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Corrosion behaviour of AISI 316L steel in artificial body fluids

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Materials

ABSTRACT

Purpose: The paper presents the comparison of corrosion resistance of AISI 316L stainless steel in various corrosive media such as artificial urine, Tyrode's physiological solution and artificial plasma.
Design/methodology/approach: The tests were carried out on samples of the following surfaces: grinded – average roughness Ra = 0.31 μm and electropolished and chemically passivated average roughness Ra = 0.10 μm. The corrosion tests were realized by recording of anodic polarization curves with the use of the potentiodynamic method. The VoltaLab® PGP 201 system for electrochemical tests was applied. The tests were carried out in electrolyte simulating urine (pH = 6-6.4), Tyrode's physiological solution (pH = 6.8-7.4) and plasma (pH = 7.2-7.6) at the temperature of 37±1°C.
Findings: Surface condition of AISI 316L stainless steel determines its corrosion resistance. The highest values of breakdown potentials were recorded for all electropolished and chemically passivated samples in all simulated body fluids. The highest values of anodic current density were recorded for samples tested in artificial urine, the lowest values were recorded for samples tested in Tyrode's physiological solution.
Research limitations/implications: The obtained results are the basis for the optimization of physicochemical properties of the AISI 316L stainless steel.
Practical implications: On the basis of the obtained results it can be stated that stainless steel meets the basic biocompatibility criteria and can be applied in reconstruction surgery, operative cardiology and urology.
Originality/value: The paper presents the influence of various corrosive media simulating human body fluids on corrosion resistance of AISI 316L stainless steel.
Keywords: Metallic alloys; Biomaterials; Corrosion; Body fluids

1. Introduction

The latest trends of research in biomedical engineering centers are focused on problems connected with surface engineering of implants. Surface treatment method that ensure minimal postoperative complications are developed. Biocompatibility of implants in tissue environment is determined by inseparable biochemical, biomechanical and bioeletronic factors. Biological reactions are analyzed with respect to metabolic, bacteriological, immunological and oncological processes [1, 3-6, 8-10, 13-19, 24].

Current chemical compositions of the stainless steel (Cr-Ni-Mo) should ensure good pitting corrosion resistance and monophase austenitic structure. The austenite grain size (less than 4 acc. to ISO) and non-metallic inclusions (max. 1.5 acc. to ISO) are limited. Fine grain and low level of non-metallic inclusions ensure good mechanical properties and reduce crackability, specially in implants with small cross-sections. They also increase corrosion resistance of implants [9, 10, 17].

Great number of „sum-up" publications is focused on generalization of corrosion failure of implants. These analyses are focused on implants commonly used in reconstruction in the orthopedic, dental surgery, operative cardiology and urology. These implants are mainly made of austenitic stainless steel [1, 2, 5, 7, 11, 22-24].

Long-term research on corrosion of implants made of the mentioned steel show the complexity of corrosion processes depending on the implant form, its chemical and phase composition, surface condition, surgical procedure and implantation period [9, 10, 17].

Corrosion products infiltrate tissues. This press is called metalosis [10]. Phatomorphological changes, dependent on the type and concentration of elements, occur in tissues close to implant. Histopathological changes are observed in the detoxication organs (liver, kidneys, spleen) [9].

Therefore, corrosion tests in simulated body fluids are the basis for searching optimal fields of usage and improvement of existing solutions.

2. Material and methods

The corrosion resistance of AISI 316L stainless steel intended for implants was tested. The tests were carried out on samples in the form of a rod of diameter d = 5 mm and length equal to l = 15 mm. The tested material met implantation requirements concerning the chemical composition, the structure and mechanical properties.

The tests were carried out on samples of the following surfaces:

- grinded – average roughness R_a = 0.31 μm,
- electropolished and chemically passivated average roughness R_a = 0.10 μm, in conditions worked out by the authors (Fig. 1). In order to measure the roughness the Surtronic 3+ surface analyzer was applied.

