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The characterization of surfaces of electro polished 316L stainless steel for orthopedic implant applications

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The characterization of the surface of electro polished 316L stainless steel by using poly(O-2-hydroxyethyl) starch (PETA) in physiological serum (PS) is discussed according to electrochemical measurements, scanning electron microscopy and Mössbauer Spectroscopy. The results obtained through polarization curves indicate that critical potential in pitting (E_{cp}) are shifted to a higher values with the increase in PETA concentration; PETA reduces anodic dissolution and also decrease of the corrosion current (i_{corr}). Decrease of the corrosion current (i_{corr}) was associated with a shift of corrosion potential (E_{corr}) to a less negative values. The polarization resistance(R_p) increases for the surfaces which were electro polished in physiological serum in the presence of PETA. Scanning electron microscopy(SEM) shown no evidence of corrosion pits on Surfaces of Electro polished 316L Stainless Steel, but the formation of a thick film on the steel surface was observed. The surface Mössbauer spectrometry proves the uniformity, compactness and stability of the passive films.

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Keywords: 316 stainless steel, Electro polished, SEM, Mössbauer Spectroscopy

1. Introduction

The metal materials used as implants must be biocompatible. Biocompatibility means absence of corrosion or alergic reactions. Corrosion is one of the most important processes that affects the functionality and the duration of medical devices made of metals and their aloys and used as implants. The failures of the implants made of stainless steel were due to significant phenomena of localised corrosion. Corrosion as a test of biocompatibility is a very important factor, which produces metal ions in the biological medium and leads to the degradation of implants [1-11].

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 surface roughness, texture and localized corrosion resistance are the most important characteristics for stabilizing tissue-implant interface. The electro polishing is the method of obtaining extremely smooth surfaces. It is also observed that electro polishing of stainless steel by using some polymers have enhanced localized corrosion resistance as compared to mechanically prepared surfaces. For biomedical applications such as orthopedic implants it is required that near zero defects surface is ensured [12,13] .

Enhancing the biocompatibility of the 316L stainless steel surfaces motivates us to characterize the electro polished surface by using poly(O-2-hydroxyethyl) starch (PETA) and compare those with mechanically polished and physiological serum passivated surface.

In this study the behavior of surface of electro polished 316L stainless steel in physiological serum is discussed according to electrochemical measurements, scanning electron microscopy and Mössbauer Spectroscopy.

2. Experimental

2.1 Electrochemical measurements

For electrochemical measurements a standard cell has been used with a cylindrical working electrode (surface 1 cm^2) made of stainless steel 316L, a platinum auxiliary electrode (surface 1 cm^2) and a calomel reference electrode (SCE). The electrode made of stainless steel 316L was polished with metalographic paper, washed in distilled water, degreased in acetone and dried in warm air. Chemical composition of 316L stainless steel employed in this study is: (wt%): 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. For each determination the samples were introduced time of 30 minutes, at room temperature in following solutions: physiological serum(PS) passivant surface;PS/0.2mM PETA; PS/0.3mM PETA; PS/0.4mM PETA PS/0.5mM PETA. In the potentiostatic polarization measurements several degree of potential of 50 mV/10 s have been applied. The device used was of type Keithley, model 2420 3A Source Meter. Five determinations were made for each solution, taking into consideration the most reproducible responses for the same current densities. The characterization of the electro polished surfaces of 316L stainless steel by using poly (O-2-hydroxyethyl) starch (PETA) in different conscentrations:0.2 mM ; 0.3 mM; 0.4mM; 0.5mM were compared those with only mechanically polished in physiological serum passivant surface. The morphology of steel surface after treatment in the above mentioned solutions was examined by scanning electron microscope (VEGA TESCAN).

2.2 Mössbauer Spectroscopy

Transmission [TMS] and electron conversion

spectroscopy [CEMS] Mössbauer spectroscopy measurements were performed on uncorroded test sample and on sample corroded in a solution of physiological serum. The Mössbauer spectra were recorded at room temperature using a conventional constant-acceleration spectrometer with a ^{57}Co-Rh source. The CEMS measurements [14,15] 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 method (electron conversion) 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 200 nm [15]. The parameters of the Mössbauer spectra were calculated using a computer fitting program, which assumes a Lorentzian line shape. The isomer shifts were referred to α-Fe.

