Surface treatment and corrosion behaviour of austenitic stainless steel biomaterial

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Abstract. In this article results from corrosion behaviour of austenitic stainless steel AISI 316L after different surface treatments are published. “As received” surface and surface after grinding resulted in lower resistance to pitting corrosion in physiological solution than electrochemically polished in H3PO4+H2SO4+H2O. Electropolishing also improved the surface roughness in comparison with the “as received” surface. Deposition of Al2O3 nanometric ALD coating improves the corrosion resistance of stainless steel in chloride-containing environment by shifting the breakdown potential toward more positive values. This oxide coating not only improves the corrosion resistance but it also affects the wettability of the surface, resulting in hydrophobic surface.

1. Introduction

Austenitic stainless steels are still widely used as biomaterials to replace structural components in the human body. They possess more superior tensile strength, fatigue strength, and fracture toughness compared to polymeric and ceramic materials. Such, austenitic biomaterials are used in medical devices such as artificial joints, bone plates, screws, intramedullary nails, spinal fixations, external fixators, stents, and dental implants. These steels have very good mechanical and technological properties combined with good corrosion resistance. The corrosion resistance of the steel increases with increase of chromium content. Their excellent resistance to uniform corrosion depends on formation of passive oxide layer on the surface. Metallic biomaterials have a tendency to spontaneously form stable oxide layer in the reaction with atmospheric oxygen or most aqueous environments and this passive layer is just few nanometers thick. The biocompatibility of the metallic biomaterial mainly depends on the properties of their surface quality and quality of native oxides that forms on the surface. Aggressive ions that are present in human body environment (chlorides and bromides) can cause local breakdown of this protective film, and enable a progress of the local pitting corrosion. This stainless orthopedic implant can corrode in body environment and release iron, chromium, and nickel ions [1-4].

Resistance of stainless steels to pitting corrosion is affected by a number of factors such as chemical composition, structure, quality of surface, concentration of aggressive ions, temperature and pH. The quality of the surface passive film is one of the most important factors of corrosion behavior of stainless steels. The passive film properties are strongly influenced by mechanical and chemical finishing processes. The mechanical treatment (grinding, polishing) affects the electrochemical and
mechanical stability of the passive film and near surface layers by changing the surface reactivity. By mechanical, wearing, grinding or mechanical polishing an amorphous layer forms on the surface of metals called the "Beilby" layer. To avoid creating this layer electrochemical polishing can be used.

During the process of electrochemical polishing a high quality passive oxide film is created on the surface. This process also improves the resistance against contamination and bacteria. This treatment is very useful in medicine whereas surgical instruments and devices, joint replacements, stents and other implantable materials are electrochemically polished. Also several coating methods have been used to deposit the material's surface and to increase the corrosion resistance. One of the deposition methods can be oxide coatings realized by the method called atomic layer deposition. By this method a few nanometers high protective oxide layer is applied on the metal's surface. The thickness of this oxide layer affects the homogeneity, the roughness, the surface energy and the wettability. The surface wettability is important for the adsorption of proteins and cell adhesion and can dictate the biocompatibility of the implanted material. Depending on the material's application there is a need to achieve hydrophobic or hydrophilic surfaces in the case of biomaterial's wettability. For instance stents used in cardiology, they need to have hydrophobic surfaces. The higher the hydrophobic surfaces it more suppresses protein and platelet adsorption and ensures good blood compatibility [3-7].

2. Atomic layer deposition
Atomic layer deposition (ALD) is a modification of chemical vapor deposition (CVD) method used for depositing surface controlled thin films one atomic layer at a time. During the coating, two or more chemical vapors or gaseous precursors react sequentially on the substrate surface and produces a solid thin film. This technology provides the ability to obtain very thin, almost defect-free nanometric coatings on the surface of different materials. In order to increase the corrosion resistance of austenitic stainless steel biomaterials, thin layers of $\text{Al}_2\text{O}_3$ or $\text{TiO}_2$ can be applied on the materials surface by ALD technology [8-9].

