in different physiological simulated mediums. The measurements for determination of corrosion resistance were made at potential in an open circuit, in orange fresh juice, unpasteurized. For the study of electrochemical behaviour, was used the citric acid (orange fresh juice, unpasteurized), because it is considered the one of the five acid which tempts most often to entire in human body, 5-9 %.The spectrum interpretation for experimental alloys, based on cobalt, was made by data modelling, with an equivalent circuit whose circuit elements describe the physical and electrochemical properties at the alloy surface immersed in solution. Based on obtained results, behind the measurements for corrosion resistance determination, it is found that once the increase of silicon content, the resistance of passive layer are increase, that means it does not catalyze the oxidation process at superficial layer level.

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1. Introduction

The physical, chemical and mechanical properties have a high importance in desire support to prognosis and design the device assemble of new materials. The general mechanical properties and surface properties for CoCrMo alloys system directly influence their usage in medical applications. In some cases, may control the dynamic at the tissue interface, from initial placement on live until the final removal.

X-ray diffraction is a non-destructive analytical technique, and with his help may obtain information about the identification and quantitative determination for different crystalline compounds, which are present in biomaterials [1].

X-ray diffraction represents the process in which the radiation, without modification of wave length, is transformed by interference with crystalline network in a high number of reflections observable with spatial characteristic directions.

Indexation of diffractogram represents the association between a maximum – diffraction peak and a plan. Indexation of diffractogram emphasizes the following: the nano-crystalline character and phase composition (major phase, minor phase) for the analyzed sample [2]. By this röentgen – structural method, based on X-ray diffraction on crystallographic plans from structure, it is analyzed and characterized, the commercial alloy from CoCrMo and new alloy CoCrMoSi4 [3].

The determination of structural constituents was made with diffractograms, in which are present the dependence between the intensity of diffracted radiation and double of diffraction angle.

The electrochemical corrosion represents assemble of physical – chemical processes, after which the alloys pass to metallic compounds (oxide, hydroxide, salts), as a result to formation of micro-cells in which the metal is subjected to anodic oxidation.

In this time, a component from solution, named depolarizing, suffer the complementary reaction of reduction [4].

Between the principal causes which determine the appearance of local elements can be mentioned [5]:

a. Contamination with noble metals, metal oxides;

b. Chemical heterogeneities, for example: multi-phases existence;

c. Physical heterogeneities, which may appear after an irregular mechanical or thermal treatment.

For the appearance of this corrosion type it is necessary to exist an anode, a cathode, an electrolyte and a conductor, so a galvanic element [6-7].

By removing of one from this condition, the electrochemical corrosion does not occur.

The thermodynamic probability for produce a chemical process on metal surface or alloy it is expressed by corrosion potential (Ecor).

This represents the potential of one corrodible surface located in an electrolyte, measured to a reference electrode

in open circuit; from this reason it is named potential in open circuit (PCD).

This name it is used especially when the electrode potential is measured directly with a mili-voltmeter with huge entrance impedance [8].

For the study of electrochemical corrosion processes it is used the spectroscopy by electrochemical impedance. Using the spectroscopy of electrochemical impedance (SIE) was obtained information about the passive process, which occurs at the maintaining of CoCrMo and CoCrMoSi4 alloys, in solution.

The advantage of this method (in alternative current) toward to other electrochemical methods (polarization methods – in continuous current) is that it can monitor some electrochemical modifications in time, being in same time a non-destructive method.

The spectroscopy of electrochemical impedance is a stationary method able to access the relax phenomena, whose relax times varies at different size orders and allow mediation in same experiment, to obtain a high level of precision [9].

The objective of this study is the improvement of cobalt alloys properties, used in medical applications , by increasing of silicon content up to 4 %. The objective is determined by the necessity of manufacturing the new biocompatible materials, which resist a long period in the human body.

The CoCrMo and CoCrMoSi4 alloys were characterized in this paper, in the terms of structural aspects, by identification of structural constituents, using X-ray diffraction and in the terms of mechanical aspects, determine the hardness for alloys and in the terms of electrochemical aspects by spectroscopy of electrochemical impedance.

2. Experimental researches

2.1 Studies using X-ray diffraction

Establish of compositional phases was made by qualitative analysis with X-ray diffraction, made on Panalytical X'Pert PRO MPD X-ray diffractometer.

It is use an X-ray fascicle, characteristic to CuKα, mono-chromatic with nickel filter.

The 2θ analysis domain is between 20…100°, with step size by 0.001° and time on step being for 3 second/step.