3. Results and discussions

3.1 Electrochemical measurements

The polarization curves of the electro polished surface of 316L stainless steel by using poly(O-2-hydroxyethyl) starch (PETA) and mechanically polished surface were obtained in physiological serum as shown in Fig. 1.

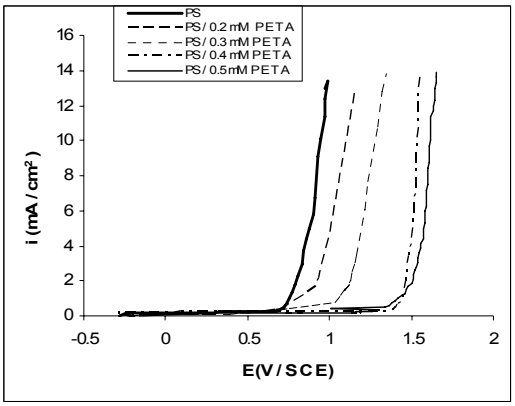

Fig. 1. Polarization curves of electro polished surface of 316L stainless steel by using PETA and mechanically polished surface obtained in physiological serum.

The study of the response of 316L material without and with various surface treatments given by polarizing those in physiological serum(PS) solution simulating the tissue fluid conditions shown a shift of corrosion potential (E_{corr}) to a higher values (Fig. 2). The addition of PETA reduces anodic dissolution and also decrease of the corrosion current (i_{corr}). The results obtained through polarization curves indicate that critical potential in pitting (E_{cp}) are shifted to a higher values with the increase in PETA concentrations (Figs. 1 and 2). This suggests that the PETA acts by adsorption at site on the metal surface and was formed a compact, adherent and uniform layer, which polished the stainless steel surface.

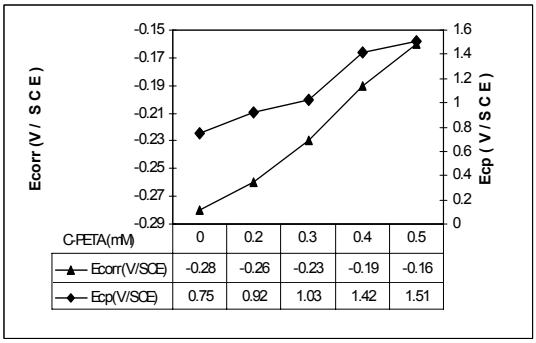

Fig. 2. Variation of corrosion potential(E_{corr}) and critical potential of pitting(E_{cp}) with the concentration of PETA for the 316L stainless steel in physiological serum.

The corrosion current was calculated at intercept of the anodic and cathodic Tafel lines resolving the system of equations which are presented in Fig. 3, for the electro polished surfaces of 316L stainless steel by using poly(O-2-hydroxyethyl) starch (PETA) in different concentrations:0.2 mM; 0.3 mM ;0,4 mM; 0.5 mM and only mechanically polished in physiological serum passivant surface. Decrease of the corrosion current (i_{corr}) was associated with a shift of corrosion potential (E_{corr}) to a less negative values ; the i_{corr} values decrease in the presence of various concentration of PETA (Fig. 3); Tafel lines of nearly equal slopes were obtained (Fig. 3).

