

Influence of electrolytic polishing on electrochemical behaviour of austenitic steel

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Materials

ABSTRACT

Purpose: The paper deals with investigations on the influence of the parameters of the electrochemical treatment of austenitic steel on their electrochemical behaviour in Tyrod solution.

Design/methodology/approach: 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.

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 $t = 60\text{ }^{\circ}\text{C}$ 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: Biomaterials; Corrosion; Surface treatment; EIS

1. Introduction

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 [1, 2].

Diffrent kinds of surface treatment for stainless steel have been developing to increase the corrosion resistance, for instance: annealling, pickling, polishing and passivation [3, 4, 5].

Metallic materials corrode in contact with aggressive body fluids; therefore, the designer must be careful when selecting materials of this type. Austenitic stainless steels as their name implies, have an austenitic microstructure (FCC) at room temperature.

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 [3].

Metallic materials used to produce implants ought to display adequate mechanical properties and must be safe for the human organism; that means that they must not exert any toxic effect on the

tissue and cause allergic reactions of the organism; neither should they corrode in the medium of the tissue and constitutional fluids. The fundamental criterion of their adaptability is their resistance to corrosion which may lead to poisoning with the corrosion products and also to patomorphological changes in the tissue.

These requirements are met to a large extent by austenitic alloy steels, chromium-nickel steels with an addition of molybdenum and, first of all, by steel of the type AISI 316L.

An important corrosive factor is also the presence of alkali metal chlorides in the constitutional fluids. Of great importance is, therefore, the morphology of the implant surface. The smoother it is, the greater is its resistance to corrosive factors [6 – 8].

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 [5]. The deformation of this 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 [9 – 11].

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 by means of AC and DC electrochemical methods.

2. Materials and methods

The investigations concerned austenitic steel type Cr – Ni – Mo, the chemical composition show in Table 1. The specimens were wire with a diameter of 30 mm and a thicknes of about 1 mm. After cleaning procedures, the surface were treated with various parameter summarized in Table 2.

Table 1.

Nominal chemical composition of Cr – Ni – Mo steel type (actual standard PN – ISO 5832 – 1:1997)

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

The process of electrolytic polishing was carried out in a phosphoric-sulphuric acid solution with an addition of organic substances. The process of chemical passivation was

run in 40% by weight nitric(V) acid solutions with an addition of oxidizing agents at 60°C for one hour. Chromic(VI) acid with a concentration of 100g/dm³ each were added. The setup of electrolytic polishing of samples were presented in Fig 1

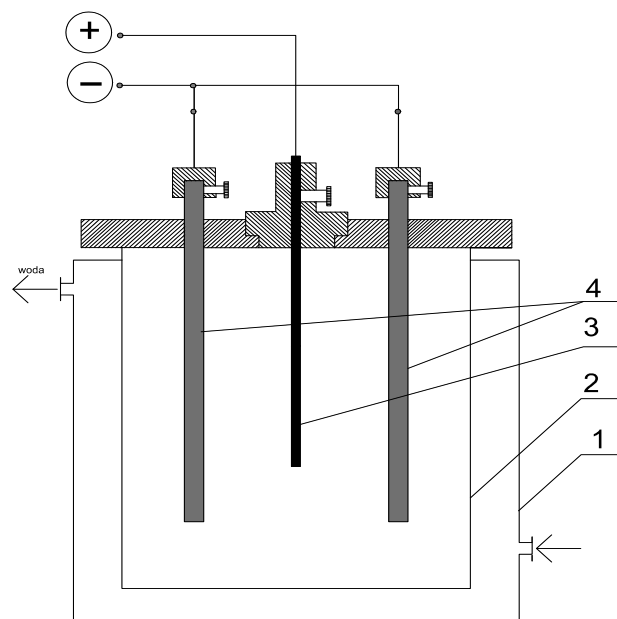


Fig. 1. The electrochemical cell for electrolytic polishing process: 1 – water jacket connected with thermostat, 2 – electrochemical cell, 3 – sample (anode), 4 – cathode

The electrochemical behavior and corrosion process were taken in physiological Tyrode solution with pH = 6.9 at a temperature of 37 °C, applying a double-chamber thermostated glass electrolyser with a volume of 150 cm³. The investigated sample were tested as to their corrosion resistance in Tyrode's solution with the following composition: NaCl-8.00 g/dm³, NaHCO₃-1.00 g/dm³, KCl-0.20 g/dm³, CaCl₂-0.20 g/dm³, MgCl₂-0.05 g/dm³ and Na₂HPO₄-0.05 g/dm³.

In its cover a Haber-Luggin capillary was attached together with a calomel electrode (SCE) as a reference electrode. A platinum plate served as an auxiliary electrode.

Solution was prepared from analytical grade reagents and deionized and demineralized water. The samples in the form of wires with were fixed in a brass holder screwed into a Teflon socket and sealed with silicon rubber. This seal served as an insulation of the brass holder. After having been fixed in the socket, the sample was rinsed twice with methanol and then placed in the lateral socket of the electrolyser and subjected to potentiostatic tests.

The electrochemical behavior of investigated alloy was performed basing on polarization curves registration using anodic polarization technique (AP) and electrochemical impedance spectroscopy technique (EIS).

Both AP and EIS tests were conducted using an Eco Chemie B.V PGSTAT30 Potentiostat and their using their accompanying software GPES (General Purpose Electrochemical System) and FRA (Frequency Response Analyzer System).