It is use a proportional detector with a single channel, the analysis was made in Gonio module [10]. In the figure 1 is presents the diffractogram obtained for commercial alloy by CoCrMo system. The initial alloy is an commercial alloy (alloy "C"), manufactured by Vaskut, Hungary. The commercial alloy was remelted and improved by the increase of silicon content up to 4 %, using an arc remelting installation, type MRF ABJ 900.

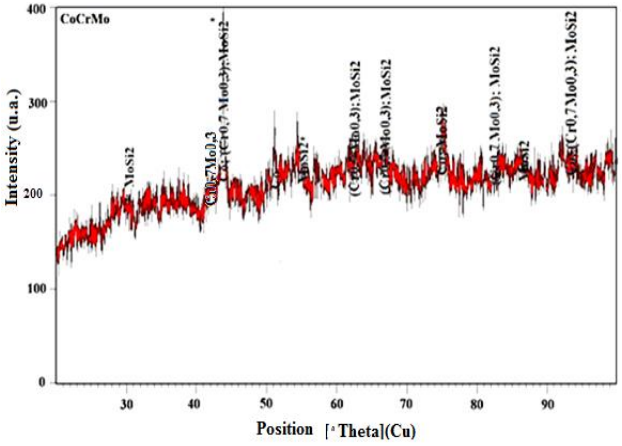


Fig. 1. X-ray diffractogram de raze X (indexed) obtained for CoCrMo commercial alloy.

In samples are present the main phases:

- Co with cubic crystalline structure, having principal maximum at 2θ = 44.19° angle;
- $Cr_{0.7}Mo_{0.3}$ with cubic crystalline structure, having principal maximum at 2θ = 43.56°.

Like minor phases is present MoSi2 compound, crystallized in tetragonal network, having principal maximum at 2θ = 44.48° angle.

In the fig. 2 is present the diffractogram obtained for CoCrMoSi4 new alloy.

In samples are present the main phases:

- Co with cubic crystalline structure, having principal maximum at 2θ = 43.90° angle;
- $Cr_{0.8}Mo_{0.2}$ with hexagonal crystalline structure, having principal maximum at 2θ = 47.24°;
- $Cr_{0.5}Mo_{0.5}$ with cubic crystalline structure, having principal maximum at 2θ = 42.54° angle.

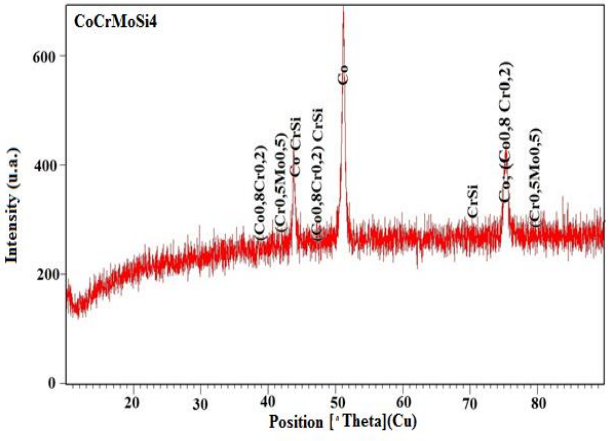


Fig. 2. X-ray diffractogram (indexed) obtained for CoCrMoSi4 alloy.

Like minor phases is present CrSi compound, crystallized in cubic structure, having principal maximum at 2θ = 43.69° angle.

2.2 Hardness measurements

The hardness measurements made on alloys by CoCrMo alloys system, provide information about the mechanical resistance, imposing or not the utility of heat treatments application.

It was chosen Vickers method, because this is a general method to determine of hardness for metallic materials and can be use without reservations in the case of experimental alloys, based on cobalt. The samples used for investigations have 10x10 mm, and analysis was made on the prepared surface (without oxides or any substances).

Table 1. Hardness for alloys based on cobalt.

Alloy	Punctual values measured (HV)	Medium value
CoCrMo	423	438.3
	446	
	446	
CoCrMoSi4	446	458.3
	458	
	471	

Hardness measurements were made on Wilson Wolpert universal hardness tester, using a pressing force by 9.807 N and a measurement time by 12 seconds.

The experiment conditions are the following:

- Sample with parallel surfaces;
- The surface on which are made the measurements was polishing with abrasive paper with 180 and 320 granulation;
- The indenter with pyramid shape, from diamond, with square base, with peak angle by 136°;
- The trace made by indenter on sample surface has a rhombic shape.

For results accuracy was realized 3 determinations on each alloy, in same conditions.

