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CORROSION BEHAVIOR OF STAINLESS STEEL COATED WITH POLY(VINYL ALCOHOL) FILM DOPED WITH STRONTIUM RANELATE

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ABSTRACT. The aim of this paper is to investigate the role of the poly (vinyl alcohol) film, doped with strontium ranelate, on the corrosion behavior of stainless steel in contact with physiological serum. The corrosion behavior was studied using two electrochemical methods: the Tafel polarization and the polarization resistance. The small current densities and high polarization resistances were obtained for stainless steel surfaces covered with PVA doped with strontium ranelate, electrochemically deposited from 0.1 M HCl solutions. It was found that the protection efficiency increased when stainless steel was electrochemically modified with strontium ranelate.

Keywords: *poly(vinyl alcohol) film, strontium ranelate, protection efficiency, stainless steel corrosion*

INTRODUCTION

Metals and their alloys are widely used as biomedical materials and they became indispensable for medical field. One of the most important properties of the biomaterials is their safety. Therefore, corrosion resistant materials are required, such as stainless steel [1-6].

Poly(vinyl alcohol) (PVA), a water-soluble synthetic polymer, has been produced for many industrial applications. It is used as emulsifier, colloid stabilizer, sizing agent, protection colloid, replacing material for leather, soil conditioner, coating in the textile, adhesives and house building industries etc. All these end-uses of PVA are based on its exceptional properties such as: water solubility, good thermal stability, good film forming, high tensile strength, no static charge, resistance to organic solvents and oils, non toxicity and non carcinogenity and good biodegradability [7-9].

The surface roughness texture and localized corrosion resistance are the most important requirements for stabilizing stainless steel / medium interface. This inconvenient can be surpassed by covering the metallic

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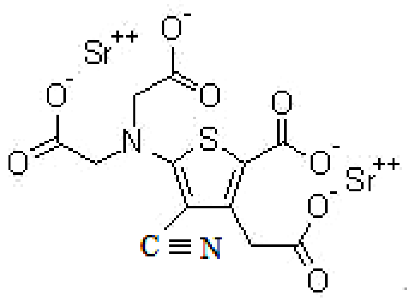
substrate with polymer coatings. The use of polymers as corrosion inhibitors has attracted considerable attention. Polymers such as poly(vinyl pyrrolidone), polyethylenimine, polyaniline and polysiloxane, poly(ethylene glycol) methyl ether have been widely investigated [10-13].

A new therapeutic agent, strontium ranelate (Osseor), was recently introduced for the treatment of postmenopausal osteoporosis [6]. It contains two strontium stable atoms connected to an organic core represented by ranelic acid.



5-[Bis(carboxymethyl)amino]-2-carboxy-4-cyano-3-thiopheneacetic acid strontium salt

It could be mentioned that approximately 26 strontium salts were investigated during the development of this agent and the ranelate salt was selected due to its physical and chemical characteristics (purity, solubility, chelating properties absence, stability) and, not lastly, due to the safety.

Multiple evidences showed that strontium ranelate has various effects in boned metabolism. Its usage in osteoporosis treatment is based on a double action mechanism: increasing bone formation and decreasing bone resortion [6].

The aim of this paper is to investigate the role of the poly (vinyl alcohol) film, doped with strontium ranelate, on the corrosion behavior of stainless steel in contact with physiological serum.

RESULTS AND DISCUSSION

Linear sweep voltammetry

The polarization curves of the stainless steel in 0.1 M HCl in absence and in presence of strontium ranelate, after the deposition of poly (vinyl alcohol) film from 2% PVA solution (by two and three immersions) are presented in Figure 1.

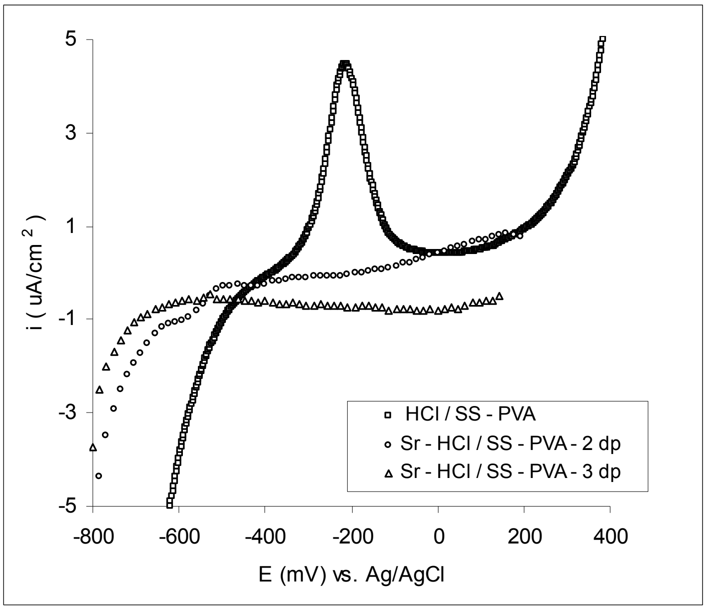


Figure 1. The polarization curves of the modified stainless steel surface with PVA film in 0.1 M HCl solution in absence and in presence of strontium ranelate (potential scan rate, 100 mV / s)