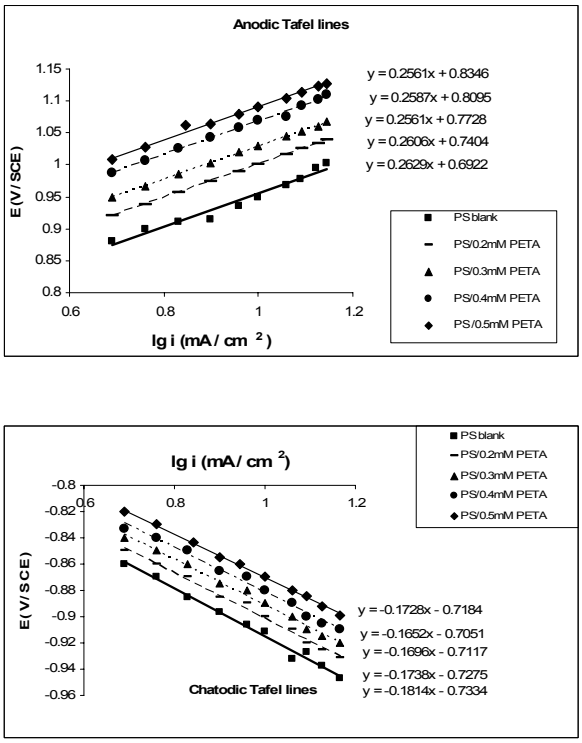

Fig. 3. Tafel diagram of electro polished surface of 316L stainless steel by using PETA and mechanically polished surface obtained in physiological serum.

The polarization resistance (R_p) represent the slope(dE/di) $\eta \rightarrow 0$ (η is over potential) of lines from Figure 4. From Fig. 4 it can be observed that R_p increases for the surfaces which were electro polished in physiological serum in presence of PETA.

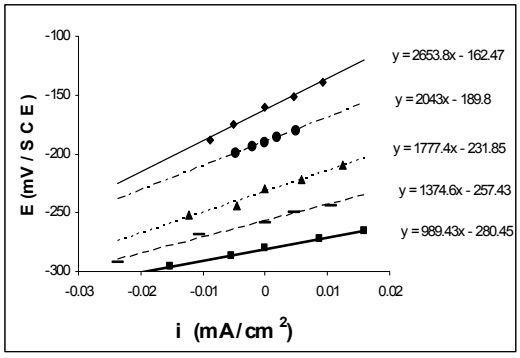

Fig. 4. *Polarization resistance(R_p) of electropolished surface of 316L stainless steel by using PETA and mechanically polished surface obtained in PS.*

The data obtained for i_{corr} and R_p are presented in Fig. 5.

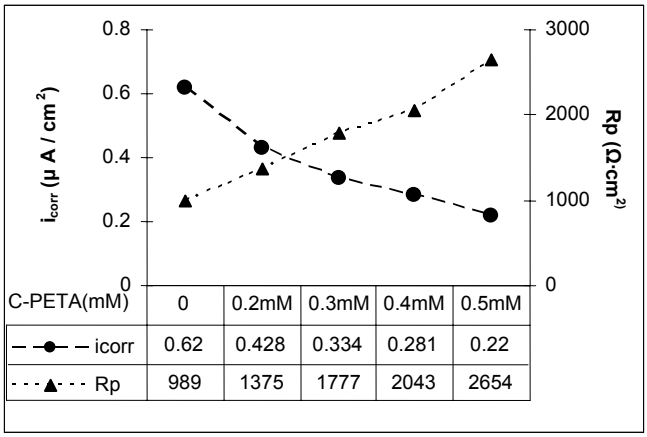

Fig. 5. Variation of corrosion current(i_{corr}) and polarization resistance(R_p) with the concentration of PETA for the 316L stainless steel in physiological serum.

The degree of coverage (θ) with a compact layer of PETA which electro polishing of surface of 316 stainless steel were calculated with the following relation:

$$\theta = \frac{i'_{corr} - i_{corr}}{i'_{corr}} \quad (1)$$

i'_{corr} and i_{corr} are the corrosion current density for the surface of 316L stainless steel in absence and presence of PETA, respectively obtained by extrapolation of the anodic and cathodic Tafel lines to the corrosion potential. The degree of coverage increases with PETA concentration and decreases with increasing in the corrosion current density (Fig. 6) .