The usage of silicon like alloying element, in the case of alloys based on cobalt, have the effect of improve of hardness values.

The obtained values, after hardness tests, confirm the hardened of experimental alloys, once the increase of silicon content (from 0.35 % Si for commercial alloy up to 4 %Si in the case of CoCrMoSi4 alloy).

In the case of dental applications, the tooth enamel has a Vickers hardness by 320 HV, and for noble alloys (biomaterials based on Au, Ag), in function by the composition and the applied heat treatment are between 180 and 300 HV.

The noble alloys hardness is much higher than tooth enamel (approximately 500 HV) [11].

From table 1, it is observed that CoCrMo and CoCrMoSi4 have a hardness which fits in reference domain (approximately 500 HV).

2.3 Characterization by electrochemical impedance spectroscopy

Determinations for corrosion resistance were made at potential in open circuit, using orange fresh juice, unpasteurized.

For the study of electrochemical behavior, is used citric acid, because it is consider the one of five acids which tempts to enter in human body, 5-9%.

In high quantity, the fresh orange juice can affect the tooth enamel, thinning him and generating thus the cavities appearance and unpleasant experiences associated to them [13].

The spectrums recorded in frequency domain between $10^{5}\ldots10^{-2}$ Hz, at a potential in alternative current, with 10 mV amplitude, using a Partsata 4000 potentiostat.

Data processing was done with ZSimpWin software, version 3.22 [13]. ZSimpWin software use a varied of electric circuits, to correlate numeric the impedance data measured.

The software analyzed the experimental dispersion data, by decomposition of complex reply in one of simply subcomponents.

The impedance spectrum was recorded after 750 seconds from samples immersion in orange juice, unpasteurized.

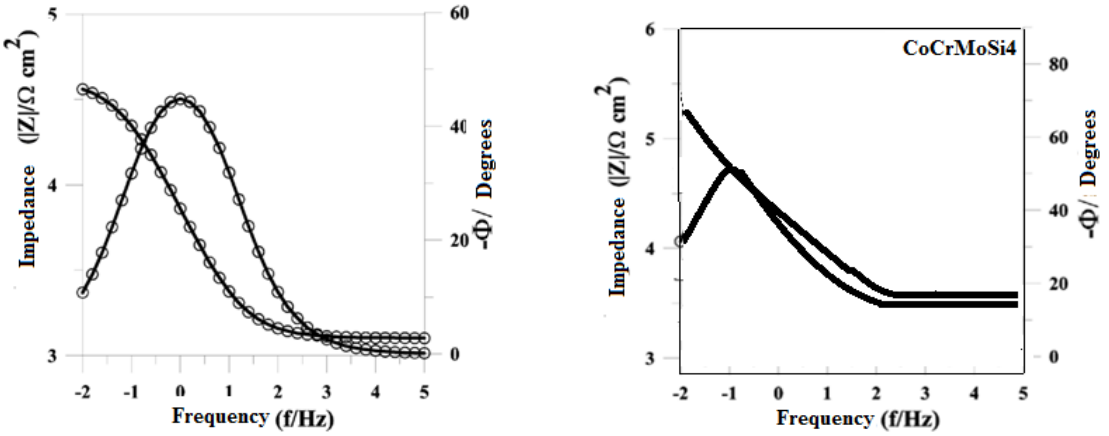
After each experiment, the impedance data was represent after Bode diagrams shape (impedance $|Z|$ vs. frequency (f) and phase angle Φ (grade) vs. frequency (f)).

The dependence between phase angle and frequency, indicate the fact that may exist one or more time constants which can be used to determinate the elements values from equivalent circuit.

The advantage of Bode diagrams is that the dates are present for all frequencies measured and can be represented the impedance values on a high interval.

It was obtained, after immersion for 750 second, in fresh orange juice, unpasteurized, the impedance spectrums represented like Bode diagrams for the 2 experimental samples from CoCrMo and CoCrMoSi4 alloys.

Bode diagrams for alloys from CoCrMo system were present in the Fig. 3.



(a) *(b)*

Fig. 3. Bode diagrams for studied alloys: (a) commercial alloy from CoCrMo system and (b) CoCrMoSi4 experimental alloys, maintaining for 750 seconds in fresh orange juice, unpasteurized.

In Bode representation for commercial alloy from CoCrMo and CoCrMoSi4, present only one constant for relaxation time, indicated by a single maximum on variation curve for phase angle with frequency.

The electrochemical cell can be represent by a single equivalent circuit, consisting from different combination of resistors, capacitors and other circuit elements.

