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Corrosion behaviour of Co-Cr-W-Ni alloy in diverse body fluids

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ABSTRACT

Purpose: The aim of the work was evaluation of corrosion resistance of implantable Co-Cr-W-Ni alloy in simulated body fluids: human blood (artificial plasma), urine (artificial urine) and bone tissue (Tyrode solution).

Design/methodology/approach: Corrosion resistance tests were carried out in the selected physiological body fluids at the temperature 37±1°C with the use of the VoltaLab® PGP 201 system for electrochemical tests. The saturated calomel electrode (SCE) was applied as the reference electrode and the auxiliary electrode was a platinum foil. The evaluation of pitting corrosion was realized by recording of anodic polarization curves with the use of the potentiodynamic method. In order to evaluate crevice corrosion resistance the samples were polarized in the potential equal to 0,8 V by 900 seconds. Roughness of all the samples was evaluated with the use of the SURTRONIC 3+ (Taylor/Hobson) surface analyzer.

Findings: Results of corrosion resistance tests of the Co-Cr-W-Ni alloy showed the diverse values of parameters obtained in the individual solutions. The suggested surface treatments ensure good crevice corrosion resistance of the Co-Cr-W-Ni alloy in all the tested physiological fluids.

Research limitations/implications: The obtained results show the necessity of selection of the appropriate physiological solution, reflecting the specificity of body environment. In order to fully characterize the material in the human body environment, additional research on stress and fatigue corrosion should be carried out.

Originality/value: The analysis of the obtained results show favorable influence of the suggested surface treatment of the Co-Cr-W-Ni alloy. Regardless of the selected physiological solution, the most favorable characteristics was observed for the electropolished and passivated samples.

Keywords: Corrosion; Working properties of materials and products; Metallic materials; Biomaterials

PROPERTIES

1. Introduction

Cobalt alloys are one of the main groups of metallic materials used as implants. They are numbered among biomaterials of good biocompatibility. Their mechanical properties and corrosion resistance are determined by chemical composition and the technology of production as well. The homogeneous structure, obtained in heat treatment and plastic working processes, is crucial for corrosion resistance. It also influence diverse properties used in implants applied in traumatology, urology or cardiology [1-8]. In recent years the increase of biocompatibility is realized by formation of surface layers. It is connected with biological activity of implanted metals and their corrosion [9-11]. The present state of the art allows to evaluate their biological activity. It is obvious that in cobalt-base alloys the main element present in corrosion products is undoubtedly cobalt. Its toxicity is small even if the concentration is 1000 higher than normal. Cobalt ions are mainly accumulated in spleen. In tissues contacting directly with the implant the cobalt concentration is 300 ÷ 6000 higher. Higher concentration of cobalt can be observed in hair,blood and urine [12, 13].

2. Materials and methods

The aim of the work was evaluation of corrosion resistance of implantable Co-Cr-W-Ni alloy. Tests were carried out on rod samples of diameter d = 5 mm and length l = 15 mm. The applied material met the standard requirements concerning chemical composition, structure and mechanical properties. in simulated body fluids: human blood (artificial plasma), urine (artificial urine) and bone tissue (Tyrode solution).

Corrosion tests were carried out on ground, electropolished and passivated surfaces in conditions worked out by the authors [2, 4, 10, 11]. The tests were performed in the following simulated body fluids: artificial plasma, artificial urine and Tyrode solution at the temperature of 37±1 °C – Table 1.

