

Electropolishing and chemical passivation of austenitic steel

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Received 08.10.2008; published in revised form 01.12.2008

Materials

ABSTRACT

Purpose: The aim of the paper is investigations a dependence between the parameters of the electrochemical treatment of austenitic steel and their electrochemical behavior in Tyrod solution.

Design/methodology/approach: Specimens (rode 30 mm × ø1 mm) were to give in to the surface treatment – mechanically polishing, electrolytic polishing and passivation with various parameter. Electrochemical investigations concerning the corrosion resistance of austenitic steel samples were carried out by means of the potentiodynamic and electrochemical impedance spectroscopy method.

Findings: The analysis of the obtained results leads to the conclusion that chemical passivation affects also the chemical composition of the passive layer of steel and changes its resistance to corrosion. Electrolytic polishing improves corrosion resistance, as can be proved by the shift of the value of the corrosion potential and breakdown potential of the passive layer and the initiation of pittings.

Research limitations/implications: The obtained results are the basis for the optimization of anodic passivation parameters of the austenitic steel as a metallic biomaterial. The future research should be focused on selected more suitable parameters of the electrochemical impedance spectroscopy test to better describe process on the solid/ liquid interface.

Practical implications: In result of the presented investigations it has been found that the best corrosion resistance can be achieved thanks to the application of electrolytic polishing of the steel in a special bath and chemical passivation in nitric (V) acid with an addition of chromic (VI) acid temperature $t = 60^{\circ}\text{C}$ for one hour.

Originality/value: The enormous demand for metal implants has given rise to a search for cheap materials with a good biotolerance and resistance to corrosion. Most commonly used are steel implants assigned to remain in the organism for some limited time only. It was compare two electrochemical methods: potentiodynamic polarization and electrochemical impedance spectroscopy.

Keywords: Metallic alloys; Biomaterials; Corrosion; Surface treatment; Electrical double layer

1. Introduction

Corrosion is a process in which metal deteriorates through a chemical reaction with the environment. Resistance to corrosion of metallic materials depends among other parameters on the surface state - chemical composition, heterogeneity, wettability, roughness. Predominantly aim of the surface treatments is to improve the passive layer by changing its composition, structure and thickness [27,30]. Type 316L stainless steel is the most popular metal for use as osteosynthesis plates for orthopaedic applications.

This popularity owes a satisfactory combination of good mechanical properties and reasonable cost. But during exposure to physiological environments the protective surface oxide inherent to 316L is not stable. Annealing, pickling, polishing and passivation have been developing to increase the corrosion resistance of austenitic steel [21,24].

Of great importance is, therefore, the morphology of the implant of the austenitic steel surface [14,16,20].

It is of advantage to polish them electrolytically, in result of which the surface layer with a deformed crystalline structure, formed in the course of mechanical treatment, is removed [18,19].

Metallic materials used to produce implants ought to display adequate mechanical properties and must be safe for the human organism; they must not exert any toxic effect on the tissue and cause allergic reactions of the organism. The fundamental criterion is their resistance to corrosion which may deteriorate with the corrosion products present.

These requirements are met to a large extent by austenitic alloy steels, chromium-nickel steels with an addition of molybdenum. The presence of higher molybdenum enhances the corrosion resistance. AISI 316L stainless steel has low carbon and high nickel and chromium. Mainly, these steels are used as implants [24].

Molybdenum hinders the active dissolution of steel, decreases the critical current of its passivation, and thus promotes the passivation. For this reason the chromium-nickel molybdenum steels of type AISI 316L, the Polish equivalent of which is 00H17N14M2A have found wide application as materials in the medical industry [21].

The deformation of passive layer causes the high electrochemical activity of the surface, and thus also its considerable susceptibility to corrosion. The technological process of producing metal implants comprises also electrolytic polishing and passivation of their surfaces.

An advantage of electrolytic polishing is, therefore, the fact that besides changes in the smoothness of the surface also its physico-chemical properties are improved [11,13,17,22].