The correlation grade of equivalent circuit for obtained experimental data is expressed by χ^2 parameter, which is directly correlated with the relative error of measured current; to one χ^2 value of the order of 10^{-4} it is correspond 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 the figure 4. For simulation it is used ZSimpWin software.

In this equivalent circuit, $R_{sol}(R_1Q_1)$, R_{sol} – represent solution resistance, and R_1 – resistance of passive layer (resistance to polarization), and Q_1 – 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_1. The impedance of this constant phase element is equal with:

$$Q = Z_{CPE} = \frac{1}{Y_0 \cdot (j \cdot \omega)^n} \quad (1)$$

Where:
Q – is a adjustable parameter (F cm^{-2} s^{n-1}),
Y_o – is a constant,
j – is a imaginary number ($j_2 = -1$),
n – is related to the slope of the lg | Z | vs. lg f, frequency from Bode graphic and ω 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 $\chi 2$ coefficient values are included between $2x10^{-4}$ and $5x10^{-4}$, which confirm that the chosen equivalent circuit describes well the physic model, adjustment of experimental values being placed in 1-3 % error limits.

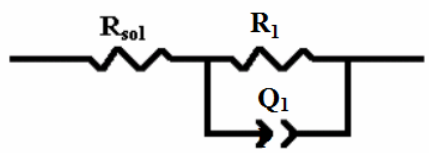


Fig. 4. Equivalent circuit (CE) used in experimental data filtering, obtained for CoCrMo commercial alloys, maintained in fresh orange juice, unpasteurized. [14].

Table 2. The electric parameters of equivalent circuit present in figure 4, obtained by the adjustment of experimental data for CoCrMo and CoCrMoSi4 studied alloys, in fresh orange juice, unpasteurized, at varied immersion times.

Alloys	10^{-3} R_1 (Ωcm^2)	$10^5 Q_1$ (S/cm^2 s^n)	n_1
	After 750 seconds from immersion		
CoCrMo	32	3.70	0.79
CoCrMoSi4	164	2.40	0.82

The resistance of solution not varied in the time of samples maintaining in these, the recorded differences for performed measurements, varies in ± 3 Ωcm^2 limits toward a medium value by 120 Ωcm^2

In the table 2 are present the values of electric parameters of equivalent circuit, for alloys of CoCrMo system, maintaining for 750 seconds in orange fresh juice, unpasteurized.

From the data present in the table 2, it is found that the resistance of passive layer increases once the increase of silicon content, for CoCrMoSi4 alloy, which means that, is not catalyzes the oxidation process at superficial layer.

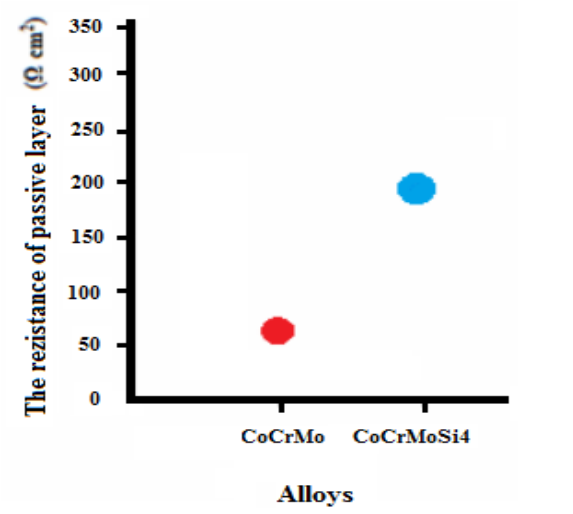


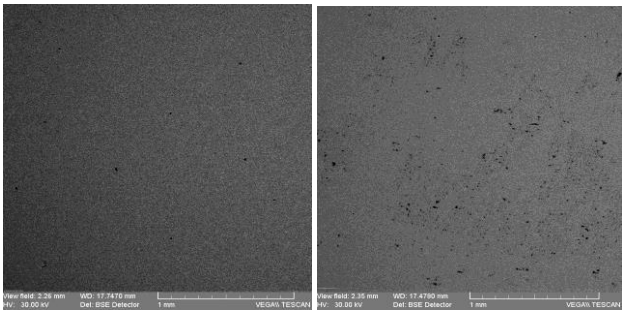
Fig. 5. Graphic representation for passive layers resistance, for new alloy, maintaining for 750 seconds in fresh orange juice, unpasteurized.

The modeling of data obtained both to CoCrMo commercial alloy and also CoCrMoSi4 new alloy (after 750 seconds from immersion in fresh orange juice) it is realize with the same equivalent circuit, present in Fig. 4.