Table 1.
Chemical compositions of body fluids used in investigations

Ingredients	Tyrode	Artificial plasma	Artificial urine
	Ingredients concentration, g/dm^3		
NaCl	8,00	6,80	13,54
$CaCl_2$	0,20	0,20	1,37
KCl	0,20	0,40	12,13
$NaHCO_3$	1,00	2,20	-
Na_2HPO_4	0,05	0,126	0,88
$MgCl_2$	0,01	-	-
$MgSO_4$	-	0,10	1,46
NaH_2PO_4	-	0,026	2,66
Na_2SO_4	-	-	4,86
NH_4Cl	-	-	4,64
$C_6H_5Na_3O_7 \cdot 2H_2O$	-	-	1,17

The electrochemical tests of the investigated alloy were performed with the use of a potentiodynamic method by recording of anodic polarization curves. The PGP 201 potentiostat with the software for electrochemical tests was applied [14]. The saturated calomel electrode (SCE) was applied as the reference electrode and the auxiliary electrode was a platinum foil. The crevice corrosion tests were carried out according to the standard [15]. The samples were polarized in the potential equal to +800 mV by 900 seconds. Roughness of all the samples was evaluated with the use of the SURTRONIC 3+ (Taylor/Hobson) roughness checker.

3. Results

3.1. Results of pitting corrosion resistance

The lowest values were observed for the samples tested in the artificial plasma (E_{tr} = +650 ÷ +680 mV) and the highest ones for the samples tested in the artificial urine (E_{tr} = +780 ÷ +790 mV) – Table 2, Fig. 1. The lowest values of polarization resistance were observed for the samples tested in the Tyrode solution (R_p = 202,9 ÷ 303,3 kΩcm) and artificial urine (R_p = 200,0 ÷ 370,0 kΩcm). However, for the samples tested in the artificial plasma, the values of the polarization resistance were in the range R_p = 442,0 ÷ 484,6 kΩcm. The values of current density were similar, regardless of the tested solution – Table 2.

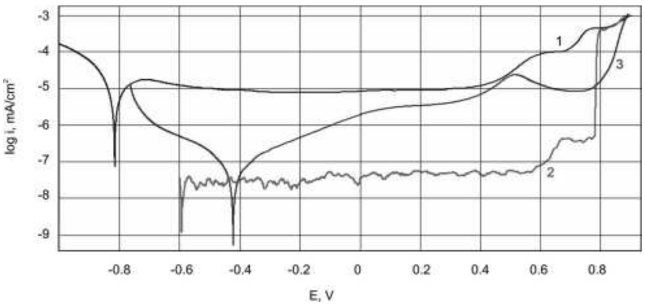

Fig. 1. Anodic polarization curves of Co-Cr-W-Ni samples of ground surface: 1 – Tyrode solution, 2 – artificial plasma, 3 – artificial urine

The tests of the electropolished samples (Ra = 0,09 ÷ 0,12 μm) revealed the favorable change of the parameters in all the tested solutions. The lowest corrosion potential values were reached for the samples tested in the artificial plasma (E_{corr} = -30 ÷ -25 mV), and the highest for the samples tested in the artificial urine (E_{corr} = +42 ÷ +54 mV). The recorded curves revealed the passive region. The obtained values of the transpassivation potentials did not reveal the significant difference and were in the range E_{tr} = +760 ÷ +815 mV – Fig. 2. The values of the polarization current and the current density are presented in Table 2.

The electrochemical tests of the ground samples (Ra = 0,25 ÷ 0,30 μm) did not reveal the significant influence of the chemical composition on the corrosion potential values. The values of the corrosion potential were in the range E_{corr} = -280 ÷ -257 mV (Tyrod solution), E_{corr} = -270 ÷ -265 mV (artificial plasma) i E_{corr} = -265 ÷ -260 mV (artificial urine) – Table 2. The trans-passivation potentials, determined for the individual solutions, were also similar.

The passivation process of the electropolished samples (Ra = 0,10 ÷ 0,12 μm) caused further favorable change of the corrosion resistance. The values of the corrosion potential were observed for the samples tested in the artificial plasma (E_{corr} = -25 ÷ -10 mV). The highest value was observed for the samples tested in the artificial urine (E_{corr} = +84 ÷ +94 mV) – Table 2.
On the basis of the recorded anodic polarization curves, no significant differences in the transpassivation potentials were observed – Fig. 3. However, the values of the polarization resistance changed considerably. The lowest values of the polarization resistance were observed for the samples tested in the artificial urine (R_p = 724,8 ÷ 996,5 kΩcm), and the highest ones for the samples tested in the artificial plasma (R_p = 2250 ÷ 2420 kΩcm) – Table 2.