The roughness of the metallic materials surface, describing the real surface structure, is an important parameter in the electrochemistry of solids state. Two parallel layers of charge are formed which are the surface itself and the layer of oppositely charged ions near the surface. This structure is called the electric double layer, which finds many important applications related to the electric field interfaces. The electric double layer and adsorption characteristics are extensive and very interesting phenomena [9,12,25].

The aim of our investigations was to determine the influence of the parameters of the process of electrolytic polishing and to test the corrosion resistance and capacity of electric double layer of polished and passivated austenitic steel samples by means of AC and DC electrochemical methods.

2. Materials and methods

Austenitic stainless steel AISI 316L type Cr – Ni – Mo with the symbol 00H17N14M2A was used during the course of this investigation, and its chemical composition is given in Table 1. All specimens (rod 30 mm × ϕ 1 mm) were given to cleaning procedures, and after the surface were treated with various parameter summarized in Table 2.

Table 1.
Nominal chemical composition of AISI 316L stainless steel

Element	Atomic concentration, %
C _{max}	0.018
Si _{max}	0.55
Mn _{max}	1.75
S _{max}	0.001
P _{max}	0.018
Cr	17.8
Mo	2.74
Ni	14.29
N _{max}	0.064
Cu _{max}	0.08

Table 2.
Parameters of surface treatment and corrosion parameters obtained in Tyrode solution

Treatment	Specimen				
	A	B	C	D	E
	Mechanically polished	Elektro-polished	Passivated in CrO ₃ +HNO ₃ solution	Passivated in CrO ₃ solution	Passivated in HNO ₃ solution
Corrosion potential, E _{cor} , V	-0.533	-0.324	0.075	-0.519	-0.281
Polarization resistance R _p , k Ω	4.32	11.26	27.11	1.151	12.45
Polarization resistance from EIS R _p , k Ω	5.7	11.8	22.21	3.11	9.1
Corrosion rate V _{cor} , mm/year	0.04	0.119	0.00412	0.051	0.0957

An applied solution in electrolytic polishing consisted of a phosphoric-sulphuric acid solution with an addition of organic substances. The process of chemical passivation was carried out in the experimentally determined conditions described in reference [6,28]. This special bath has been developed at the Department of Chemistry and Inorganic Technology, Silesian University of Technology [5]. The setup of electrolytic polishing of samples were presented in Figure 1.

The morphology of the microstructure was determined by scanning electron microscope (SEM).

The surface texture measurements were performed on a stylus profilometer (Taylor Hobson Surtronic 3+). The stylus was moving in a direction perpendicular to the direction of the samples cutting. The roughness parameter considered were Ra.

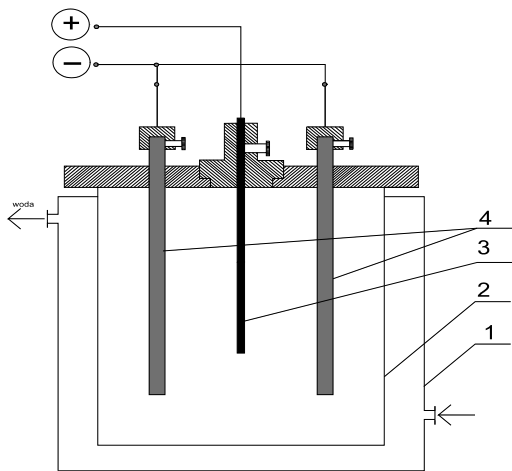


Fig. 1. The electrochemical cell for electrolytic polishing process: 1-water jacket connected with thermostat, 2- electrochemical cell, 3 -sample (anode), 4-cathode

The Tyrode solution with pH = 6.9 at a temperature of 37°C prepared from analytical grade reagents and deionized and demineralized water, was used [5,6]. The Haber-Luggin capillary was attached together with a calomel electrode (SCE) as a reference electrode and platinum plate served as an auxiliary electrode.

The samples were fixed in a brass holder screwed into a Teflon socket and sealed with silicon rubber. After having been fixed in the socket, the sample was rinsed with methanol and then placed in the lateral socket of the electrolyser and subjected to potentiostatic tests, Figure 2 [22,23].

