Corrosion behaviour of electropolished AISI 316L austenitic biomaterial in physiological solution

V Zatkalíková¹, L Markovičová¹ and M Škorvanová²
¹ University of Žilina, Faculty of Mechanical Engineering, Department of Material Engineering, Univerzitná 8215/1, 01026 Žilina, Slovakia
² Comenius University in Bratislava, Jessenius Faculty of Medicine in Martin, Malá Hora 10701/4A, 036 01 Martin, Slovakia
viera.zatkalikova@fstroj.uniza.sk

Abstract. Due to suitable mechanical properties, satisfactory corrosion resistance and relatively low cost, austenitic stainless steels are important biomaterials for manufacture of implants and various medical instruments and devices. Their corrosion properties and biocompatibility are significantly affected by protective passive surface film quality, which depends on used mechanical and chemical surface treatment. This article deals with corrosion resistance of AISI 316L stainless steel, which is the most widely used Cr-Ni-Mo austenitic biomaterial. Corrosion behaviour of five various surfaces (original, electropolished, three surfaces with combined treatment finished by electropolishing) is evaluated on the bases of cyclic potentiodynamic polarization tests performed in physiological solution at the temperature of 37±0.5 °C.

1. Introduction
Currently, austenitic stainless steels are one of three metallic biomaterials used in the manufacture of implants. Coronary stents, fracture fixation plates and screws, spinal implant devices, aneurysm clips, temporary fixation devices, dentistry and surgical instruments are the most common medical applications of austenitic biomaterials [1, 2]. Compared to titanium alloys and chromium-cobalt alloys, the advantages of stainless steels are suitable mechanical properties (strength, mechanical workability), low cost and acceptable corrosion resistance [2-4]. Due to the protective passive surface film, stainless steels are resistant to the uniform corrosion [5, 6], but possibility of local pitting or crevice corrosion have to be taken into account in an internal human body environment [1, 2]. The surface film affects an interaction between the living tissue and implant. Therefore the quality of surface (largely influenced by used mechanical and chemical surface treatment techniques) plays the major role in the biocompatibility and corrosion resistance of implants [1-3].

Polished smooth surfaces are strictly required especially for surgical and dentistry instruments, ophthalmic devices, coronary stents, fracture fixation plates and screws [7, 8]. According to studies of many authors, bright smooth surfaces have markedly higher corrosion resistance [9-11] and also provide increased resistance to microorganisms that have less chance of getting caught [8] than those with higher roughness. For the above mentioned biomedical applications, mechanical and electrochemical polishing of austenitic steels is commonly combined with pickling (acid cleaning), ultrasonic cleaning, chemical passivation [8, 12].
There are various polishing processes commonly used to obtain a smooth material surface. Traditional mechanical polishing may result in deformed layer and residual stresses on the treated surface [8]. Electropolishing is an electrochemical surface finishing process to enhance high surface brightness (mirror finish) with very low surface roughness ($R_a < 2 \, \mu m$), without residual surface tensions and with improved corrosion resistance [12]. A particular layer from the metal’s surface is removed and a high quality passive oxide film is created.

This article deals with corrosion resistance of AISI 316L stainless steel, which is the most widely used Cr-Ni-Mo austenitic biomaterial. Corrosion behavior of five various surfaces (original without additional mechanical and chemical treatment, electropolished, ground + electropolished, pickled + electropolished, ground + pickled + electropolished) is tested. Evaluation of the corrosion resistance is based on the results of electrochemical cyclic potentiodynamic polarization tests performed in physiological solution at the temperature of $37 \pm 0.5 \, ^\circ C$. After tests, the surfaces are checked by optical microscope observation.

2. Experimental material
The experimental material AISI 316L is Cr-Ni-Mo austenitic stainless steel with the chemical composition shown in Table 1. The steel was purchased in sheet (1000 x 1500 mm) of 1.5 mm thickness. Its treatment (marked as IIB/IIIC) was based on cold rolling, homogenization annealing ($1040 – 1100 \, ^\circ C$) and pickling after slightly smoothing rolling (www.italinox.sk).

| Cr  | Ni  | Mo  | Mn  | N   | C   | Si  | P   | S   | Fe  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 16.79 | 10.14 | 2.03 | 0.82 | 0.05 | 0.02 | 0.031 | 0.03 | 0.001 | balance |

Table 1. Chemical composition of AISI 316L stainless steel (wt. %).