3. Experimental material and procedures
Commercially available low-carbon austenitic stainless steel AISI 316L was used as an experimental material with the chemical composition listed in Table 1. The specimens for ALD process were cut from rectangular bars with dimension of 10x10x5 mm and the other specimens for electrolytic polishing were purchased in sheets of 1.5 mm thickness. Microstructure of the material in initial state is presented in Figure 1 - 2. Microstructure of the experimental material is formed of polyedric austenitic grains with annealing twins and parallel lines arose by rolling.

| Chemical composition (wt. %) | C  | Cr  | Ni  | Mo | Mn | Si  | S   | P   | Fe  |
|------------------------------|----|-----|-----|----|----|-----|-----|-----|-----|
| AISI 316L                    | 0.04 | 17.41 | 9.91 | 2.38 | 1.34 | 0.52 | 0.03 | 0.05 | bal. |
| AISI 316L (sheet)            | 0.02 | 16.79 | 10.14 | 2.03 | 0.82 | 0.31 | 0.001 | 0.03 | bal. |
3.1. Surface preparation

The ALD coating (Figure 3.) was deposited using PICOSUN® R-200 at the Silesian University of Technology, Gliwice. Al₂O₃ layer was obtained using trimethylaluminum and water precursors. During the Al₂O₃ ALD process, trimethylaluminum (TMA) reacts with hydroxyl groups on the surface. This reaction proceeds until the surface reaction is completed. Subsequently, TMA is carried or pumped away with the inert gas (Nitrogen). The same process is then performed with H₂O. Water reacts with methyl groups on the surface until this surface reaction is completed. The sequential exposure to TMA and H₂O represents one AB cycle. These AB cycles are repeated to achieve the desired film thickness [8-9]. The number of precursor cycles of deposition was 500 cycles. The deposition was performed at a temperature of 200°C.

Other specimens were tested after electrochemical polishing, mechanical grinding, “as received” surface and electrochemically polished surface after sensitization.

Electrochemical polishing was performed in H₃PO₄ + H₂SO₄ + H₂O electrolyte under the conditions listed in Table 2. The polished specimen was immersed into electrolyte and connected to the positive pole of the power source as an anode. A cathode was of the same material as the anode.

| Component | Content [wt. %] | Temperature [°C] | Current density [A/cm²] | Time [s] |
|-----------|----------------|-----------------|-------------------------|--------|
| H₃PO₄    | 64             |                 |                         |        |
| H₂SO₄    | 13             | 40              | 0.8                     | 420    |
| H₂O      | 23             |                 |                         |        |

3.2. Potentiodynamic polarization tests

Potentiodynamic polarization tests were carried out in a three electrode cell of corrosion measuring system (VoltaLab 10 with VSP unit). Potentiodynamic polarization curves were obtained by the EC-LAB SOFT software. The potential between the sample and the electrolyte had settled for 10 minutes before the polarization. The scan range was -0.3 V – 2.0 V vs the open circuit potential and the scan rate was 1mV/s. The surface of AISI 316L, working electrode of 1 cm² area was rinsed with ethanol before measurement. The saturated calomel electrode (SCE) was applied as the reference electrode and platinum foil as a counter electrode. All experiments were performed in physiological solution represented by 0.9 % NaCl solution (i.e. 0.15 M NaCl).

3.3. Surface wettability

The surface wettability, the wetting angle, was evaluated on the samples in initial state after polishing, then samples with ALD coating and some of the samples underwent heat treatment before the measurement and polished also. Measurement of the contact angle (θ) was performed using distilled
water. The measurement of a drop of liquid applied to the sample's surface was performed at room temperature (T = 23 °C) at the test stand incorporating SURFTENS UNIVERSAL goniometer by OEG and a computer software SurfTens 4.5 to analyze the recorded image of the drop. Five drops of distilled water, each 1.5 μl volume, was applied on the surface of each sample. The measurement started after 15 s after application of drops. The duration of one measurement was 60 s at the sampling frequency 1 Hz.

4. Results

Potentiodynamic polarization curves express dependence of the current density \( i \) [mA.cm\(^{-2}\)] on the potential \( E \) [V]. They enable determination of the passivity region and the pitting potential \( E_p \), which is an important electrochemical characteristic of the resistance to pitting. \( E_p \) can be located as the potential of the strong increase in current density on the polarization curve of direct measurement. When the potential reaches this critical value, current density suddenly increases, denoting the breakdown of the passive film and the beginning of a stable pit growth. Polarization curves of AISI 316L stainless steel of variously treated surfaces in physiological solution are shown in Figure 4.