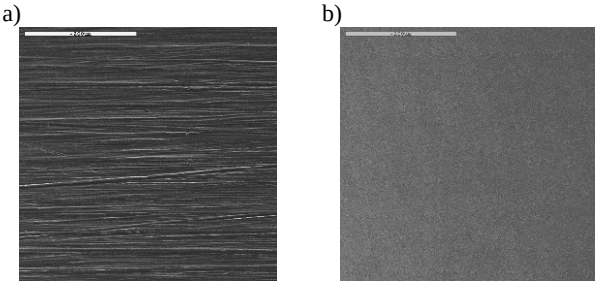

Fig. 1. View of the samples surface: a) ground R_a = 0.31 μm, b) electropolished and chemically passivated R_a = 0.10 μm

The pitting corrosion tests were realized by recording of anodic polarization curves. The VoltaLab® PGP 201 system for electrochemical tests was applied (Fig. 2) [13]. The saturated calomel electrode (SCE) of KP-113 type was applied as the reference electrode. The tests were carried out in electrolyte simulating:

- urine (pH = 6 - 6.4) [4, 6, 12, 20] (Table 1),
- Tyrode's physiological solution (pH = 6.8 - 7.4) [10] (Table 2),
- plasma (pH = 7.2 - 7.6) (Table 3).

The tests were carried at the temperature of 37±1°C.

Macroscopic observations of samples' surfaces were carried out both before and after the corrosion tests. The observations were realized with the use of the DSM 940 OPTON scanning microscope in the magnification range from 50 to 2000x.

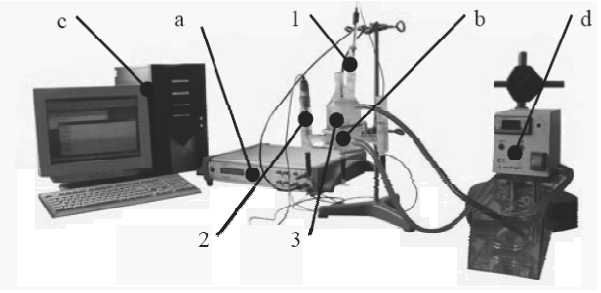

Fig. 2. Diagram of the corrosion resistance set: a) potentiostat VoltaLab® PGP201, b) electrochemical cell: 1 – SCE electrode, 2 – Pt electrode, 3 – sample, c) computer, d) termostat Medlingen

Table 1.
Artificial urine (A:B = 1:1) [4, 6, 23, 24]

Ingredients A	g/l distiled water	Ingrediends B	g/l distiled water
$CaCl_2 2H_2O$	1.765	$NaH_2PO_4 2H_2O$	2.660
Na_2SO_4	4.862	Na_2HPO_4	0.869
$MgSO_4 7H_2O$	1.462	$Na_3Cit \cdot 2H_2O$	1.168
NH_4Cl	4.643	NaCl	13.545
KCL	12.130	-	-

Table 2.
Tyrode's physiological solution [10, 25]

Ingredients	g/l distiled water
NaCl	8.000
$CaCl_2$	0.200
KCl	0.220
$NaHCO_3$	1.000
Na_2HPO_4	0.050
$MgCl_2$	0.200

Table 3.
Artificial plasma [10]

Ingredients	g/l distiled water
NaCl	6.800
$CaCl_2$	0.200
KCl	0.400
$MgSO_4$	0.100
$NaHCO_3$	2.200
Na_2HPO_4	0.126
NaH_2PO_4	0.026

3. Results

3.1. Pitting corrosion resistance results in artificial urine

Results of electrochemical tests have revealed the influence of surface preparation of the Cr-Ni-Mo steel on the corrosion resistance (Table 4). For the grinded samples, the corrosion potential was in the range E_{corr} = -250 - -134 mV (Fig. 3). Polarization of samples caused the rapid increase of anodic current for potentials in the range E_B = +565 - +657 mV (Fig. 4). The repassivation potential was in the range E_{cp} = -22 - +272 mV. Average polarization resistance of the samples was equal to $R_{p\,av}$ = 536 kΩcm^2.

