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The study of the passive film formed on the surface of 316L stainless steel in artificial physiological media

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This work is aimed at providing a better understanding of the biocompatibility of 316L stainless steel in the human body, where various biomolecules are able to bind metal ions and convey them from the surface of orthopaedic implant to various parts of the body. The passivation behavior of orthopaedic 316L implant was studied by associating the electrochemical methods (Differential Pulse Voltammetry and Cyclic Voltammetry) with the surface Mössbauer spectroscopy as a function of type of physiological media; glucydic, proteic and lipidic. Was studied the electrochemical behaviour of steel in three artificial media: Aminosteryl, Intralipid and Kabiven in the concentrations corresponding to the administration dosages. The results were discussed in the context of the formation of passive film which stability strongly depends on the corrosive activity of the physiological media in the order: Aminosteryl < Kabiven < Intralipid.

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Keywords: Artificial physiological media, 316L stainless steel, Electrochemical measurements, Mössbauer spectroscopy

1. Introduction

There have been made electrochemical studies „in vitro" in order to determine the corrosion reactions, which are necessary for foreseeing the behavior of the materials used in implantology. The degradation of metals and alloys in the human body is a combination of effects due to corrosion and mechanical activities. The orthopaedic implants must to resist to weariness corrosion, cleaving corrosion under mechanical tension, friction, pitting, crevasse.

The weariness corrosion represents metal fracture, which appears because of the combined interaction between electrochemical reactions and the mechanical destruction of the metal [1-3]. The corrosion human medium can produce a local attack, which makes different imperfections worse, thus initiating the process of fracturing. The cleaving corrosion under mechanical tension appears when the metal has to resist to the tensional effort and corrosive action of the aggressive metal [4]. The fretting corrosion can appear between the plates and the implant sutures, by destroying the passive films of the implanted metals, film that ensure their resistance to corrosion [5-6]. The crevasse corrosion [7-10] is a local type of corrosion, which appears under the form of pits or crevasses when the metal is partially destroyed by the aggressive medium. The corrosion in pitting [11-16] can be observed only in case of passivable steels and in the presence of halogen or sulphur ions; in saline media like the human body this type of corrosion propagates under the form of small pits, which give off to a significant quantity of metal ions, being very dangerous to the body and a threat to safely using the prosthesis.

The metal ions resulted from the corrosive processes have allergic, carcinogenic and cytotoxic effects. Thus, Takeda [17] advocates that the cytotoxic effect of metals components of the different alloys utilised as implants follows the order: Cr>Co>V>Fe>Mn>Cu>Ni>Mo.

The aim of this work was to investigate the role of the artificial physiological media (Aminosteril, Intralipid, Kabiven) on the surface of the 316L stainless steel by using electrochemical measurements and Mössbauer spectroscopy.

2. Experimental

The corrosion behavior and biocompatibility of metallic biomaterials must be evaluated in order to understand the properties of materials in "vivo". Electrochemical measurements are useful to characterize the corrosion behavior and the interface structure of metal and solution. In order to effect the experimental measurements a standard electrochemical cell has been used with a cylindrical working electrode (surface 1 cm^2) made of 316L stainless steel, a platinum auxiliary electrode with a plate shape (surface 1 cm^2) and a saturated calomel reference electrode (SCE). The electrode made of stainless steel 316L was polished with ultrafine metalographic paper, washed with distilled water, degreased in acetone and dried. Chemical composition of 316L stainless steel employed in this study was (at%): Cr 16-18; Ni 10-15; Mo 2-3; Mn 2; P 0,04; C 0,035; Si 0,03; S 0,03; Fe balance.

The artificial physiological media have the compositions rendered in table1.

Table 1. Chemical composition of Aminosteryl, Intralipid and Kabiven solutions.