Table 2.
Results of pitting corrosion resistance in body fluids

Kind of solution	Samples	Corrosion potential E_{corr}, mV	Transpassivation potential E_{tr}, mV	Corrosion current density $i_{corr.}$, nA/cm^2	Polarisation resistance R_p, kΩcm	Corrosion rate, nm/year
Tyrode	ground	-280 ÷ -257	+680 ÷ +700	1,59 ÷ 6,11	202,9 ÷ 303,3	16 ÷ 18
	electropolished	+20 ÷ +25	+760 ÷ + 780	0,52 ÷ 0,86	445,5 ÷ 455,6	6 ÷ 8
	electropolished and passivated	+40 ÷ +60	+800 ÷ +820	0,25 ÷ 0,85	995,2 ÷ 1 050,6	11 ÷ 12
Artificial plasma	ground	-270 ÷ -265	+650 ÷ +680	4,52 ÷ 6,11	442,0 ÷ 484,6	16 ÷ 18
	electropolished	-30÷ -25	+760 ÷ +780	1,28 ÷ 2,06	1 305,0 ÷ 1 365,0	9 ÷ 11
	electropolished and passivated	-25 ÷ -10	+800 ÷ +810	0,78 ÷ 0,96	2 250,0 ÷ 2 420,0	8 ÷ 10
Artificial urine	ground	-265 ÷ -260	+780 ÷ +790	2,28 ÷ 8,24	200,0 ÷ 370,0	22 ÷ 24
	electropolished	+42 ÷ +54	+805 ÷ +815	1,14 ÷ 1,96	724,8 ÷ 928,0	18 ÷ 20
	electropolished and passivated	+84 ÷ +94	+830 ÷ +840	1,08 ÷ 1,42	724,8 ÷ 996,5	15 ÷ 17

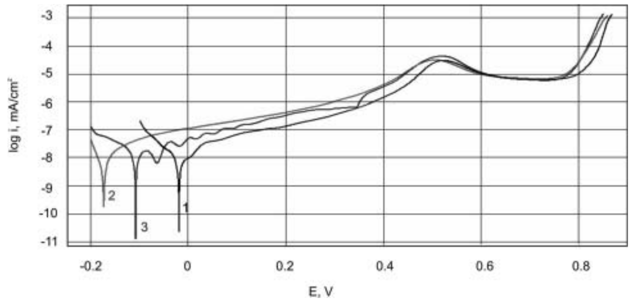

Fig. 2. Anodic polarization curves of Co-Cr-W-Ni samples of electropolished surface: 1 – Tyrode solution, 2 – artificial plasma, 3 – artificial urine

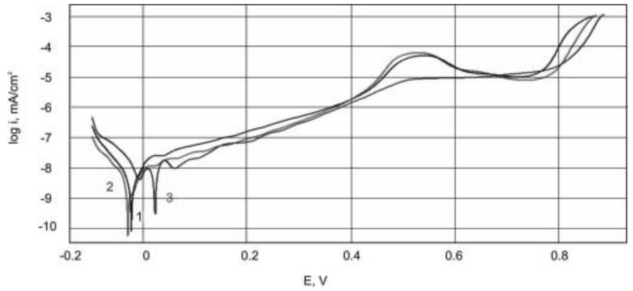

Fig. 3. Anodic polarization curves of Co-Cr-W-Ni samples of electropolished and chemically passivated surface: 1 – Tyrode solution, 2 – artificial plasma, 3 – artificial urine

3.2. Results of crevice corrosion resistance

The tests of the ground samples revealed their good crevice corrosion resistance in the all tested solutions. Sudden decrease of the anodic current density in function of time for the potential equal to +800 mV was observed – Fig. 4a. Furthermore, diverse current densities for the individual solutions were observed. The lowest values were obtained for the samples tested in the Tyrode solution (i = 0,16 ÷ 0,24 mA/cm^2), and the highest for the samples tested in the artificial plasma (i = 1,17 ÷ 1,27 mA/cm^2).