Table 4.
Pitting corrosion resistance of Cr-Ni-Mo alloy in artificial urine

Surface preparation method	Corrosion potential Ecorr (mV)	Break-down potential EB (mV)	Repassivation potential Ecp (mV)	Average polarization resistance $R_{p\,av}$ (kΩcm^2)
Grinded	-250 - -134	+565 - +657	-22 - +272	536
Electropolished and passivated	-61 - -38	+1257 - +1296	-48 - +20	1940

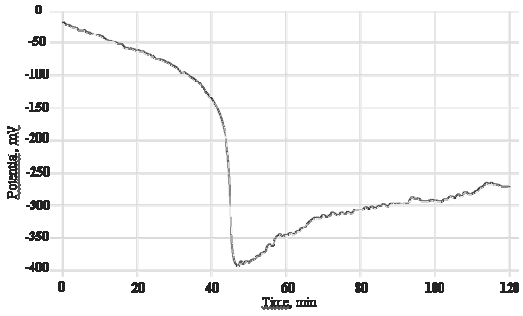

Fig. 3. Corrosion potential changes in time for grinded samples

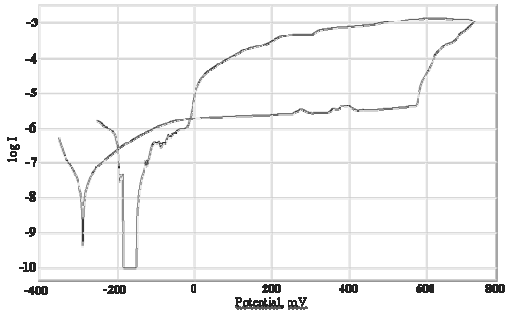

Fig. 4. Anodic polarization curve for grinded samples

For the electropolished and passivated samples, the corrosion potential was in the range E_{corr} = -61 - -38 mV (Fig. 5). Polarization of samples caused the rapid increase of anodic current for potentials in the range E_B = +1257 - +1296 mV (Fig. 6), The repassivation potential was in the range E_{cp} = -48 - +20 mV. Average polarization resistance of the electropolished and passivated samples was equal to $R_{p\,av}$ = 1940 kΩcm^2.

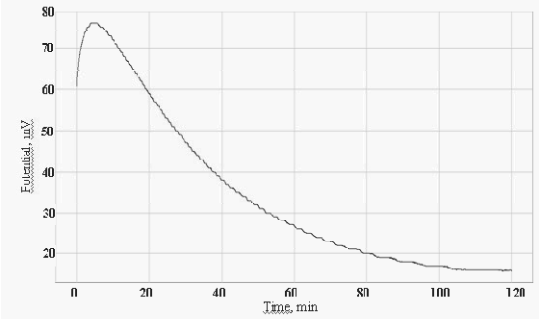

Fig. 5. Corrosion potential changes in time for electropolished and chemically passivated samples

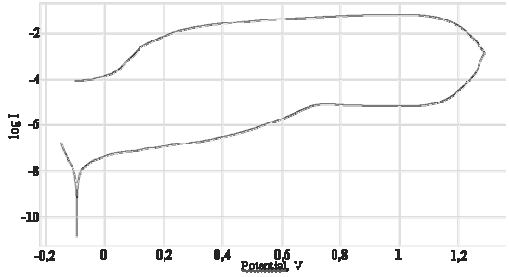

Fig. 6. Anodic polarization curve for electropolished and chemically passivated samples

Exciding the breakdown potential (for electrochemically polished and chemically passivated samples) caused a damage of the passive layer and rapid development of corrosion pits.