Chemical composition	Concentration (g/L)		
	Aminosteryl	Intralipid	Kabiven
Glucose	-	-	67,36
Glycine	15,95	-	8,00
Alanine	15,00	-	16
Serine	-	-	4,66
Proline	15,00	-	6,66
Valine	5,92	-	7,33
Threonine	4,21	-	5,66
Isoleucine	4,67	-	5,66
Leucine	7,06	-	8,00
Aspartic acid	-	-	3,33
Malic acid	8,08	-	-
Lysine monochlorohydrate	7,46	-	-
(lysine)	5,97	-	9,00
Glutamic acid	-	-	5,66
Methionine	4,10	-	5,66
Histidine	2,88	-	6,66
Phenylalanine	4,82	-	8,00
Arginine	10,64	-	11,33
Tyrosine	-	-	0,23
Natrium Glycerophosphate anh.	-	-	5,00
Triptophan	1,82	-	1,90
Soy oil (purified)	-	200	200
Egg phospholipids (purified)	-	12,16	12,16
Glycerole	-	21,96	21,96
NaOH	1,200	→ pH=8	-
KCl	0,683	-	6,00
KOH 85%	0,716	-	-
$MgCl_2 \cdot 6H_2O$	1,017	-	-
$CaCl_2$	-	-	0,73
$MgSO_4$	-	-	1,60
CH_3COONa	-	-	5,00
Distilled water to	1000 mL	1000 mL	1000 mL

The apparatus used was an electronic multimeter of Keithley type, model 2420 3A SourceMeter which can generate and measure currents and/or potentials with different sweeps. The potential of the work electrode was measured as compared to the reference electrode with a digital milivoltmeter of type MS8221C, MASTECH.

In order to register the polarization curves through cyclic voltammetry potential steps of 50mV/10sec. were applied. The mode of potential application in differential pulse voltammetry (DPV) is schematized in figure 1.

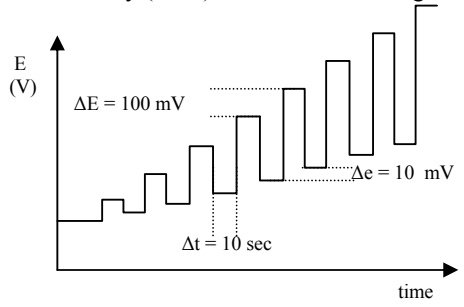

Fig. 1. The diagram of potential generation in differential pulse voltammetry.

Mössbauer spectroscopy was performed at room temperature in conversion electron spectroscopy (CEMS) using a conventional constant-acceleration spectrometer with a ^{57}Co-Rh source. The CEMS measurements were conducted at a high degree of accuracy, ensuring the same geometry of the detection space and the same gas flow rate for all samples. The information obtained by scattering methods is restricted to the layer to which the secondary radiation employed in the measurement can penetrate from the surface of the sample. In the ^{57}Fe Mössbauer spectroscopy the penetration depth maximum of conversion electron is of the order of 250 nm. The parameters of the Mössbauer spectra were calculated using a computer fitting program, which assume a Lorentzian line shape. The isomer shifts were referred to α-Fe.

3. Results and discussion

The biomolecules influence the corrosion processes of metals and metallic alloys and their presence can inhibit or accelerate the corrosion phenomena.

By associating the electrochemical measurements (open circuit potentiommetry, cyclic voltammetry and differential pulse voltammetry) with surface Mössbauer spectrometry was studied the influence of adsorption processes of biomolecules over the 316L bioimplant corrosion and the stability of passive film formed on the alloy surface.

3.1 Electrochemical study

At equilibrium, the open circuit potentiograms registered at room temperature are represented in figure 2 and denotes a passivant behavior of artificial physiological media because of the biomolecules adsorption on metallic surface.

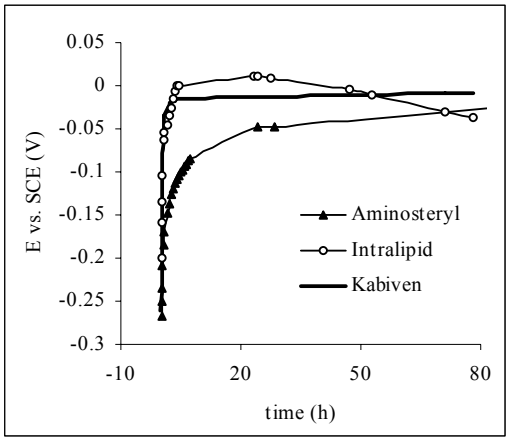

Fig. 2. Open circuit potentiogram of 316L implant in Aminosteryl, Intralipid and Kabiven solutions.

In Aminosteryl solution, the 316L bioimplant presents the negative corrosion potential (E_{corr}=-380 mV) and the higher stabilization time of open circuit potential (7-8 h). This fact is due to the predominant ionic form of aminoacids in the experimental conditions of analysis of

pH=5,5. Aminoacids molecules act by adsorption on the surface of the stainless steel.

The open circuit potentiometric measurements indicate a small time (2-2,5 h) of potential stabilization for 316L implant in Kabiven and Intralipid solutions. After this period of time, the potential of -10 mV is maintained unchanged until the end of experiment. This denotes the formation of a compact and adherent passive film with a great stability.