From Figure 1 it can be noticed that in the case of poly(vinyl alcohol) film the polarization curve exhibits three domains: the first part is an active region between -600 mV and -200 mV, the current densities reaching high values; then the curve presents a passive region until approximately 200 mV, while the current densities values are maintained constantly at zero. This is followed by a transpassive domain. In case of PVA films doped with strontium ranelate the active region is shifted between -800 mV and -600 mV, and is followed by the surface passivation, indicating the electrodeposition of strontium.

Tafel polarization

For the modified stainless steel surface with PVA film and PVA film doped with strontium ranelate, deposited at different pulling speeds (0.045 cm/s and 0.065 cm/s) and electrodeposited from 0.1 M HCl solution, the corrosion tests were recorded in physiological serum (PS).

The anodic and cathodic Tafel lines corresponding to the stainless steel corroded in physiological serum solution were represented in figure 2.

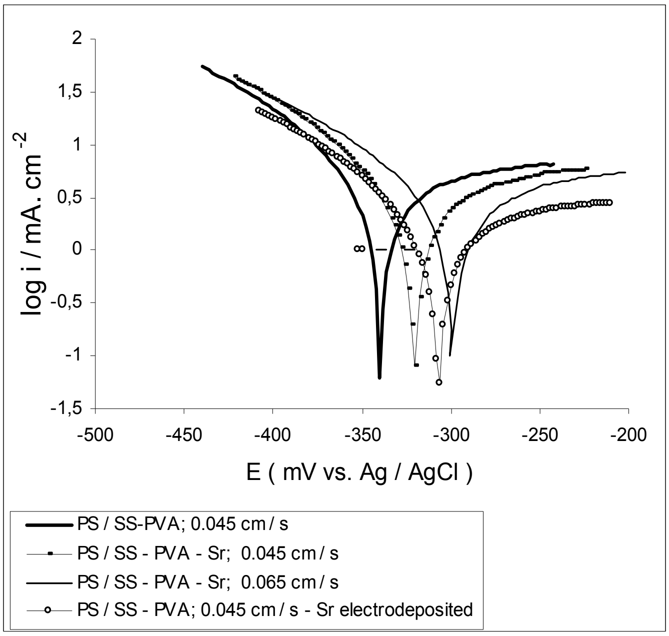


Figure 2. Tafel plot of the modified stainless steel surfaces with PVA and Sr-PVA films, corroded in physiological serum solution (potential scan rate of 10 mV/s)

From Figure 2 it can be noticed that the corrosion potential *(E_{corr})* shifts to less negative values when the speed of pulling from 2 % PVA solutions containing 1 % strontium ranelate increases. At the same time, the current densities decrease for the modified surfaces with Sr-PVA film. Sr-PVA film increased both the cathodic and anodic overvoltages and caused mainly a parallel displacement to the more negative and positive values, respectively. The corrosion current density ($i_{corr.}$) decreased in the case of Sr-PVA film, with increasing the pulling speed for deposition of PVA, and shifts towards lower values for the modified stainless steel surface with PVA – strontium ranelate electrodeposited, which indicates that the degree of protection depends on the film type and deposition method (Figure 3).

The protection efficiency *(P)* of Sr-PVA film was also determined from the polarization measurements according to the following equation:

$$\mathbf{P} = \frac{\mathbf{i'_{corr} - i_{corr}}}{\mathbf{i'_{corr}}} \times \mathbf{100} \tag{1}$$

where i'_{corr} and i_{corr} are the corrosion current densities for stainless steel in presence of PVA film and in presence of PVA doped with strontium ranelate film, respectively. These values were obtained by extrapolation of the anodic and cathodic Tafel lines to the corrosion potential.