In the case of curves of “as received” surface, ground surface and the surface with Al\(_2\)O\(_3\) the passivity region and strong increase of current density occurred at pitting potential 0.343 V for the sample with “as received” surface; 0.439 V for the sample after mechanical grinding; 0.561 V for the sample with ALD coating. Passivity region of electropolished sample is very broad, no breakdown of passivity, which indicates initiation of pitting corrosion, was recorded. Current density suddenly increases at the potential approximately 1.2 V, which can be considered as transpassivation potential \( E_t \). If potential is equal or higher than \( E_t \), the passive surface film is dissolved, and active corrosion of material starts. The rise of current density at the transpassivation potential \( E_t \) points to the beginning of Cr\(_2\)O\(_3\) dissolution and formation of soluble chromates or other compounds arose from the electrolyte which do not create a protective barrier between the metal and the electrolyte or prevents from creating the passive film on the surface. However, it should be noted that an active corrosion of tested biomaterial in transpassive region in internal human's body environment is not an option because of high \( E_t \) value, which cannot be reached spontaneously under given conditions. Electropolishing did not reveal sensitization of austenitic stainless steel which could be observed by almost the same course of polarization curve as the curve of electropolished sample without sensitization (Figure 4).

After 7 min of electrochemical polishing in electrolyte with the applied current density 0.8 A.cm\(^{-2}\) around 0.08 - 0.09 mm layer was removed from the sample's surface. This amount of removed
material corresponds with the time and current density in comparison with the layer (0.02 mm) removed from the sample after electrolytic polishing published in [10].

The surface roughness of electropolished and “as received” surface of the sample was measured. The surface roughness is an arithmetic mean average stating the surface roughness parameters (Rₐ - roughness average, Rₛ - root mean square roughness, Rₚ - mean roughness depth) listed in the Table 3. For surface roughness measurement portable Mitutoyo SJ-210 tester was used with the standard measurement conditions: 4 x 10⁻³ N measuring force, VDA= 0.5 mm/s and λₖ= 0.8 mm. We can conclude from the results below that there is an evident decrease in surface roughness average value in the case of electropolished sample in comparison with the “as received” sample.

Table 3. Average surface roughness parameters

| Surface Type           | Rₐ [µm] | Rₛ [µm] | Rₚ [µm] |
|------------------------|---------|---------|---------|
| Electropolished surface| 0.078   | 0.096   | 0.474   |
| “As received” surface  | 0.256   | 0.363   | 2.290   |

The results of wettability and examples of drops on the sample’s surface in initial state and samples with Al₂O₃ are presented in Figure 5. and Figure 6. The ALD deposition resulted in an increase of the wetting angle above 90°. The polished surfaces in initial state are hydrophilic and the surfaces have a very low surface wettability (θ = 82.87°) and applying the ALD coating on the sample’s surface resulted in a hydrophobic surface. Steel with the deposited Al₂O₃ layer showed higher wetting angle (θ = 94.39°) as compared to the values obtained in surfaces in initial polished state.

Figure 5. Results of the contact angle measurements of AISI 316L

Figure 6. Sample measurement of wetting angle; a) initial state, b) with ALD coating
5. Conclusion
The results show following conclusions:

- Electrochemical polishing is a conventional chemical surface finish which improves the corrosion resistance, results in higher surface quality with high surface brightness and decreases the surface roughness. Surface roughness is decreased due to the removal of particular layer from the metal's surface.
- Electrochemical polishing carried out in $\text{H}_3\text{PO}_4 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ electrolyte according to recommended conditions is an efficient chemical surface treatment to increase AISI 316L resistance to pitting corrosion in physiological solution.
- “As received” surface and surface after grinding showed lower resistance to pitting corrosion than electrochemically polished ones. Therefore, such treated surfaces are not recommended for the internal human's environment.
- Deposition of $\text{Al}_2\text{O}_3$ nanometric ALD coating improves the corrosion resistance of stainless steel in chloride-containing environment by shifting breakdown potential towards more positive values.
- Sensitization induced by heat treatment (700 °C/10 hours) does not decrease resistance to pitting corrosion.
- Electropolishing of specimen improved the surface roughness because the “as received” surface had the average value of surface roughness $R_a = 0.256 \, \mu\text{m}$ and the electropolished surface reached the surface roughness $R_a = 0.078 \, \mu\text{m}$.
- The $\text{Al}_2\text{O}_3$ layer improved the wettability because the sample's surface resulted in a hydrophobic character.

Acknowledgement
This work has been supported by Scientific Grant Agency of Ministry of Education of Slovak republic VEGA 1/0683/15.

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