The cyclic voltammetry is one of the standardized methods used for electrod processes studies and allowed as to register the critical potential of pitting (E_{cp}) and of repassivation against pitting (E_{pp}) for 316L implant in artificial media. Figure 3 shows the cyclic voltammograms of 316L implant in Aminosteryl, Intralipid and Kabiven solutions.

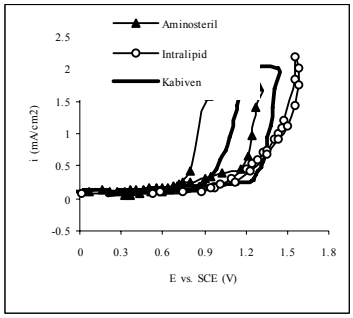

Fig. 3. Cyclic voltammograms of 316L implant in Aminosteryl, Intralipid and Kabiven solutions.

Starting from the open circuit potential in anodic direction of potential with a rate of 50mV/10sec was observed that in the potential domain 0 ÷ 800 mV the values of current densities are small and constant (100 – 140 $\mu A/cm^2$) indicating that a spontaneous passivation of bioimplant in this artificial media. This domain of potentials corresponds to the passivity of steel and is due to a competitive processes of anorganic and/or organic species with the formation of superficial film and to the adsorption processes of biomolecules on the metallic surface.

The resistance of steel to pitting corrosion, which depends to the passivant metals from the alloy content, can be evaluated through the width of hysteresis cycle, measured by difference $\Delta E = E_{cp} - E_{pp}$. Generally, small differences of these potentials indicate a higher resistance to pitting corrosion. Experimentally was observed that the tendency to corrosion in pitting follows this order: Aminosteryl > Kabiven, corresponding to ΔE values: 400>300 mV.

In the case of cyclic voltammogram of 316L implant in Intralipid solution the absence of hysteresis indicate the presence of a very stable passive film with a great capacity of regeneration.

The phospholipids and the soy oil in the Intralipid present great affinity for metal, are adsorbed on its surface and lead to the stoppage of the dissolvation process. In Aminosteryl the induction time for pitting is partly explained by the slow process of the competitive adsorbtion of the aminoacids on the steel surface, due to the difference in the polarization capacity, their influence on the dissolvation kinetics of the metal is changed as compared to the Intralipid. Kabiven contains aminoacids, soy oil and phospholipids. Thus the competitive process of adsorption requires a shift of the critical potential of pitting towards positive values as compared to the one of the Aminosteryl, which should allow the aminoacids to reach a concentration in the double layer capable to destabilize the surface film and to destroy its passivity locally.

Using electrochemical methods more sensitive at small variations of current densities, e.g. differential pulse voltammetry (Fig. 4) was observed a slow depassivation of metallic surface at potentials higher then 600 mV.

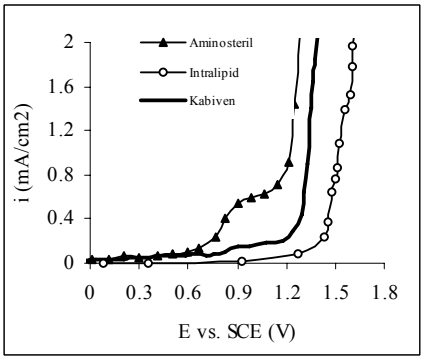

Fig. 4. Differential pulse voltammograms of 316L implant in Aminosteryl, Intralipid and Kabiven solutions.

This indicate that under an increasing overpotentials the accumulation of corrosion products and the presence of aggressive anions like Cl^-, SO_4^{2-}, OH^-, NO_3^- can influence the corrosion processes observed at implant surface. Seeing like cumulative effect, the increase of current densities in the potentials domain 600 ÷ 1200 mV is due to the slow depassivation and to the electrooxidation processes of biomnolecules.

3.2 Mössbauer spectrometric study

The passive films formed on implant surface in Aminosteryl and Intralipid solutions was studied by Mossbauer spectroscopy. In Fig. 5 is presented the CEMS spectrum of an uncorroded steel.