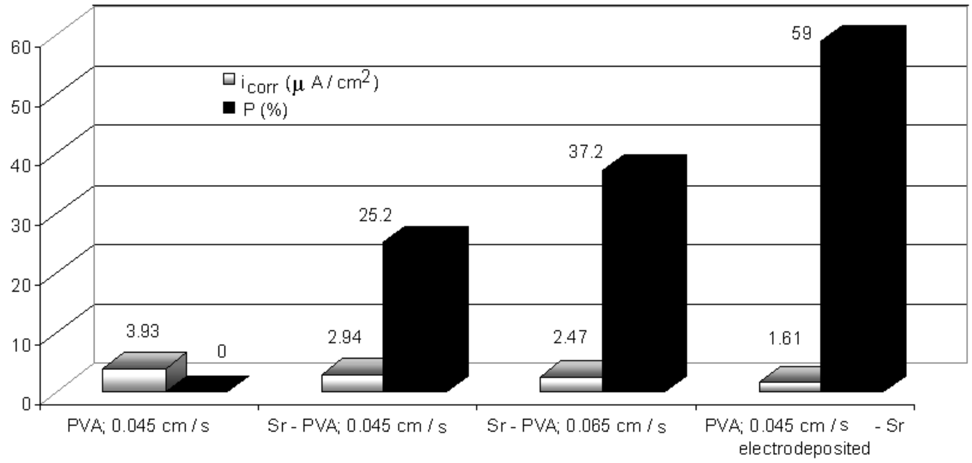


Figure 3. Variation of corrosion current density and protection efficiency (estimated using Tafel polarization) on the deposition method of Sr-PVA films.

Polarization resistance technique (Stern Method)

The polarization curves corresponding to the potential domain close to the corrosion potentials were recorded with a scan rate of 10 mV/s. Their linearizations were performed in the domain of overvoltages values of ± 10 mV (Figure 4).

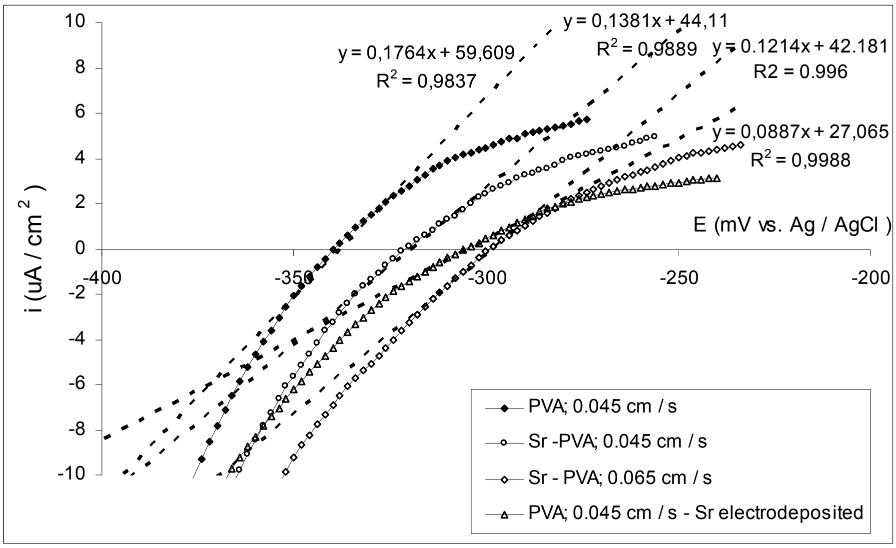


Figure 4. Polarization resistance (R_p) of the stainless steel surfaces modified with PVA and Sr-PVA films, corroded in physiological serum solution.

The slopes $(di/dE)_{E \to Ecorr}$ of the lines from Figure 4, represent the polarization conductance. Polarization resistance (R_p, kΩ.cm^2) was calculated using relation 2:

$$\left(\frac{\mathbf{di}}{\mathbf{dE}}\right)_{\mathbf{E \to E_{corr}}} = \frac{\mathbf{1}}{\mathbf{R_p}} \tag{2}$$

As it can be seen from figure 4, the polarization resistances increase with the increase of stainless steel pulling speed. The polarization resistance for the modified surfaces with Sr-PVA film reaches the highest values for the surfaces modified with PVA deposited at 0.045 cm/s pulling speed and for the surfaces where strontium ranelate was electrodeposited.

The protection efficiency *(P')* of Sr-PVA film was calculated according to the following equation:

$$\mathbf{P'} = \left(\mathbf{1} - \frac{\mathbf{R_p}^{\mathbf{0}}}{\mathbf{R_p}}\right) \times \mathbf{100} \tag{3}$$

where R^o_p is polarization resistance of the unmodified stainless steel electrode and R_p is the polarization resistance of stainless steel electrode modified with PVA doped with strontium ranelate. The numerical values of the polarization resistances (R_p) and protection efficiencies *(P')* are presented in Figure 5.