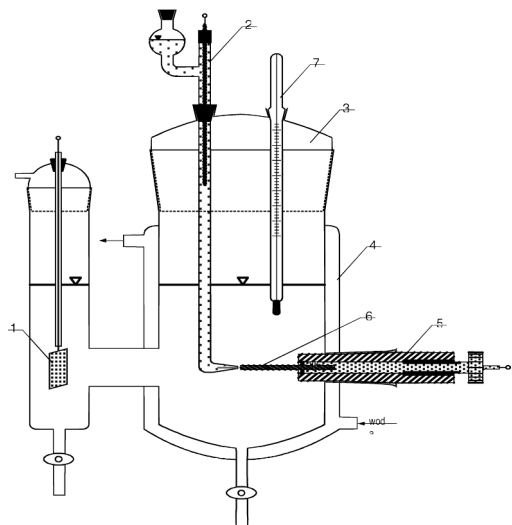


Fig. 2. Scheme of cell for electrochemical test: 1-auxiliary electrode, 2- Habber – Luggin capillary with reference electrode, 3- covering plate, 4- water jacket, 5- branch piece with holder, 6- working electrode (sample), 7- thermometer

The electrochemical behavior of investigated alloy was identified with the aid of polarization curves registration using

anodic polarization technique (AP) and electrochemical impedance spectroscopy technique (EIS).

Electrochemical measurements were performed at open circuit potential after holding the samples for 60 minutes in the solution by means of an Eco Chemie B.V PGSTAT30 Potentiostat and their accompanying software: GPES (General Purpose Electrochemical System) and FRA (Frequency Response Analyzer System) [1,2].

A fitting of obtained data were carried out [3,6,7,10, 26].The frequency range were between 50 kHz and 0.1 Hz with perturbation amplitude of 0.05 mV.

A potentiodynamic polarisation scan was performed after EIS measurement. The samples were scanned at the rate 0.05 V/sec from negative (cathodic) overpotential and ending at positive (anodic) overpotential. Double layer capacitance were measured as a function of potential from -0.5 V to 1 V with step potential 0.05 V.

The passivation ability and corrosion resistance of alloy have been determined basing on the measurement of the following values:

- corrosion potential E_{corr} [mV],
- polarization resistance R_p [kΩ]

The surface area (SA), equivalent weight (EW) and the density (D) of electrode material are used to calculate the corrosion rate in terms of current density (i_{corr}) and millimeters/year (v_{corr}), Equation 1 and 2.

The Tafel plot extrapolated to the zero current/potential gives a set of co-ordinates relating to E_{corr} and i_{corr} . The i_{corr} value may be calculated using the Tafel constants ($\beta_a + \beta_c$) and R_p .

The value for β_a can be determined by taking the slope for the anodic portion of the curve and β_c for the corresponding cathodic part.

Using the R_p value and the Stern-Geary equation the value for i_{corr} can be determined. The corrosion rate can then be calculated from this value in mm per year.

$$I_{corr} = i_{corr} / SA, A/cm^2 \quad (1)$$

$$v_{corr} = 3272 \cdot i_{corr} \cdot EW / (SA \cdot D), mm/year \quad (2)$$

3. Results

The quality of the grounded, polished and passivated surface was observed in the surface roughness tester (Surtronic), and were observed in the scanning electron microscope before and after passivation process, Figures 3 and 4. The ground surface - average roughness $R_a = 0.31 \mu m$ and passivated surface - average roughness $R_a = 0.11 \mu m$.

The average polarization resistance of this sample was equal to $R_p = 27.11 k\Omega$ and the average corrosion rate was equal to $v_{corr} = 0.00412 mm/year$. The information concern corrosion parameters are present in Table 2. The most electronegative potential was observed for mechanically polished sample, equal to $E_{corr} = -0.533 V$. The average polarization resistance of this sample was equal to $R_p = 4.32 k\Omega$.