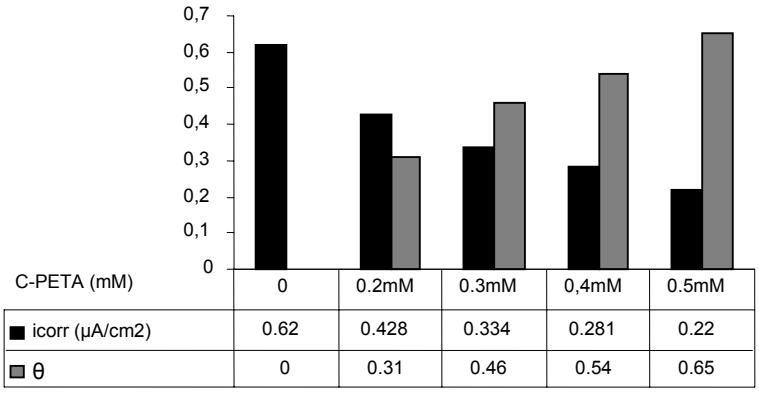

Fig. 6. Variation of corrosion current(i_{corr}) and degree of coverage with the concentration of PETA for the 316L stainless steel in physiological serum.

3.2 Application of adsorption isotherm

Studying the surface of 316L stainless steel we reached the conclusion that the experimental data characterize an adsorption isotherm of Langmuir type expressed by the relation 2.

$$\frac{\theta}{1-\theta} = K \cdot c \quad (2)$$

where θ is degree of coverage, K is the equilibrium constant of the adsorption-desorption process, c is the concentration of the PETA.

The data gave straight lines with slopes of K. It can be observed that K has a high value of 3583 M^{-1} L. Figure 7 illustrates the results of a Langmuir diagram for corrosion inhibition. The equilibrium constants K vary towards the same direction, in the sense that higher values of K imply a better adsorption.

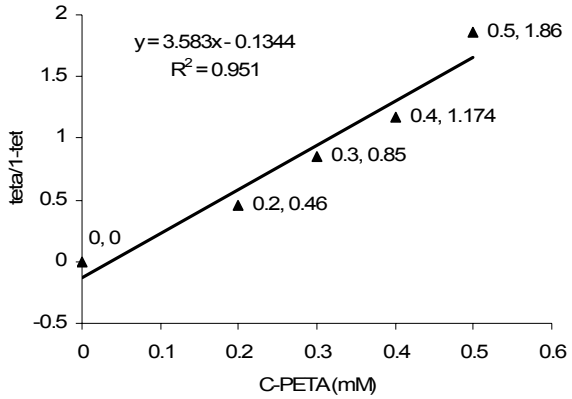

Fig. 7. The results of a Langmuir diagram in case of electro polished surface of 316L stainless steel by using PETA obtained in physiological serum, at room temperature.

The standard free energy of adsorption (ΔG^0_{ads}) can be calculated from the equation 3.

$$K = \frac{1}{55.5} \cdot \exp\left(-\frac{\Delta G^0_{ads}}{R \cdot T}\right) \quad (3)$$

where 55.5 is the molar concentration of water in the solution, R is the universal gas constant, T is temperature (K). The values of ΔG^0_{ads} are negative(-30.2 kJ/ M), which shows that the process of adsorption is spontaneous.

3.3 Scanning electron microscopy

SEM examination of stainless steel surface corroded in physiological serum solution in absence and presence of PETA was carried out (Figure 8). In the absence of PETA the data showed that the surface was covered with a large number of pits, as shown in figure 8a. In the presence of PETA the micrograph shown no evidence of corrosion pits, but the formation of a thick film on the steel surface was observed (Fig. 8c). The results are due to the adsorption of PETA molecules around the corrosion pits in the early stage of formation (initiation and propagation). Also it can be concluded that there is a competitive adsorption between the PETA molecules and aggressive anion (Cl^-) on surface of stainless steel.