3.2. Pitting corrosion resistance results in the Tyrode's physiological solution

Results of electrochemical tests have revealed the influence of surface preparation of the Cr-Ni-Mo steel on the corrosion resistance (Table 5). For the grinded samples, the corrosion potential was in the range E_{corr} = -33 - +20 mV (Fig. 7). Polarization of samples caused the rapid increase of anodic current for potentials in the range E_B = +596 - +654mV (Fig. 8). The repassivation potential was in the range E_{cp} = -5 - + 200 mV. Average polarization resistance of the samples was equal to $R_{p\,av}$ = 311 kΩcm^2.

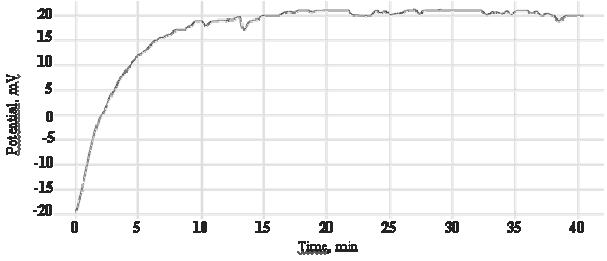

Fig. 7. Corrosion potential changes in time for grinded samples

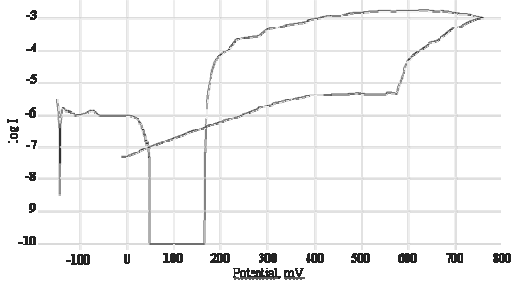

Fig. 8. Anodic polarization curve for grinded samples

Table 5.
Pitting corrosion resistance of Cr-Ni-Mo alloy in the Tyrode's physiological solution [8]

Surface preparation method	Corrosion potential E_{corr} (mV)	Break-down potential E_B (mV)	Repassivation potential E_{cp} (mV)	Average polarization resistance $R_{p\,av}$ (kΩcm^2)
Grinded	-33 - +20	+596 - +654	-5 - + 200	311
Electropolished and passivated	-28 - +37	+887 - +1016	+1 - +76	1040

For the electropolished and passivated samples, the corrosion potential was in the range E_{corr} = -28 - +37mV (Fig. 9). Polarization of samples caused the rapid increase of anodic current for potentials in the range E_B = +887 - +1016 mV (Fig. 10), The repassivation potential was in the range E_{cp} = +1 - +76 mV. Average polarization resistance of the electropolished and passivated samples was equal to $R_{p\,av}$ = 1040 kΩcm^2.

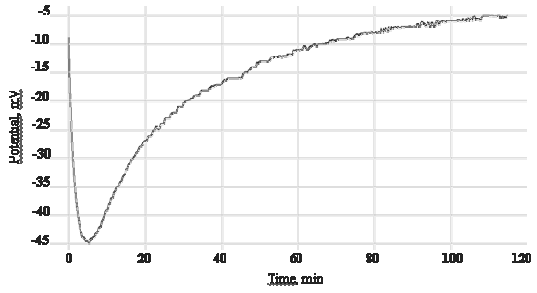

Fig. 9. Corrosion potential changes in time for electropolished and chemically passivated samples

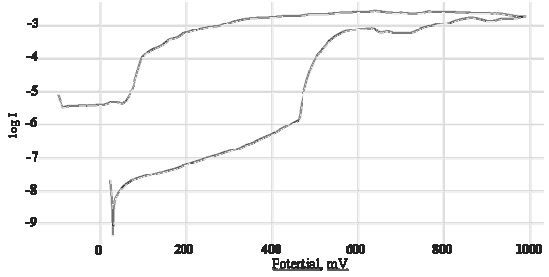

Fig. 10. Anodic polarization curve for electropolished and chemically passivated samples

Tests carried out in the Tyrode's physiological solution showed (similarly to the tests carried out in artificial urine) that exciding the breakdown potential (for electrochemically polished and chemically passivated samples) caused a damage of the passive layer and rapid development of corrosion pits.