The shape of the anodic polarisation curves were similar for samples after grounding, electropolishing and passivating. The anodic polarization curves of samples obtained in Tyrod solution are given in Figure 5. It was observed the most noble corrosion potential, equal to $E_{corr} = 0.075 V$ for passivated in $CrO_3 + HNO_3$ solution.

Results have been presented in Bode plots - a combination of a Bode magnitude plot and Bode phase plot. The Bode plots are

used because it has been argued that they are more informative than the conventionally popular Nyquist plots [15].

EIS spectra typical for tested samples are presented shown in Bode plot in Figure 6. It can be observed that the modulus and the phase angle of the impedance are strongly depend on the surface pretreatment.



Fig. 3. The surface fractography of the surface of as received sample before the corrosion test, magnitude 200x

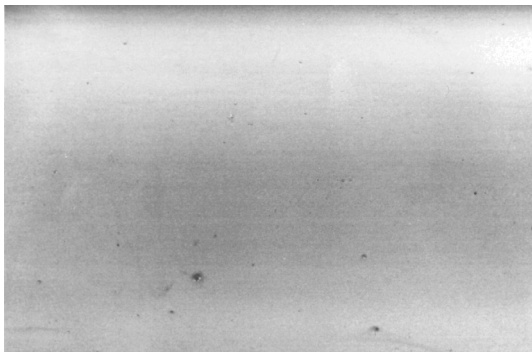


Fig. 4. The surface fractography of the electropolished and passivated surface of sample before the corrosion test, magnitude 200x

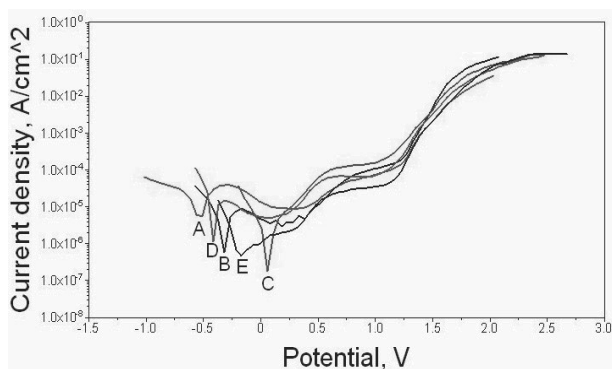


Fig. 5. Potentiodynamic polarization curves corresponding to the mechanically polished (A), electropolished (B), passivated in HNO₃ + CrO₃ (C), passivated in CrO₃ (D), passivated in HNO₃ (E) specimens

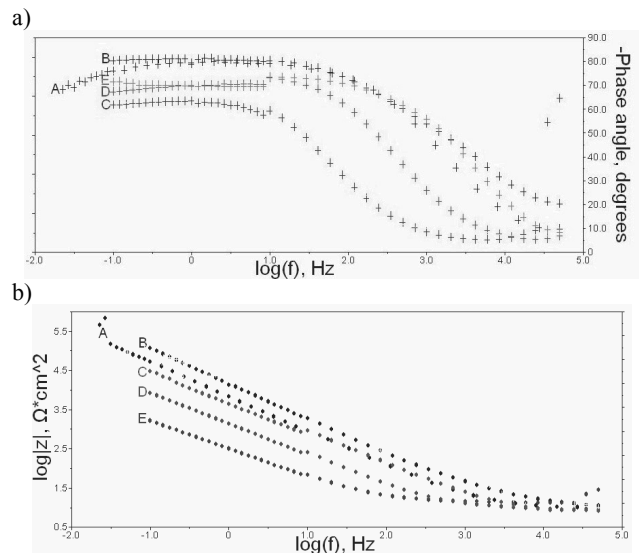


Fig. 6. Bode plots obtained in Tyrod solution corresponding to the mechanically polished (A), electropolished (B), passivated in HNO₃ + CrO₃ (C), passivated in CrO₃ (D), passivated in HNO₃ (E) specimens

The measurement of capacitance of electronic double layer can be also useful methods which show the changes in the surface after different pretreatment process. The relatively high value of C_s obtained, could be attributed to an association of effects including the non – homogenous aspect of the surface, the presents of pores and adsorption of intermediate compounds [8].