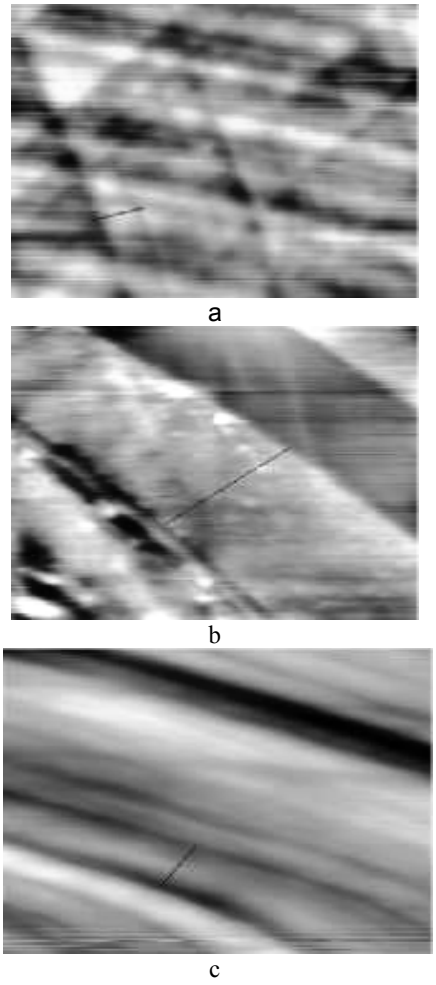

Fig. 8. Scanning electron micrograph of the 316L stainless steel surface treated in: (8a) PS; (8b) PS/0.4 mM PETA; (8c) PS/0.5 mM PETA.

It can be concluded that:

-the increase in PETA concentrations leads to a decrease in the corrosion current for both examined samples, indicating that the presence of PETA retards the general corrosion rate of samples in physiological serum solution. This suggests that the inhibition of the 316L stainless steel corrosion in the presence of PETA occurs by adsorption at site on the metal surface.

- the polymeric compounds electro polishing the surface of 316L stainless steel by adsorbing at the metal/solutions interface. The main types are electrostatic adsorption, chemo-sorption and adsorption resulting in π bond interaction with the metal.

- chemosorption of macromolecules on a metal involves the displacement of water molecules from the metal surface and the eventual charge sharing or even actual charge transfer.

-the molecular structure, type and concentration of PETA, mode of adsorption and chemical nature of "anchoring" and the composition of stainless steel determine the degree of coverage θ .

3.4 Mössbauer Spectroscopy

All spectra (TMS and CEMS) show a central broad line, typical for austenitic stainless steels. We will present and discuss the CEMS spectra. We used for them 3 variants for data fit: single line, doublet and two lines. The best fitting of the spectra was obtained for single line. The parameters of this line for uncorroded mechanically polished surface sample of 316L stainless steel (Figure 9) were following: position –0,11 mm/s; width 0,41 mm/s; effect 5,84%. The best fitting of the CEMS spectra obtained for mechanically polished sample in physiological serum(PS) passivant surface (Fig. 10) and electropolished sample in physiological serum/0.5mM PETA, respectively (Figure 11) gives, practically, identical parameters within experimental errors excepting the effect.

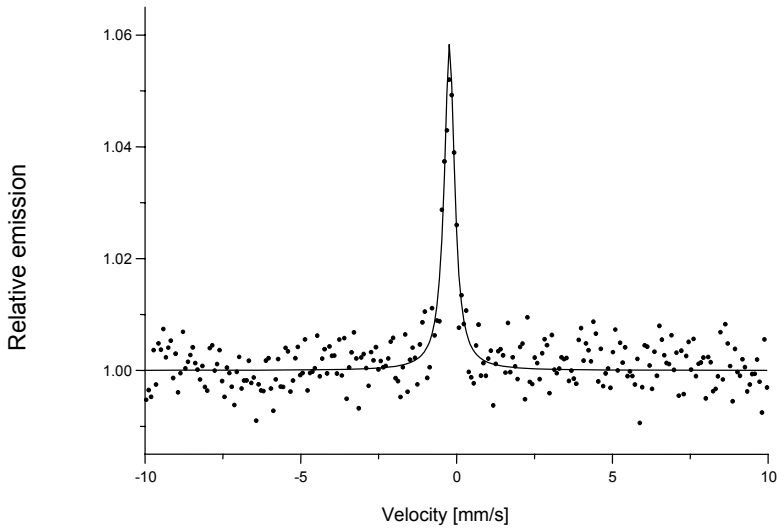

Fig. 9. Conversion electron Mössbauer spectra of uncorroded mechanically polished surface sample of 316L stainless steel (• data; — fit).