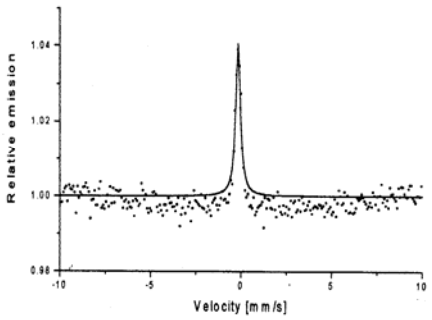

Fig. 5. Conversion electron Mössbauer spectrum of the uncorroded stainless steel (• data; — fit).

The best fitting of the spectrum shows the presence of a single line, typically for stainless steel, which is paramagnetic at room temperature [18-20]. In Figs. 6 and 7 are presented the CEMS spectra of 316L implant in Kabiven and Intralipid solutions.

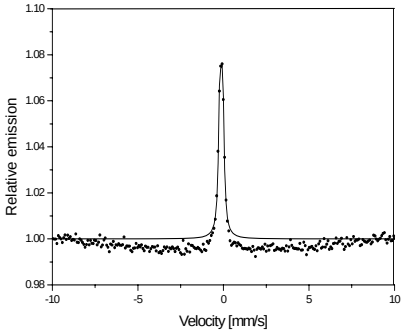

Fig. 6. Conversion electron Mössbauer spectrum of the corroded stainless steel in Aminosteryl solution (• data; — fit).

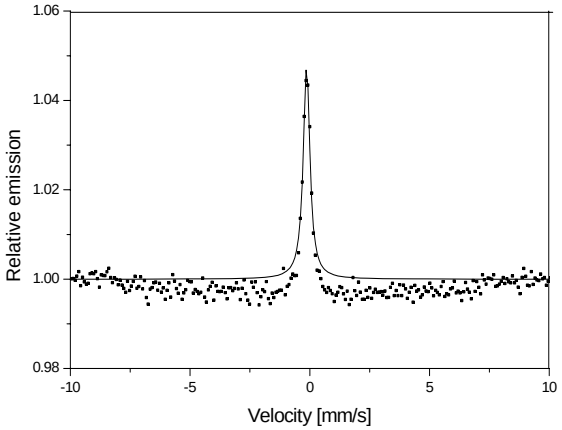

Fig. 7. Conversion electron Mössbauer spectrum of the stainless steel sample after corrosion in Intralipid solution (• data; — fit).

Mössbauer spectrometry confirms and andure the uniformity, compactness and stability of passive film with the possible exception of some iron vicinities where the superficial layer is affected thus showing the presence of pits. The parameters of the line (isomer shift and line width) are the same, within experimental errors, as for a reference sample. This proves the corrosion resistance of our stainless steel in the tested conditions.

The electrochemical parameters of 316L stainless steel in artificial physiological media used are presented in Table 2.

Table 2. Electrochemical parameters of 316L implant in Aminosteryl, Intralipid and Kabiven.

Artificial media	Methode / Parameters							
	OCP			CV				DPV
	E_{in} (mV)	E_f (mV)	T (h)	E_{cor} (mV)	E_{cp} (mV)	E_{pp} (mV)	ΔE (mV)	E_{cp} (mV)
Aminosteryl	-380	-25	7-8	-380	1200	800	400	1200
Intralipid	-195	0	1-1,5	-195	-	-	-	-
Kabiven	-260	-10	2-2,5	-260	1300	1000	300	1300

4. Conclusions

The potentiograms obtained from the open circuit potentiommetry of 316L implant in physiological media indicate the minimum time for potential stabilization in Intralipid solution and to a very stable open circuit potential in Kabiven solution indicating the formation of a compact and stabile passive film. The metallic implant in physiological media passives at a passivation current of 90-100 $\mu A/cm^2$, being stable in the potential domain of 0 ÷ 800 mV.

The data obtained from the cyclic voltammetry (E_{corr}, E_{cp}, E_{pp}) confirm and endure the results obtained through linear electrochemical methods, configuring a critical potential of pitting of 1200 mV (Aminosteryl), 1300 mV (Kabiven), a maximum potential of protection

against pitting of 800 mV (Aminosteryl) and of 1000 mV in Kabiven solution.

The corrosion potentials of –380 mV (Aminosteryl), -195 (Intralipid) and –260 mV (Kabiven) which are lower then the pitting critical potential and the protection potential against pitting, confirms that this alloy is safe for the human body and there is no risk of corrosion in pitting in the conditions of utilization "in vivo" of this alloy, because such potentials cannot be reached in the physiological media in the human body.

The Mössbauer spectrometry proves the uniformity, compactness and stability of the passive films, except for closeness to some iron vicinities, which confirms the apparition of the corrosion in pitting.

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