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Influence of medium and surface modification on corrosion behaviour of the cobalt alloy

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Materials

ABSTRACT

Purpose: The work presents the influence of artificial urine environment and surface treatment of Co-Cr-W-Ni alloy, intended for implants applied in urogenital surgery, on their corrosion resistance. The tests were carried out in three artificial urine solutions that differed in chemical composition at the temperature 37±1°C and pH = 5.6-6.4. In particular, the pitting and crevice corrosion resistance tests were carried out.
Design/methodology/approach: 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 = 5.6-6.4) at the temperature of 37±1°C.
Findings: The obtained results indicate diverse corrosion resistance of the Co-Cr-W-Ni alloy depending on the applied surface treatment and chemical composition of the artificial urine that can be connected with individual reactivity of patients.
Research limitations/implications: The obtained results are the basis for optimization of physicochemical properties of the Co-Cr-W-Ni alloy and allow to select only one artificial urine solution for further corrosion tests.
Practical implications: On the basis of the obtained results it can be stated that Co-Cr-W-Ni alloy can be applied in urology.
Originality/value: The paper presents the influence of artificial urine environment and the surface treatment on corrosion resistance of Co-Cr-W-Ni alloy.
Keywords: Metallic alloys; Biomaterials; Corrosion

1. Introduction

Development of minimally invasive methods in treatment of stenosis in urogenital system with the use of urological stents is the effect of searching of alternative solutions and new surgery procedures with reference to traditional methods. New methods are characterized by less physical and psychological trauma. Basis requirements for stents are: appropriate mechanical properties of biomaterial, corrosion resistance and good biocompatibility in environment of urological tissues and fluids. Another requirements are related with insusceptibility to incrustation, epithelialization (for permanent stents) and assuring the appropriate flow of urine [1-3].

Quantitative and qualitative description of corrosion processes decide on effectiveness and clinical usefulness of every geometrical form of implant and postoperative, reactive complications [4-10].

It is also important to analyze corrosion processes taking into consideration patient's individual reactivity. Hence, the work presents corrosion resistance tests carried out three artificial urine solutions that differed in chemical composition [10]. The differences in the composition can be connected with different disease states both in urogenital system as well as in general [11,12].

2. Material and methods

The corrosion resistance of Co-Cr-W-Ni alloy intended for implants applied in the little invasive surgery of urogenital system was tested. The tests were carried out on samples in the form of a rod of diameter d = 6 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: ground, electropolished, electropolished and chemically passivated in conditions worked by the authors, chemically pasivated and sterylizated and after 6 months exposure in artificial urine. The in vitro test was carried out in artificial urine at the temperature of 37±1 °C and pH = 5.6-6.4 – Table 1.

Sterilization was carried out in the Mocom Basic Plus autoclave in the given parameters: temperature 121°C, pressure 1.1 bar, time 30 minutes.

Table 1.
Artificial urine [15-18]

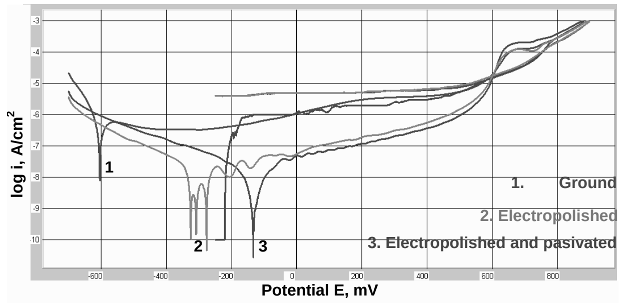
Solution		g/dm^3 distilled water
Solution I	Ingredients A	
	$CaCl_2 \cdot 2H_2O$	1.765
	Na_2SO_4	4.862
	$MgSO_4 \cdot 7H_2O$	1.462
	NH_4Cl	4.643
	KCl	12.130
	Ingredients B	
	$NaH_2PO_4 \cdot 2H_2O$	2.660
	Na_2HPO_4	0.869
	$C_6H_5Na_3O_7 \cdot 2H_2O$	1.168
	NaCl	13.545
Solution II	$CaCl_2$	0.490
	$MgCl_2 \cdot 6H_2O$	0.650
	NaCl	4.600
	Na_2SO_4	2.300
	$C_6H_5Na_3O_7 \cdot 2H_2O$	0.650
	$C_2Na_2O_4$	0.020
	$KH_2PO_4 \cdot 2H_2O$	2.800
	KCl	1.600
	NH_4Cl	1.000
	CH_4N_2O	25.000
Solution III	NaCl	6.165
	KCl	4.749
	NaH_2PO_4 H_2O	0.504
	Na_2SO_4	2.407
	$MgSO_4$	0.949
	$C_6H_5Na_3O_7 \cdot 2H_2O$	0.944

The pitting 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 [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 at the temperature of 37±1 °C – Table 1.

