

Physicochemical properties of Cr-Ni-Mo steel and Co-Cr-W-Ni alloy applied in urology

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Materials

ABSTRACT

Purpose: The main purpose of this study was to evaluate physical and chemical properties of Cr-Ni-Mo steel and Co-Cr-W-Ni alloy with modified surface, used for implants in human urinary system.

Design/methodology/approach: Evaluation of physical and chemical properties of biomaterials was made on the ground of corrosion resistance tests and analysis of chemical composition of surface layer. Resistance to pitting corrosion was evaluated on the ground registered anodic polarisation curves by means of potentiodynamic method. Chemical composition investigations of the passive layer have been carried out with the use of X-ray Photoelectron Spectroscopy (XPS).

Findings: Obtained test results show more favourable physical and chemical characteristics of Co-Cr-W-Ni alloy when compared to Cr-Ni-Mo steel. Suggested processes of surface treatment guarantee the improvement of corrosion resistance, and hence – biocompatibility of both metallic biomaterials in artificial urine.

Research limitations/implications: Obtained test results indicate the necessity to select such physiological solution for corrosion tests, that would reflect specificity of the environment in which the implant will be functioning. Complementation of presented tests with measurements of stress and fatigue corrosion resistance will enable complex evaluation of behaviour of those biomaterials in urinary system environment.

Practical implications: Analysis of test results shows favourable influence of suggested surface treatment of Co-Cr-W-Ni alloy. Samples with electrolytically polished and chemically passivated surface featured the best physical and chemical characteristics.

Originality/value: After 30 days' exposure in artificial urine solution passive layer created on the surface of Co-Cr-W-Ni alloy has better combination of physical and chemical properties than passive layer created on steel.

Keywords: Biomaterials; Artificial urine; Corrosion resistance; XPS

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1. Introduction

Dynamic development of urinary system diseases treatment methods brought about a variety of choices related to diagnostics or treatment for each individual case. At present it is estimated that urological treatment makes a great part, ca. 30%, of all surgical interventions. They are less and less frequently performed as open surgeries, endoscopic treatment or various types of techniques requiring minimum intervention are used instead. Application of external source of light together with a system of light pipes to illuminate urinary system from inside was a genuine breakthrough in modern urology. Development of new techniques and miniaturisation of optical equipment enabled endoscopy and performance of operations inside all sections of urinary tract, and most of all – abandonment of open surgical methods in favour of less invasive treatment [1].

Thanks to endoscopic methods, by means of special urological equipment, namely all kinds of probes and urethral expanders, cystoscopes and nephroscopes, electro-resectoscopes, lithotriptors as well as urethrotoms, a wide range of urological operations is carried out. Such low-invasive treatment methods include among other things electro-resection of prostate cancer, bladder cancer or bladder neck cirrhosis, and also trans-urethral electro-resection. They are performed under visual supervision. Recently, special cameras that enable visual observation of the operation on a TV monitor, have been introduced. Endoscopic methods are low-invasive, save the organs and most of all they reduce hospitalisation time and costs of therapy [2].

Endoscopic treatment methods are also used for urethra contraction. As far as this method is concerned, the revolution took place in 1974, when Sachs designed optical urethrotom which is a kind of cystoscope equipped with a delicate knife for cutting urethra. After making an incision, it is necessary to perform urethra catheterization, usually by means of Foley's catheter. But is also involves the risk of urine infection and obstructs drainage of urethra discharge. That is why in 1987 an original spiral device was created, for urethra catheterisation after making the incision, which enabled regeneration of mucous membrane and prevention of infection.

In 1988 for the first time metal stent was used in urology. It was used for urethra contraction treatment. First stents were used as a part of palliative treatment of people suffering from cancer in its last stage. Now, they are used for treatment in such diseases as: BPH (benign prostate hyperplasia), urethral contraction, contraction of ureteroenterostomy or ureteropelvic junction obstruction [3].

Development of modern urology requires improvement of surgical techniques, which in turn determines the necessity to produce modern equipment and a range of auxiliary materials for treatment. One should mention here guide wires. Thanks to their application during operation, it is possible to insert endoscopes, catheters or urological stents efficiently. Both, guide wires and stents, are made of stainless steel. They must feature suitable application properties for individual applications (among other things mechanical properties and resistance to corrosion in urinary environment, which features depend to a great extent on wire production technology and determination of physical and chemical characteristics of their surface layer) [5,8,11,13,17,18].

General criteria of metal biomaterial applicability for urological implants (urological stents) is biocompatibility

[4,9,10]. It is mainly connected with physical and chemical properties of implant surface, which should be adjusted to the features of human urinary system tissues environment [15]. In order to improve biocompatibility of Cr-Ni-Mo steel and Co-Cr-W-Ni alloy, conditions of passive layer creation on their surface were determined [16]. Passive layer creation included the stage of electrolytic polishing and passivation. Such method of surface treatment of both materials provided their roughness of $R_a \leq 0,16 \mu\text{m}$ required for this kind of implants. In this study special attention is paid to the analysis of long-term influence of artificial urine environment on physical and chemical characteristics of selected biomaterials [6,7].

2. Materials and methods

The following materials were selected for experimental tests: Co-Cr-W-Ni alloy in accordance with PN-ISO 5832 – 6 made by Fort Wayne Metals in annealed condition and Cr-Ni-Mo steel in accordance with PN-ISO 5831 – 1, made by Sandvik, in supersaturated condition, generally used for production of urological stents. Chemical composition of tested biomaterials and strength properties are presented in Tables 1 and 2.