Because obtained impedance spectra is relatively simple with one time constant it was modeled by a simple parallel combination of a resistor (polarization resistance) and capacitor (double layer) in series with a resistor (uncompensated solution resistance) [1,2,15,26,29,30]. The circuit in the Figure 7 represent a single charge transfer reaction.

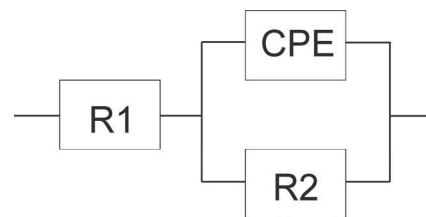


Fig. 7. Equivalent circuit model represent a single charge transfer reaction

The experimental capacitor – potential curves were shown in Figures 8 a– e.

For the passivated samples a capacitance of electric double layer was the lowest and equal to C_s = 0.01 μF, Figure 8 e. The highest capacitance was typical for grounded specimen. The potential of zero charge, at the capacitor – potential curve is no excess charge upon the metal. If we consider the absorption of a cations, this will tend to be adsorbed at an electrode if its potential is negative, with respect to the potential of zero charge, but to be desorbed if its potential is positive.

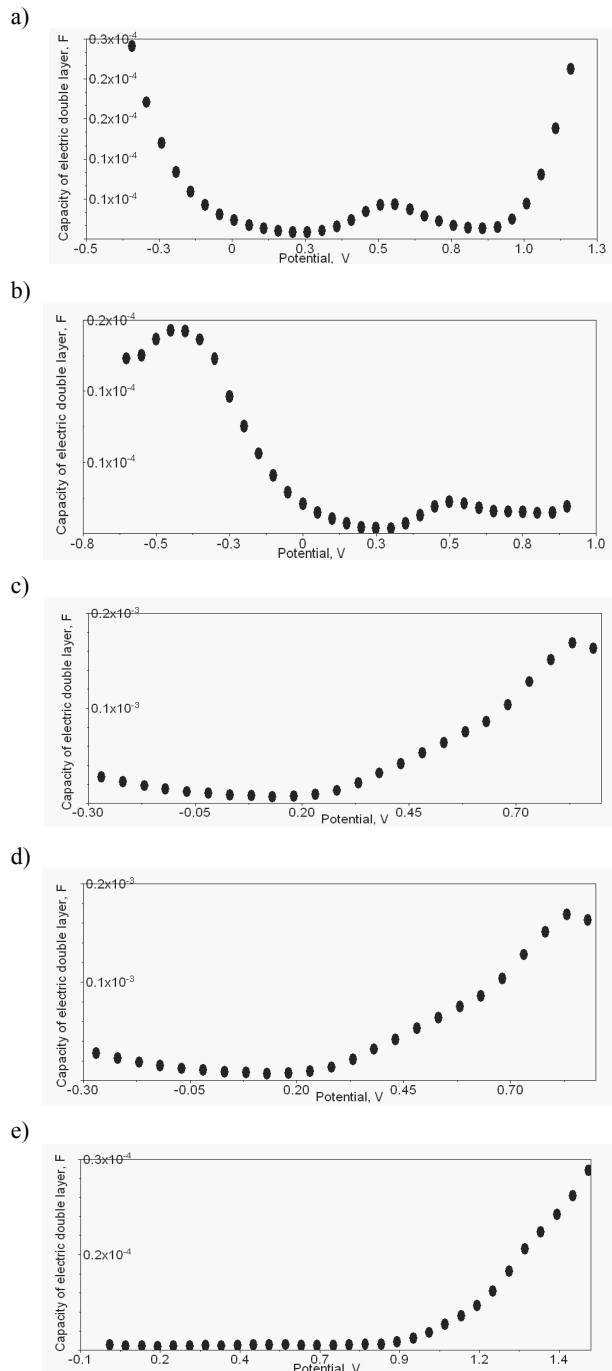


Fig. 8. Experimental capacitance - potential curve referred to the calomel electrode a- sample mechanically polished, a- sample electrochemically polished, b- sample passivated in $\text{CrO}_3 + \text{HNO}_3$ solution, c- sample passivated in CrO_3 solution, d- sample passivated in HNO_3 solution

The potential of zero charge tends to represent the dividing line between adsorption and desorption for given ions at the particular electrode [9].