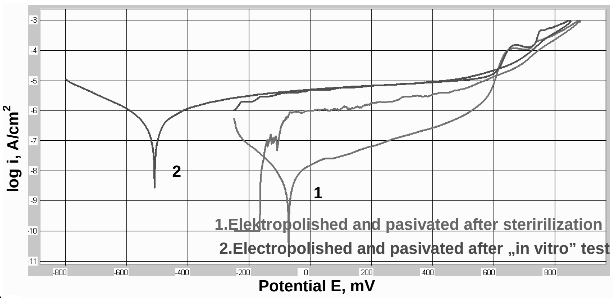
Crevice corrosion resistance was carried out in accordance to the ASTM G5-94:1999 standard [14]. The samples were polarized in the potential of 0,8 V for 900 seconds.

3. Results

As a result of the tests carried out in three artificial urine solutions for diverse surface treatment methods, values of corrosion potential E_{corr}, transpassivation potential E_{tr}, polarization resistance R_p and corrosion rate W_{corr} were determined – Table 2, Fig.1.



a)



b)

Fig. 1. Anodic polarization curves of Co-Cr-W-Ni samples after diverse surface preparation: a) grounded, electropolished and electropolished and pasivated, b) sterilization and in vitro test

The tests carried out on Co-Cr-W-Ni samples with differently modified surfaces showed advisability of the surface treatment. Formation of the passive layer caused increase of the corrosion potential of about 200 mV, in comparison to the ground samples (solution I, II and III). Increase of the transpassivation potential (50 – 100 mV) for both electropolished and passivated samples (solution I, II and III) in comparison to the ground samples was also observed.

Electropolishing and passivation caused additionally significant decrease of anodic current densities in the potential range 0.2-0.6 V – Fig. 1 a, b and increase of polarization resistance from R_p = 19-32 $k\Omega \cdot cm^2$ (solutin II) for the ground samples to R_p = 5446-7000 $k\Omega \cdot cm^2$ (solution I) for the electropolished and passivated samples. Decrease of corrosion rate was also observed W_{corr} = 51-60 nm/year (solution III).

Table 2.
Piting corrosion resistance of Co-Cr-W-Ni

Artificial urine	Surface preparation method	Corrosion potential E_{corr}, mV	Transpasivation potential E_{tr}, mV	Polarization resistance R_p, kΩ·cm2	Corrosion intensity W_{corr}, nm/year
Solution I	ground	-201--196	+654-+671	23-44	8906-9233
	electropolished	-229--27	+700-+797	449-1510	321-763
	electropolished and passivated	+54-+89	+669-+687	5446-7000	211-285
	electropolished and pas-sivated after sterilization	+32-+88	+786-+840	3891-4550	68-87
	electropolished and passivated after „in vitro" test	-505--441	+710-+731	110-312	5023-5647
Solution II	ground	-286--225	+609-+721	19-32	11020-11875
	electropolished	-210--194	+875-880	155-513	898-1088
	electropolished and passivated	+68-+75	+716-+723	1390-2040	470-538
Solution III	ground	-235--182	+621-+680	19-151	10112-13390
	electropolished	-272-+19	+693-+873	211-356	1083-2282
	electropolished and passivated	+19-+54	+714-+719	1190-1240	51-60

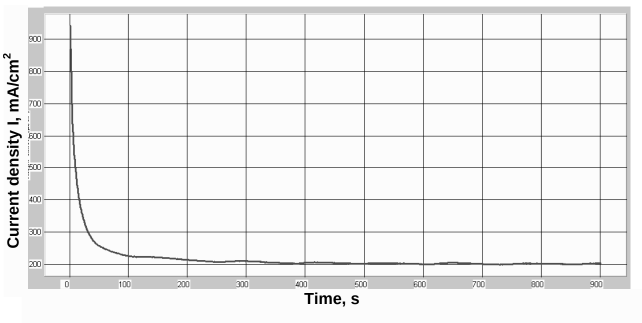


Fig. 2. Change of anodic current in a function of time for Co-Cr-W-Ni samples electropolished and chemically passivated, E = +800 mV