3.3. Pitting corrosion resistance results in artificial plasma

Results of electrochemical tests have revealed the influence of surface preparation of the Cr-Ni-Mo steel on the corrosion resistance (Table 6). For the grinded samples, the corrosion potential was in the range E_{corr} = -298 - -176 mV (Fig. 11). Polarization of samples caused the rapid increase of anodic current for potentials in the range E_B = +370 - +570 mV (Fig. 12). The repassivation potential was in the range E_{cp} = +84 - +323 mV. Average polarization resistance of the samples was equal to $R_{p\,av}$ = 572 kΩcm^2.

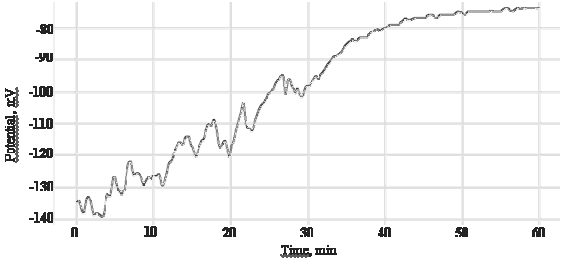

Fig. 11. Corrosion potential changes in time for grinded samples

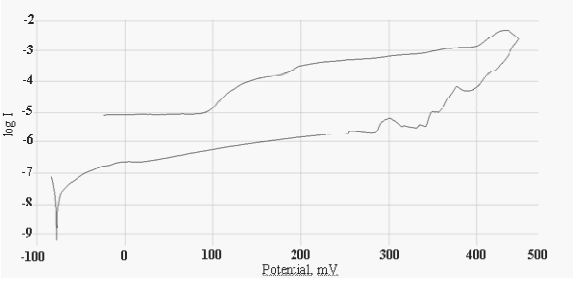

Fig. 12. Anodic polarization curve for grinded samples

For the electropolished and passivated samples, the corrosion potential was in the range E_{corr} = -85 - +21 mV (Fig. 13). Polarization of samples caused the rapid increase of anodic current for potentials in the range E_B = +1180 - +1220 mV (Fig. 14), The repassivation potential was in the range E_{cp} = 0 - +75 mV. Average polarization resistance of the electropolished and passivated samples was equal to $R_{p\,av}$ = 837 kΩcm^2.

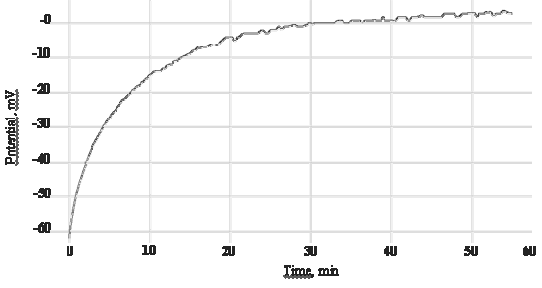

Fig. 13. Corrosion potential changes in time for electropolished and chemically passivated samples

Table 6.
Pitting corrosion resistance of Cr-Ni-Mo alloy in artificial plasma

Surface preparation method	Corrosion potential E_{corr} (mV)	Break-down potential E_B (mV)	Repassivation potential E_{cp} (mV)	Average polarization resistance $R_{p\,av}$ (kΩcm^2)
Grinded	-298 - -176	+370 - +570	+84 - +323	572
Electropolished and passivated	-85 - +21	+1180 - +1220	0 - +75	837