Microstructure of experimental material (Figure 1) is created by polyedric austenitic grains with numerous twins, which could be created by annealing or by rolling.

![Figure 1. Microstructure of AISI 16L stainless steel, cross-section (Kallings etch.).](image-url)
3. Experimental procedure

Five types of steel surfaces were used for potentiodynamic tests:
1. “as received“ surface, i.e. original surface without additional mechanical and chemical treatment;
2. electropolished surface;
3. ground (1200 mesh) + electropolished surface;
4. pickled + electropolished surface;
5. ground (1200 mesh) + pickled + electropolished surface.

Electropolishing was performed in $\text{H}_3\text{PO}_4 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ electrolyte under the conditions listed in table 2 [13, 14]. 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 [13, 14].

| Component | Content (wt.%) | Temperature (°C) | Current density (A.cm$^{-2}$) | Time (s) |
|-----------|----------------|------------------|-----------------------------|----------|
| $\text{H}_3\text{PO}_4$ | 64             |                  |                             |          |
| $\text{H}_2\text{SO}_4$ | 13             | 40               | 0.8                         | 420      |
| $\text{H}_2\text{O}$   | 23             |                  |                             |          |

Pickling (acid cleaning) was performed under the conditions recommended for AISI 316L implants, namely coronary stents (Table 3) [7].

| Component | Content (wt.%) | Volume (ml) | Temperature (°C) | Time (s) |
|-----------|----------------|-------------|------------------|----------|
| HF        | 48             | 3           | 22 ± 3           | 3600     |
| $\text{HNO}_3$ | 65             | 9           |                  |          |
| $\text{H}_2\text{O}$ | -             | to 100 ml   |                  |          |

0.9 % sodium chloride solution was used as the corrosion environment for electrochemical cyclic potentiodynamic tests at the temperature of 37 ± 0.5 °C to simulate the internal environment of the human body.

Cyclic potentiodynamic polarization tests (ASTM G61) were carried out in a three electrode cell of corrosion measuring system (VoltaLab 10 with VSP unit). Polarization curves were obtained by the EC-LAB SOFT software. Potential between the sample and the electrolyte has been settled for 10 minutes before the polarization. Scan range was -0.3V – 1.2V vs the open circuit potential and the scan rate was 1 mV/s. The surface of working electrode AISI 316L of 1 cm$^2$ 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. At least five experiment repeats were carried out for each specimen. Surfaces of working electrode AISI 316L were observed by the optical microscope (Zeis Axio Imager A1m) after potentiodynamic measurements.

4. Experiment results and discussion

According to ASTM G61 standard method, the pitting potential ($E_p$) and the repassivation potential ($E_{rp}$) are the most important electrochemical characteristics of the cyclic potentiodynamic polarization curve. $E_p$ potential can be determined as the potential of a sudden, strong increase of current density on the curve of the direct measurement, which denotes the breakdown of the passive film and the beginning of stable pit growth. The shift of $E_p$ to more noble value means the rise of resistance to pitting [5, 6]. $E_{rp}$ is obtained as the potential at which the backward measurement curve crosses the direct measurement curve.
If the passive film is highly resistant and current density is very low in whole passive region (according to Pourbaix diagram for Cr in neutral 0.9 % NaCl solution, the passive region reaches up to potentials 0.7 - 0.8 V) [15], it means that the pitting corrosion is not initiated during measurement. In this case the cyclic curve is not of typical loop shape and the current density increases at the trans-passivation potential ($E_t$). If the potential overrun $E_t$ value, the surface passive film is dissolved, and an active corrosion of material starts (Cr$^{3+}$ is converted to Cr$^{6+}$) [5, 15].

The corrosion potential ($E_{corr}$) and the corrosion current density ($i_{corr}$) are additional electrochemical characteristics which can be determined according to Tafel analysis of the potentiodynamic curve [15]. The lower $E_{corr}$ points to the lower thermodynamic stability of material. The $i_{corr}$ value has the relationship to the kinetics of the corrosion process. The higher $i_{corr}$ value means the higher corrosion rate.