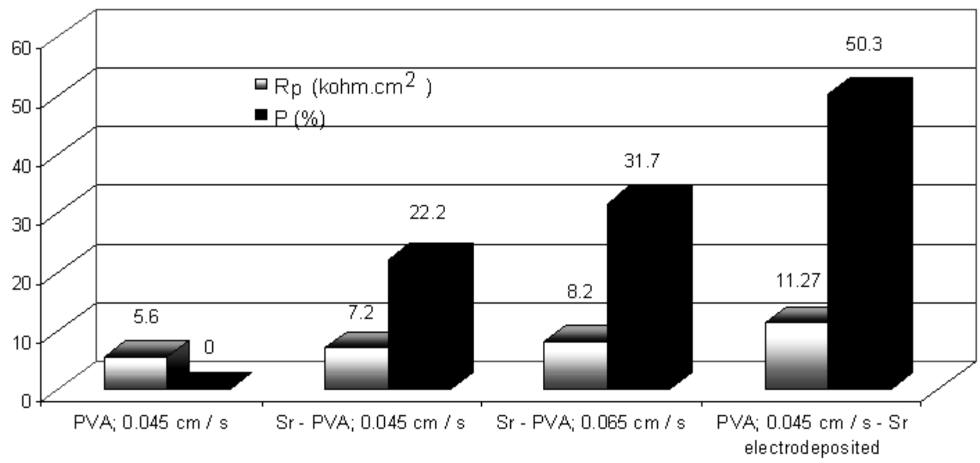


Figure 5. Variation of polarization resistance and protection efficiency (using polarization resistance technique) on the deposition method of Sr-PVA film.

The values of protection efficiency obtained from Tafel polarization and resistance polarization technique were found in good agreement.

CONCLUSIONS

The aim of this paper was to investigate the role of the poly (vinyl alcohol) film, doped with strontium ranelate, on the stainless steel corrosion behavior in contact with physiological serum.

The corrosion current density ($i_{corr.}$) decreased in the case of Sr- PVA film, with the increase of the pulling speed for PVA deposition, and shifts to lower values for stainless steel surfaces modified with electrodeposited PVA – strontium ranelate. This behavior indicates that the protection degree depends on the film type as well as on the deposition method.

The polarization resistance for the modified surfaces with Sr-PVA film reaches the highest values for the surfaces modified with PVA deposited at 0.045 cm/s pulling speed and for the surfaces where strontium ranelate was electrodeposited.

The values of protection efficiency obtained from Tafel polarization are in good agreement with those provided by the technique of resistance polarization.

EXPERIMENTAL SECTION

Films were deposited on the stainless steel surfaces from 2 % PVA solutions containing 1 % strontium ranelate with a DipCoater at different speeds of pulling: 0.045 cm/s and 0.065 cm/s. Also, PVA films were initially deposited with DipCoater through consecutive immersions, 2 dips or 3 dips, with the same pulling speed (neclar!!). Then these were doped with strontium from 0.1 M HCl solutions containing 1% strontium ranelate by using linear sweep voltammetry. Poly (vinyl alcohol) was obtained from Fluka.

The chemical composition (wt %) of the stainless steel employed in this study was determined by using SEM/EDS analysis (Figure 6). The stainless steel contains Cr 18-20 and Ni 8-10.

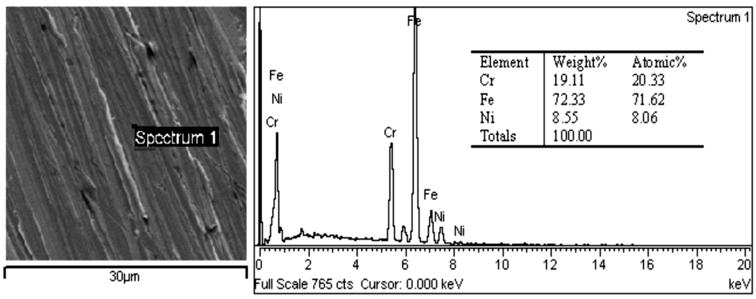


Figure 6. SEM/EDS analysis of the 304L stainless steel sample

For the electrochemical measurements, Tafel polarization and polarization resistance technique were used. For electrochemical measurements a standard cylindrical cell (made of glass) has been used, provided with a plate working electrode (surface 2 cm2) made of stainless steel, a platinum auxiliary electrode (surface 1 cm2) and an Ag/AgCl reference electrode. The stainless steel electrode was polished with metallographic paper, washed in distilled water, degreased in acetone and dried in warm air. A VoltaLab 40 potentiostat connected to a personal computer, using VoltaMaster 4 as software, were used to perform electrochemical measurements in physiological serum solution.

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