Table 7.
Corrosion resistance of Cr-Ni-Mo steel in simulated body fluids

Electrolyte	Surface preparation method	Corrosion potential E_{corr} (mV)	Average value of corrosion potential $E_{corr\,av}$ (mV)	Breakdown potential E_B (mV)	Average value of breakdown potential $E_{B\,av}$ (mV)
Artificial urine	Grinded	-250 - -134	-192	+565 - +657	+611
	Electropolished and passivated	-61 - -38	-49,5	+1257 - +1296	+1276
Tyrode's physiological solution	Grinded	-33 - +20	-6,5	+596 - +654	+625
	Electropolished and passivated	-28 - +37	+4,5	+887 - +1016	+951
Artificial plasma	Grinded	-298 - -176	-237	+370 - +570	+470
	Electropolished and passivated	-85 - +21	-53	+1180 - +1220	+1200

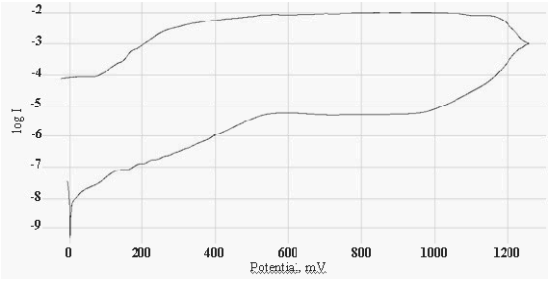

Fig. 14. Anodic polarization curve for electropolished and chemically passivated specimens

Similarly to the tests carried out in artificial urine and Tyrode's physiological solution, exciding the breakdown potential (for electrochemically polished and chemically passivated specimens) caused a damage of the passive layer and rapid development of corrosion pits.

3.4. Comparison of corrosion tests results

Comparison of corrosion tests results of the Cr-Ni-Mo steel in different simulated body fluids, depending on surface conditions were presented in Table 7 and Figs 15, 16.

For the grinded specimens, the highest value was recorded for samples tested in the Tyrode's physiological solution and was equal to +20 mV. The lowest value of the corrosion potential was recorded for the grinded samples tested in the artificial plasma. For the electrochemically polished and chemically passivated specimens the highest value was recorded for grinded samples tested in the Tyrode's physiological solution and was equal to +37 mV however the lowest value -85 mV was recorded for the artificial plasma.

For both the grinded and electropolished and chemically passivated specimens, tested in the artificial urine, the mean value of the corrosion potential was imperceptibly higher than for the artificial plasma.

The recorded anodic polarization curves for the grinded specimens showed different values of breakdown potentials EB for the different media. The lowest values were recorded for the specimens tested in the artificial plasma and were equal to +470 mV. The breakdown potentials for the specimens tested in the Tyrode's physiological solution and the artificial urine were similar and equal to +611 for artificial urine and +625 for Thyrode's physiological solution mV (Fig. 15).

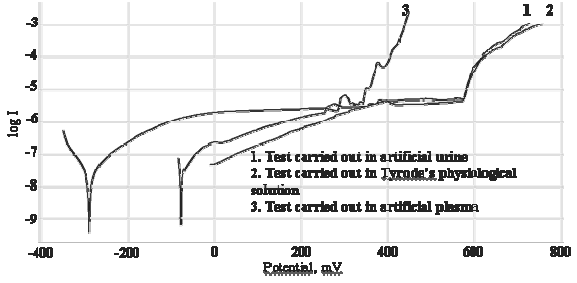

Fig. 15. Anodic polarization curves for grinded specimens in different simulated body fluids

Average values EB av for electrochemically polished and chemically passivated specimens (Fig. 16) – were significantly

higher than for the grinded samples. The lowest average values of the corrosion potential for the psssivated samples were recorded in the Tyrode's physiological solution and were equal +951 mV. The highest values of the corrosion potential were recorded in the artificial urine and were equal +1276 mV. Breakdown potentials recorded for the specimens tested in the artificial plasma were similar to the values obtained in the artificial urine and were equal +1200 mV.