For the electropolished and passivated samples subjected to sterilization and 6 months exposure to artificial urine, positive influence of the sterilization process on the corrosion and trans-passivation potentials (increase of about 150 mV) was observed. Decrease of corrosion rate was also observed (W_{corr} = 68-87 nm/year) for similar values of the polarization resistance with reference to the initial samples – Table 2. Long-time exposure to artificial urine caused decrease of the corrosion potential (about 500 mV) and the polarization resistance to the range R_p = 110-312 kΩ·cm^2.

Significant increase of the corrosion rate (W_{corr} = 5023-5647 nm/year) with reference to the electropolished and passivated samples before "in vitro" tests, was also observed.

Furthermore, for these samples no significant change of the transpassivation potential was observed – Fig. 1b, Table 2.

Another stage of the corrosion tests was determination of crevice corrosion resistance of the Co-Cr-W-Ni alloy.

The samples of ground, electropolished and passivated surface were characterized by the corrosion potential: E_{corr}= -234 mV, E_{corr} = -227 mV and E_{corr} = -67 mV respectively. Anodic current for the preselected potential equal to E = +800 mV was very low, independently on the applied surface treatment – Fig. 2.

During the course of research it was stated that the Co-Cr-W-Ni alloy of differently modified surfaces, tested in the solution I, is resistant to crevice corrosion. For all the samples no increase of anodic current (in 900 seconds) was observed.

4. Conclusions

The aim of the work was determination of the proposed surface treatment and long-time exposure to artificial urine on corrosion resistance of the Co-Cr-W-Ni alloy, intended of stents applied in urology.

The tests were carried out in three artificial urine solutions that differed in chemical composition. Obtained results indicate the favorable influence of the proposed surface treatment on corrosion resistance of the investigated alloy in all applied solutions. The best anticorrosive parameters were observed for the electropolished and passivated samples as well as the electropolished, passivated and sterilized samples.

No corrosion pits were observed on the Co-Cr-W-Ni alloy surfaces what indicates good corrosion resistance in artificial urine. Contemporaneously, it was observed that the passive layer on the surface does not prevent the incrustation with mineral compounds present in urine. Depending on individual reactivity of patients and susceptibility to urolithiasis, this can lead to incrustation of stents surface, decreasing the corrosion resistance of the applied biomaterials – Fig. 3 a and b. This phenomenon causes also progressive stenosis which can lead to retention of urine.

It should be concluded that metallic biomaterials should be characterized by good biocompatibility ensuring fast epithelialization of urological stents, preventing incrustation and inflammatory ractions.

a)

b)

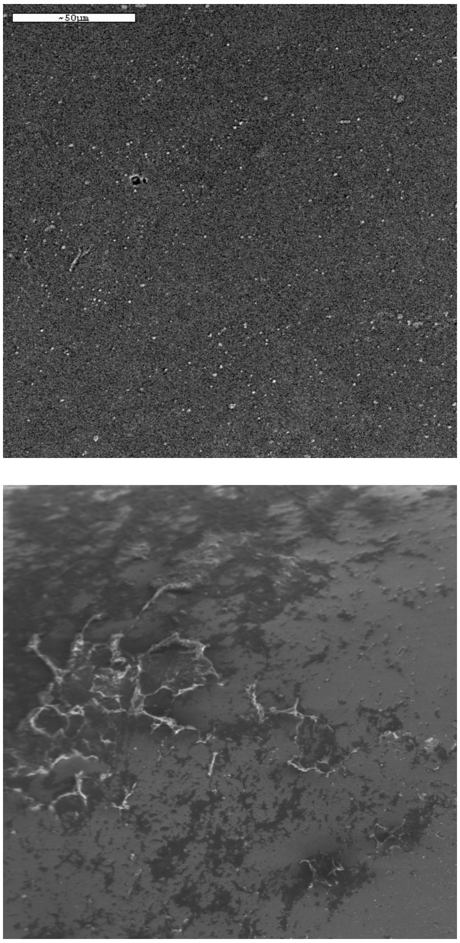


Fig. 3. View of the samples surface: a) before in vitro test, b) after in vitro test

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