The polarization curve and impedance data were obtained after holding the samples at open circuit potential for 60 minutes. The electrochemical impedance experiment was performed at open circuit potential. The measurements were made in the frequency range between 50 kHz and 0.1 Hz with perturbation amplitude of 0.05 mV. A potentiodynamic polarisation scan was performed after EIS measurement.

The FRA software allows simulate responses of equivalent circuit and fit the circuit parameters to the measured data. Circuit models were built with the help of well – known elements such as resistors R, capacitors C, inductors L, constant phase element CPE [12-14].

Double layer capacitance were measured as a function of potential from – 0.5V to 1V with step potential 0.05V.

In the anodic polarization tests, the alloy was scanned at the rate 0.05 V/sec. from negative (cathodic) overpotential and ending at positive (anodic) overpotential.

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 [k Ω]

GPES program using 1st Stern – Tafel method, enabled to set corrosion rate express by v_{corr} [mm/year]. 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.

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

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

3. Results

The alloy was subjected to anodic polarisation after grounding, electropolishing and passivating. The anodic polarisation curves of samples obtained in Tyrod solution are given in Fig 1.

The shape of the curves was similar. It was observed the most noble corrosion potential, equal to $E_{corr} = 0,075$ V for passivated in $CrO_3 + HNO_3$ solution.

The average polarization resistance of this sample was equal to $R_p = 27,11k\Omega$ and the average corrosion rate was equal to $v_{corr} = 0,00412$ mm/year. 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 $R_p = 4,32k\Omega$. The rest information concern corrosion parameters are present in table 2.

EIS spectra typical for mechanically polish, electropolished and passivated specimens are shown in Bode plot in Fig 3.

Impedance spectra have been presented as Bode phase and Bode magnitude plots. The Bode plots are used because it has been argued that they are more informative than the conventionally popular Nyquist plots.

It can be observed that the modulus and the phase angle of the impedance are strongly depend on the surface pretreatment. The spectra are relatively simple with one time constant. Nonlinear regression was used to curve fit the analogous circuit model to the spectra.

It was choosing the simpler model that fits the data – the more likely it represents the physical process. The circuit in the Fig. 4 represents a single charge transfer reaction.

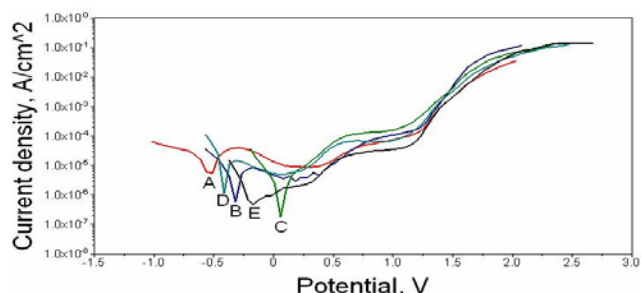


Fig. 2. Potentiodynamic polarization curves corresponding to the mechanically polished (A), electropolished (B), passivated in $HNO_3 + CrO_3$ (C), passivated in CrO_3 (D), passivated in HNO_3 (E) specimens

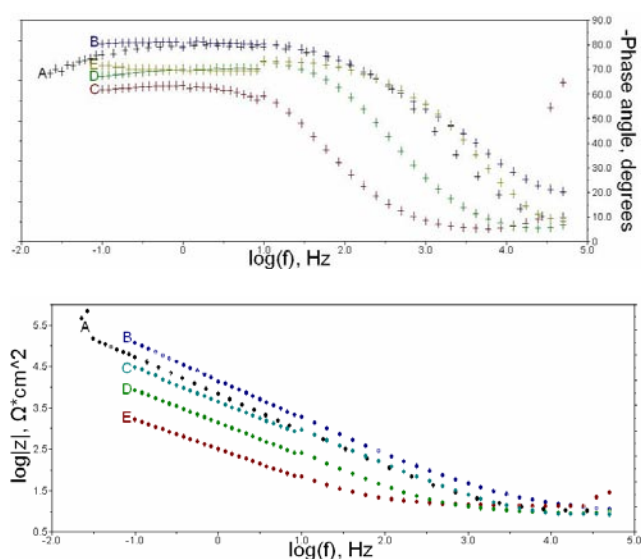


Fig. 3. Bode plots obtained in Tyrod solution corresponding to the mechanically polished (A), electropolished (B), passivated in $HNO_3 + CrO_3$ (C), passivated in CrO_3 (D), passivated in HNO_3 (E) specimens

All impedance spectra were modeled by a simple parallel combination of a resistor (polarisation resistance) and capacitor (double layer) in series with a resistor (uncompensated solution resistance).

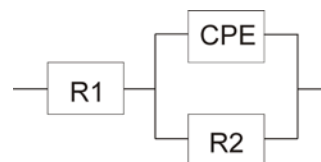


Fig. 4. Equivalent circuit model represent a single charge transfer reaction

Table 2.

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

Treatment	Specimen				
	A	B	C	D	E
	Mechanically polished	Electropolished	Passivated in $\text{CrO}_3 + \text{HNO}_3$ 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 , $\text{k}\Omega$	4.32	11.26	27.11	1.151	12.45
Polarization resistance from EIS R_p , $\text{k}\Omega$	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

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