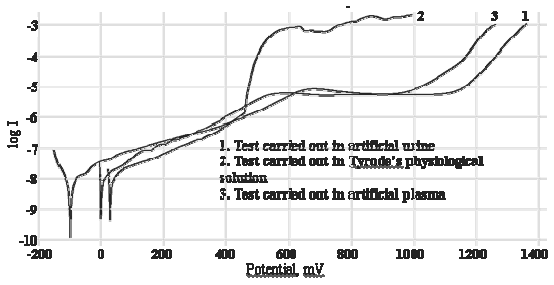

Fig. 16. Anodic polarization curves for electropolished and chemically passivated specimens in different simulated body fluids

The recorded curves of the anodic polarization (Figs 15, 16) were characterized by lower values of the anodic current density for electropolished and chemically passivated specimens then grinded ones in the range of potentials occurring in human body (0 - 400 mV). However there were no significant differences between the group of electropolisched and chemically passivated specimens and the same situation were referred to the grinded specimens.

Observations of specimens surfaces with the use of the scanning microscope were carried out after the corrosion tests. Single pits were observed on every sample (Fig. 17).

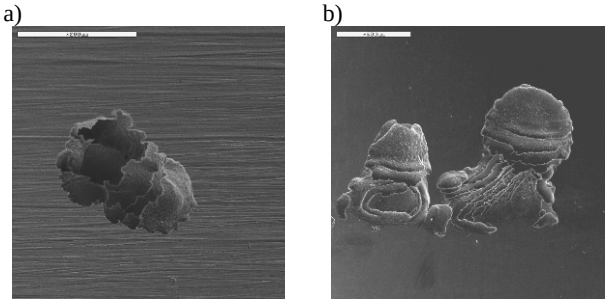

Fig. 17. Single pits on the specimens surface after test in artificial urine: a) grinded specimen, b) electropolished and chemically passivated specimen

4. Conclusions

The aim of the research was the usefulness evaluation of the AISI 316L stainless steel, commonly used for implants.

To sum up the performed corrosion tests of the AISI 316L stainless steel intended for short-term implants, it can be stated that chemical composition of artificial body fluids influences corrosion resistance. Also the obtained results have shown favorable influence of the applied surface treatment process on the corrosion resistance of samples made of the AISI 316L. This influence was notably apparent for the electropolisched and chemically passivated specimens in comparation with grinded specimens.

The highest values of breakdown potentials were observed for the specimens tested in the artificial urine. However these samples were also characterized by the highest values of the anodic current density in the passive range. High values of the anodic current density indicate the high surface activity in the medium. Contemporaneously it indicates less biocompatibility of AISI 316L steel in the mentioned medium.

The lowest values of breakdown potentials, both for the grinded and electropolished specimens, were observed in the Tyrode's physiological solution (with respect to the artificial plasma and urine). The recorded values of the anodic current density were lower that indicates the better corrosion resistance of the AISI 316L stainless steel in comparison to the other solutions.

The tests carried out in the artificial plasma showed that values of both breakdown potentials and anodic current densities were in between with respect to the values obtained for the artificial urine and the Tyrode's physiological solution.

Differences in the corrosion resistance in various media simulating body fluids can be caused by different concentration of chloride ions.

Furthermore, a legitimacy of the surface layers on metallic biomaterials increasing biocompatibility and corrosion resistance was confirmed.

In order to fully characterize the corrosion resistance of AISI 316L stainless steel alloy in artificially body fluids additional tests of electropollshed and chemically passivated samples after sterilization and in vitro tests are needed. Sterilization conditions should reflect the conditions applied for the final product.

In general the comparison tests showed the influence of the corrosive medium on the corrosion resistance of the tested biomaterial.

To this end it seems to be necessary to carry out analogous corrosion resistance tests in artificial body fluids for other metallic biomaterials, e.i. cobalt alloys, titanium alloys and Ni-Ti shape memory alloys in order to better understand corrosion phenomena.

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