There was no satisfactory explanation of differences in experimental and theoretical shape of potential vs electric double layer capacitance. If there were specific absorption ions in the electrolyte solution it could be observed. Due to roughness of the investigated surface the curve in Figure 8 a and b has shows two minimums [6]. The interpretation is difficult because of the limited data.

The smoothest surface has been characteristic for electropolishing and passivated in HNO_3 solution.

Investigations were limited to the examination of case only - samples kept for 60 minutes and 21 days in Tyrode solution. There were not significant differences. It is necessary to carry out analogous tests after longer time of exposition.

It is clear that any interface will disrupt the electrolyte solution since the interactions between the solid and the electrolyte will be considerably different to those in solution. For electrodes which are under potentiostatic control there will also be the additional influence of the charge held at the electrode. These different factors result in strong interactions occurring between the ions/molecules in solution and the surface of the steel.

This gives rise to a region called the electrical double layer. Many models have been put forward to explain the behavior observed when electrochemical measurements are performed in electrolyte solutions.

The distance of approach between ions and steel's surface is assumed to be limited to the radius of the ion and a single sphere of solvation round each ion. The overall result is two layers of charge (the double layer) and a potential drop which is confined to only this region (termed the outer Helmholtz Plane, OHP) in solution. The result is absolutely analogous to an electrical capacitor which has two plates of charge separated by some distance (d) with the potential drop occurring in a linear manner between the two plates. The model of Helmholtz does not account for many factors such as, diffusion or mixing in solution, the possibility of absorption on to the surface and the interaction between solvent dipole moments and the investigated specimen. A later model put forward by Stern, Figure 9.

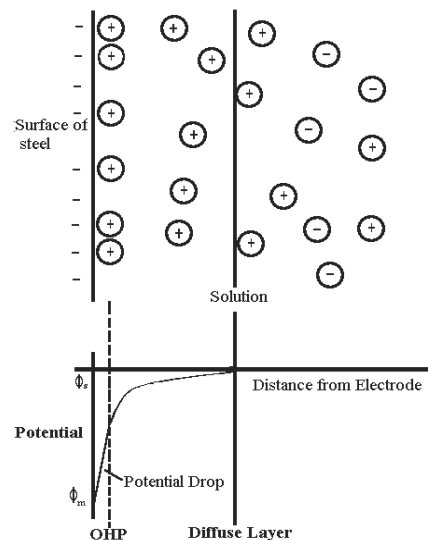


Fig. 9. The model of electrical double layer between steel's surface and electrolyte solution

4. Conclusions

In conclusion we can say that the performed corrosion tests of the Cr – Ni – Mo steel intended for medical applications, surface treatment increases corrosion resistance in the Tyrod physiological fluid. The following methods were used: anodic polarisation curves, electrochemical impedance spectroscopy and scanning electron microscope and roughness measurement.

The shape of the curves were similar. It was observed the most noble corrosion potential, equal to $E_{\text{corr}} = 0.075$ V for passivated in $\text{CrO}_3 + \text{HNO}_3$ solution.

The impedance spectra obtained by EIS measurement were relatively simple with one time constant. It was chosen the simpler model. The circuit represent a single charge transfer reaction. All impedance spectra were modeled by a simple parallel combination of a resistor (polarization resistance) and capacitor (double layer) in series with a resistor (uncompensated solution resistance). For the passivated samples a capacitance of electric double layer was the lowest and equal to $C_s = 0.01$ μF .

The highest capacitance was typical for grounded specimen. Investigations were limited to the examination of case only – samples kept for 60 minutes and 21 days in Tyrode solution. There were not significant differences. It is necessary to carry out analogous tests after longer time of exposition.

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