The cyclic potentiodynamic curves of tested AISI 316L surfaces are shown in Figures 2 – 4. The obtained electrochemical characteristics are presented in Table 4.

**Figure 2.** Cyclic potentiodynamic curve of AISI 316L working electrode with “as received” surface.

**Figure 3.** Cyclic potentiodynamic curves of AISI 316L working electrode with electropolished surface.
Figure 4. Cyclic potentiodynamic curves of AISI 316L working electrode with combined surface treatment finished by electropolishing

The “as received” surface curve (Figure 2) is of a typical loop shape with clearly observable pitting potential. According to electrochemical characteristics (namely $E_p$, table 4) this type of surface is least thermodynamically stable compared to other tested surfaces. The pitting corrosion damage was visible to the naked eye and also observed by an optical microscope (Figure 5A).

Table 4. The electrochemical characteristics of tested AISI 316L surfaces.

| Type of surface                        | $E_p$ (V) | $E_{pp}$ (V) | $E_t$ (V) | $E_{corr}$ (V) | $i_{corr}$ (μA/cm$^2$) |
|----------------------------------------|-----------|--------------|-----------|----------------|------------------------|
| “as received”                          | 0.381     | -0.052       | -         | -0.071         | 0.078                  |
| electropolished                        | 0.476     | 0.128        | 1.121     | -0.069         | 0.062                  |
|                                        | 1         |              |           | 0.027          | 0.035                  |
| ground + electropolished               | -         | -            | -         | -0.108         | 0.044                  |
| pickled + electropolished              | -         | -            | 1.060     | -0.035         | 0.265                  |
| ground + pickled + electropolished     | -         | -            | 1.103     | 0.059          | 0.016                  |

The electropolishing of the original surface (Figure 3) improved the quality of the passive layer, but obtained curves fluctuated between the typical loop shape (1) and the shape with low current density, without depassivation in passive region and with an increase of current density at the trans-passivation potential $E_t$ (2). The passive film was apparently not uniform enough, chloride ions could penetrate through the weakened places and the stable growing corrosion pits were formed. The course of the measured curve depended on the particular area selected for the potentiodynamic test. Similar curves measured for the electropolished surface of the same steel were also found by the authors [14].

The typical corrosion pit on the electropolished surface is shown in Figure 5 B. The high corrosion resistance was reflected on surfaces that have been mechanically/chemically treated before electropolishing (Figure 4). The obtained curves were without depassivation in passive region and with transition to the transpassivity state. The display of the respective curves at one scale and their comparison showed some differences in the passive state current density and in approximate values of the $E_t$ potentials.

It is worth recalling that the threshold value of the current density signaling the transition from the passivity state to the active dissolution of the metal is usually assumed to be 0.05 mA/cm$^2$ [6]. Generally, a passive state with high stability exhibits a low passive current density without large fluctuations on the direct measurement curve and the transition to the transmissivity (reflected by a significant increase in current density) at the high $E_t$ potential [5].
Taking into account the above mentioned facts, the ground + pickled + electropolished surface exhibits the best resistance to pitting. On the contrary, grinding + electropolishing can be considered the worst from three surface treatment tested combinations. On the ground + electropolished surface the passive state appears the least stable - current density slightly increases throughout the passive area (Figure 4). Microscopic observation of these combine-treated surfaces after cyclic potentiodynamic tests did not reveal any pitting corrosion damage (Figure 6).
Very good quality of electropolished surfaces is probably connected with the newly grown, uniform and compact oxide film with higher chromium and oxygen content [16]. The authors [3] documented chromium enrichment in surface passive film of AISI 304 steel after electropolishing. According to the authors [3, 16], the increase of Cr/Fe ratio is caused by selective dissolution leading to the formation of a passive layer during the electropolishing process.