This means that the surface was, practically, insignificantly changed during the corrosion process. Mössbauer measurements do not point out micro-structural changes in the investigated samples. The effect decreases slowly, especially for electro polished sample corroded in physiological serum. This proved the presence of a thin superficial layer on corroded samples. The Mössbauer spectroscopy proves, thus, the uniformity, compactness and stability of the surface passive films.

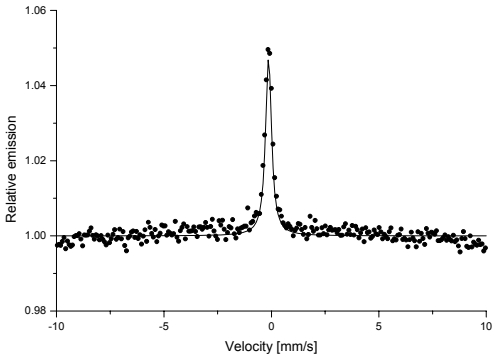

Fig. 10. Conversion electron Mössbauer spectra of corroded mechanically polished surface sample of 316L stainless steel in physiological serum (• data; — fit)

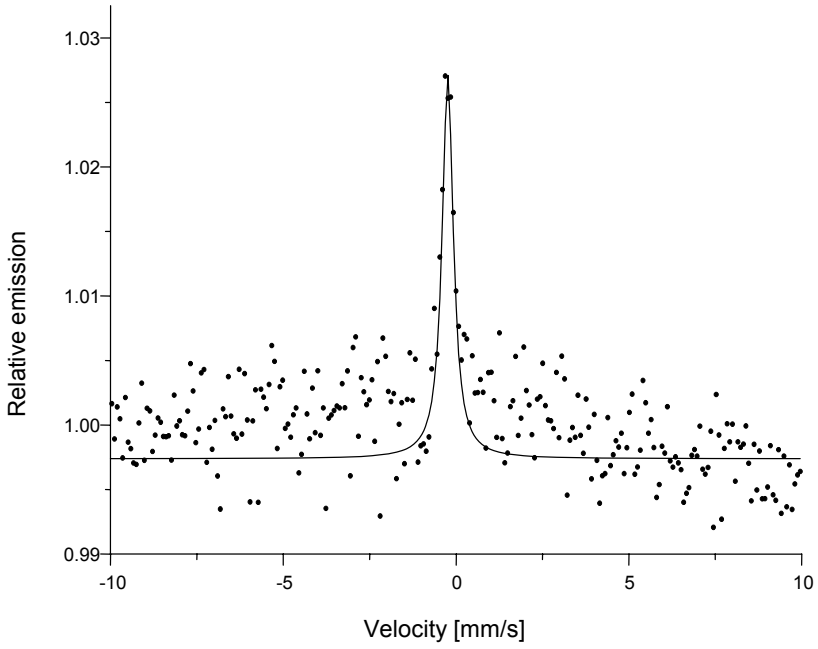

Fig. 11. Conversion electron Mössbauer spectra of electro polished surface sample of 316L stainless steel corroded in physiological serum /0.5 mM PETA (• data; — fit).

4. Conclusions

The polymeric compounds as an example PETA electro polishing the surface of 316L stainless steel by adsorbing at the metal/solutions interface.

The study of the response of 316L material without and with various surface treatments given by polarizing those in physiological serum(PS) solution simulating the tissue fluid conditions shown a shift of corrosion potential (E_{corr}) and critical potential in pitting (E_{cp}) to higher values. The addition of PETA reduces anodic dissolution and also decrease of the corrosion current (i_{corr}). This suggests that the PETA acts by adsorption at site on the metal surface and was formed a compact, adherent and uniform layer, which polished the stainless steel surface. The results of scanning electron microscopy (SEM) are due to the adsorption of PETA molecules around the corrosion pits in the early stage of formation (initiation and propagation). In the presence of PETA the micrographs show no evidence of corrosion pits, but the formation of a thick film on the steel surface.

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