Can mention that in the Fig. 3, the experimental data are present like individual points, and by continuous line are represent the theoretic spectrums obtained after simulation, using the equivalent circuit, from figure 4.

2.4 The effect of corrosion on surface layer

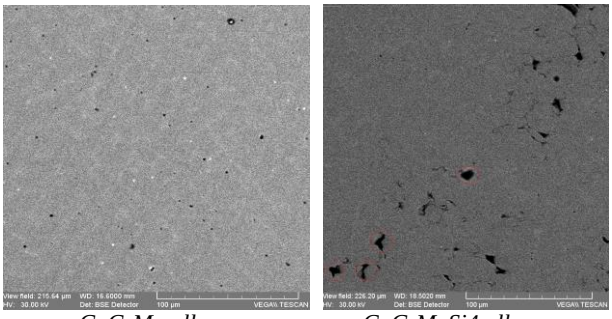
For identification of the corrosive effect on surface layer was used the SEM, equipped with BSE detector (Back Scattered Electrons – 2D image of surface, best contrast of various phases), at 100X and 1000X magnitude.



CoCrMo alloy *CoCrMoSi4 alloy*

Fig. 6. Microstructure of investigated alloy – 100X BSE magnitude.

The analyzed samples at 100X BSE magnitude, by cobalt based alloys, in cast state was subjected to electrochemical corrosion study, using orange fresh juice unpasteurized like corrosive medium.



CoCrMo alloy *CoCrMoSi4 alloy*

Fig. 7. Microstructure of investigated alloy - 1000X BSE magnitude.

By analyzing of samples structures after electrochemical corrosion tests, in orange fresh juice unpasteurized, at 1000X BSE magnitude, is found the appearance, on surface, of fine points by corrosion (red circles), randomly distributed and oriented by dendrite direction.

3. Results

The X-ray diffractometric analysis confirm the structural modifications and allow an precise determination of phases and structural constituents (Co_xCr_y, Cr_yMo_z, Cr_yMo_zSi, $Co_xCr_yMo_z$), that are found both in commercial alloy and also in CoCrMoSi4 new alloy.

Hardness measurements made on alloy from CoCrMo system, provide information about mechanical resistance, imposing or not the utility of some heat treatments application.

By spectroscopy of electrochemical impedance (SIE), it is obtained new information about the passive process, which occurs at testing of CoCrMo and CoCrMoSi4 alloys, in fresh orange unpasterurized juice. CoCrMoSi4 new alloy present an increase for corrosion resistance, at a determined value for alloying element.

This case is confirmed by forming of complex structures, like Co_xCr_y, with hexagonal crystalline network and CrSi with cubic crystalline structure, identified with phase qualitative analysis, by X-ray diffractometric investigations.

4. Discussions

It was observed that by silicon addition for CoCrMo system alloys, it is obtained structures and properties which lead to influencing the corrosion resistance.

The properties modifications can lead, in essentially mode, at the increase of corrosion resistance for alloys of CoCrMo system.

The increase of corrosion resistance for CoCrMoSi4 alloy, at a determined value for alloying element, it is explained by the formation of complex structures, like $Co_{0.8}Cr_{0.2}$ with hexagonal crystalline network and

$Cr_{0.5}Mo_{0.5}$ with cubic crystalline structures, identified with phase qualitative analysis by diffractometric investigations with X-ray radiations. These structures form the films enriched atoms on CoCrMoSi4 experimental alloys surfaces.

Based on SEM micrographs, at 100X magnitudes, after corrosion studies, can affirm that the samples not present strong traces of corrosion, these appeared on surface in the form of tiny dots.

At 1000X BSE magnitude, the micrographs of analyzed samples, highlight fine points by corrosion, oriented on dendrite direction and randomly distributed.

To be used with success in medical applications, it is recommend the testing of the new alloy for determination of mechanical characteristics and biocompatible tests.

5. Conclusions

Adding of silicon to the commercial alloy from CoCrMo system improve the mechanical characteristics, especially hardness, by forming of solid solution with cobalt and chemical compounds, like Co_xCr_y and Cr_xMo_y, also favoring a structure with fine grains.

For establish the electrochemical behavior of the two alloys from Co-Cr-Mo system it is used for experiment the citric acid.

The experimental researches made both on CoCrMo commercial alloy and also CoCrMoSi4 new alloy highlights improvements in the terms of surface, but also mechanical and electrochemical resistance.

These advantages recommend CoCrMoSi4 alloy to be used in different medical applications, his characteristics being higher than the commercial alloy.

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