5. Conclusion
Based on the results of performed experiments can be concluded:

- The “as received” surface state is least thermodynamically stable. The pitting corrosion damage was visible to the naked eye.
- Single polishing without pre-treatment does not appear as a surface treatment that would provide a sufficiently uniform and resistant passive film.
- Surfaces with combined treatment finished by electropolishing (ground + electropolished, pickled + electropolished, ground + pickled + electropolished) exhibit better corrosion resistance than single electropolished surface. The least suitable combination is grinding + electropolishing. The best combination is grinding + pickling + electropolishing, which provides the highest corrosion resistance.

Potentiodynamic tests are convenient and fast, but at least two independent tests are needed to assess clearly the corrosion resistance of a given biomaterial (especially when intended for long-term implantation). Although the surface is properly treated, it is important to avoid mechanical damage during implantation (e.g. by surgical instrument). The passive film breakdown could cause dangerous local corrosion in the internal environment of the human body.

Acknowledgement
The research was supported partially by Scientific Grant Agency of Ministry of Education, Science and Sport of Slovak Republic and Slovak Academy of Sciences, grant VEGA No. 1/0683/15 and grant KEGA No. 049ŽU-4/2017.

References
[1] Ratner B D, Hoffmann A S, Schoen F J and Lemons J E 2004 *Biomaterials Science* Elsevier, San Diego USA
[2] Nagase M 1995 Host Reactions to Particulate Biomaterials. *Encyclopedic handbook of biomaterials and bioengineering* I Part A New York
[3] Ghanavati S, Shishesaz M R, Farzam M and Danaee I 2015 Effects of Surface Treatment on Corrosion Resistance of 304L and 316L Stainless Steel Implants in Hank’s Solution *Iranian Journal of Oil & Gas Science and Technology* 5 1 65-72
[4] Uhrčíč M, Oravcová M, Palček P, Sapieta M and Chalupová M 2016 *The stress detection and the fatigue lifetime of stainless steel AISI 316L during three-point bending cyclic loading* (Conference Paper) EAN 2016 - 54th International Conference on Experimental Stress Analysis
[5] Szklarska–Smialowska Z 2005 *Pitting and crevice corrosion* NACE International Houston Texas
[6] Liptáková T 2009 *Bodová korózia nehrdzavejúcich ocelí. (Pitting corrosion of stainless steels.)* EDIS Žilina
[7] Zhao H, Van Humbeeck J, Sohier J and De Scheerder I 2002 Electrochemical Polishing of 316L Stainless Steel slotted tube coronary stents *Journal of Materials science: materials in medicine* 13 911-916
[8] Lee S J and Lai J J 2003 The effects of electropolishing (EP) proces parameters on corrosion resistence of 316L stainless steel *Journal of Material Processing Technology* 140 206-210.
[9] Liptáková T, Alaskari A and Halamová M 2012 Surface treatment of the AISI 316L after welding and study of corrosion behaviour Periodica Polytechnica Transportation Engineering, 41 2 143-147
[10] Hong T and Nagumo M 1997 Effect of surface roughness on early stages of pitting corrosion of Type 301 stainless steel Corros. Sci. 39 9 1665–1672
[11] Sasaki K and Burstein G T 1996 The generation of surface roughness during slurry erosion-corrosion and its effect on the pitting potential Corros. Sci. 38 12 2111–2120
[12] Nuñez P J, Garcia-Plaza E, Hernando M and Trujillo R 2013 Characterization of Surface Finish of Electropolished Stainless steel AISI 316L with Varying Electrolyte Concentrations Procedia Engineering 63 771-778
[13] Vaňa D 2014 Porovnanie technologických možností plazmového a elektrochemického leštenia antikorózných ocelí v elektrolyte AlumniPress Trnava
[14] Oravcová M, Palček P, Zatkalíková V, Tański T and Król M 2017 Surface treatment and corrosion behaviour of austenitic stainless steel biomaterial IOP Conference Series: Materials Science and Engineering 175 1
[15] Hadzima B and Liptáková T 2008 Základy elektrochemickej korózie kovov (The bases of electrochemical corrosion of metals) EDIS Žilina
[16] Hashimoto K, Asami K, Kawashima A, Habazaki H and Akiyama E 2007 The role of Corrosion-resistant alloying Elements in Passivity Corros. Sci. 49 1 42-52