The electropolishing and passivation processes did not considerably changed the crevice corrosion resistance. No increase of the anodic current densities was observed. It shows good crevice corrosion resistance of the tested samples. Diverse values of the anodic current density were observed after 900s, like for the ground samples. Regardless of the surface modification, the lowest values of the current density were observed for the samples tested in the Tyrode solution and the highest for the samples tested in the artificial plasma – Fig. 4b and c.

4. Conclusions

Corrosion resistance of metallic biomaterials is one of the basic criteria determinig their usefulness. Problems of corrosion resistance of Co-Cr-W-Ni alloy in simulated body fluids are not well recognized. In the presented work, the authors focused on two basis types of corrosion – pitting and crevice. Furthermore, the influence of surface treatment on corrosion resistance in the selected body fluids was also analyzed.

The analysis of the pitting corrosion results shows the favorable influence of the suggested surface treatment. Regardless of the applied physiological solution, the most favorable corrosion characteristics is observed for the electropolished and passivated samples. The research revealed insignificant influence of the applied physiological solution on the corrosion resistance of the analyzed alloy. Differences of the corrosion parameters result from the diverse chemical composition (diverse reactivity of the individual solutions) – Table 2.

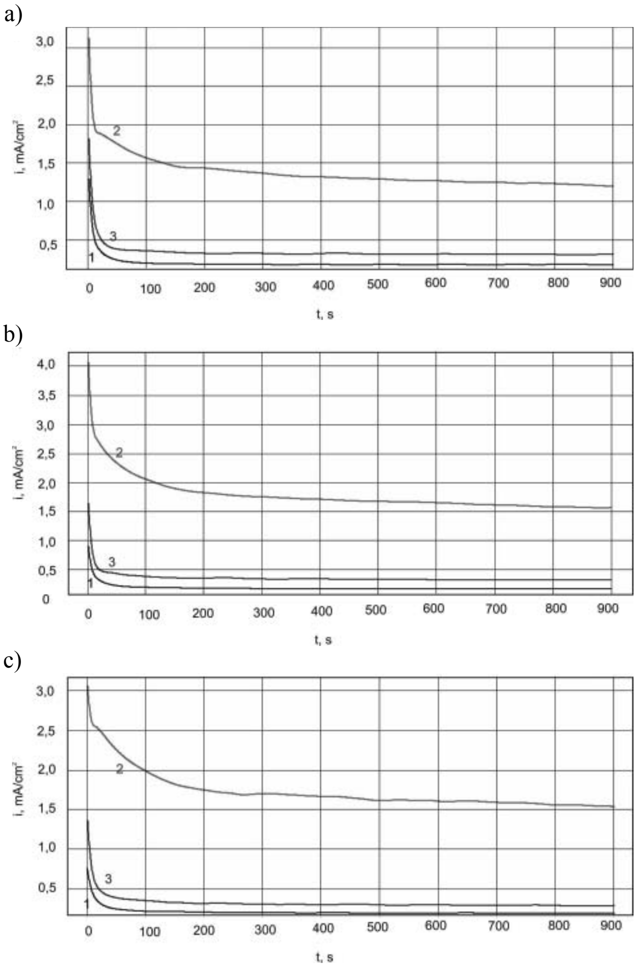

Fig. 4. Change of anodic current in a function of time for Co-Cr-W-Ni samples of surface (potential +800 mV): a – ground, b – electropolished, c – electropolished and passivated, 1 – Tyrode solution, 2 – artificial plasma, 3 – artificial urine

All variants of the applied surface treatment ensure good crevice corrosion resistance of the Co-Cr-W-Ni alloy, regardless of the used physiological solutions – Fig. 4.

On the basis of the research it can be stated that corrosion behavior of implants should be considered with respect to the appropriate environment of body fluids. In order to fully characterize the corrosion resistance of the analyzed alloy in simulated body fluids, stress and fatigue corrosion test should be carried out.

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