Table 1.

Chemical composition of the investigated materials

Element	Co-Cr-W-Ni alloy		Cr-Ni-Mo steel	
	Acc. to ISO	Ladle analysis	Acc. to ISO	Ladle analysis
	% mass.	% mass.	% mass.	% mass.
C	<0.15	0.08	<0.03	0.01
Co	balance	50.56	-	-
Cr	19.0-21.0	20.45	17.0-19.0	17.49
Fe	<3.0	1.88	balance	balance
Mn	<2.0	1.24	<2.0	1.68
N	-	0.019	0.1-0.2	0.087
Ni	9.0-11.0	10.16	14.0-16.0	14.49
P	<0.04	0.002	<0.025	0.017
S	<0.03	<0.001	<0.01	0.003
Si	<1.0	0.01	<1.0	0.21
W	14.0-16.0	15.14	-	-
Mo	-	-	2.35-4.20	2.76
Cu	-	-	<0.5	0.05

Table 2.

Mechanical properties of the investigated materials

Material	Yield stress $R_{p0.2}$, MPa	Tensile strength R_m , MPa	Elongation A_5 , %
Cr-Ni-Mo steel	252	604	40
Co-Cr-W-Ni alloy	476	917	35

Samples for tests, taken both from Cr-Ni-Mo steel and Co-Cr-W-Ni alloy, were subject to the following treatment: mechanical grinding, which was made by means of hydrous abrasive paper with granularity of 120 - 500 grains/mm²; electrochemically polished:

for steel it was performed in the solution with chemical composition presented in Tab. 3 in the period of 4 minutes; for the cobalt alloy - performed in the solution with chemical composition presented in Tab. 4 in the period of ca. 5 minutes; chemical passivation for both biomaterials was made in 40 % solution of HNO₃ in the temperature of 65 ± 1 °C in the period of 60 minutes.

Table 3. Chemical composition of the solution polishing for Cr-Ni-Mo steel

Component	Amount	Conditions
H ₃ PO ₄	55 - 60 % mass.	T = 60 ± 1 °C, i = 40 ± 1 A/dm ²
H ₂ SO ₄	35 - 45 % mass.	
C ₂ H ₂ O ₄	40 - 60 g/dm ³	
C ₈ H ₉ NO	40 - 60 g/dm ³	
Inhibitor of corrosion	3 g/dm ³	

Table 4. Chemical composition of the solution polishing for Co-Cr-W-Ni alloy

Component	Amount	Conditions
H ₂ SO ₄	0.12 - 0.18 dm ³	T = 60 ± 1 °C, i = 55 ± 1 A/dm ²

Tests of physical and chemical properties of metallic biomaterials with modified surface were carried out in two stages. The first stage consisted in determination of corrosion resistance of samples in solution simulating urine – Tab. 5, which the tested alloy may come into contact with in clinical practice. The purpose of the second stage was determination of corrosion resistance of samples that were subject to 30 days' exposure in artificial urine on samples surface. For this purpose, a testing station was designed and created. This designed station enabled simulation of conditions prevalent in patient's organism. Flow of physiological medium was realised by means of a pump which secures suitable flow intensity, adequate to physiological conditions. Moreover, designed station enabled constant control of pH and ensured constant temperature of 37±1°C. Surface of samples in initial condition as well as after the time of immersion in artificial urine was also tested for its chemical composition.

2.1. Corrosion resistance testing

The pitting corrosion tests were realized with the use of potentiodynamic method by means of recording of anodic polarization curves [12,14]. The VoltaLab® PGP 201 system (Radiometr) for electrochemical tests was applied. The saturated calomel electrode (SCE) of KP-113 type was applied as the reference electrode. The PtP-201 platinum electrode was the auxiliary electrode. Corrosion resistance of all samples was investigated. The corrosion tests were undertaken in artificial urine of chemical composition presented in Table 5. Temperature of the solution was equal to 37 ± 1 °C and pH = 7.0 ± 0.2. Both solutions A and B that artificial urine was composed of were mixed together in the proportion 1:1. The solution featured mol concentration of chlorine ions of 0.46.

The measurements were carried out after 60 min immersion in the artificial urine while the open circuit potential (OCP) was

recorded. The potential scan was started at 100 mV more cathodic potential than the OCP, increasing toward the anodic values at a constant rate of 1 mV/s up to 1 mA/cm², and then a reverse scan was carried out toward the cathodic value.

Table 5. Chemical composition of artificial urine

Component	Amount of distilled water, g/l
Solution A	
CaCl ₂ · H ₂ O	1.765
Na ₂ SO ₄	4.862
MgSO ₄ · 7H ₂ O	1.462
NH ₄ Cl	4.643
KCl	12.130
Solution B	
NaH ₂ PO ₄ · 2H ₂ O	2.660
Na ₂ HPO ₄	0.869
C ₆ H ₅ Na ₃ O ₇ · 2H ₂ O	1.168
NaCl	13.545

On the basis of the recorded curves the following corrosion parameters were assessed: corrosion potential E_{corr}, breakdown potential E_b, repassivation potential E_{cp}, polarization resistance R_p, corrosive current i_{corr}.

The breakdown potential was directly read from the graph by drawing tangent lines to the passive current and inflection of the curve. The coordinate of the intersection point was considered as E_b. Repassivation potential was determined as the intersection point of the anodic (forward) and the return curves. The Stern method was applied to calculate the polarization resistance R_p. The polarization resistance depends mostly on the anodic current density therefore it was assumed that the “b” value for anodic and cathodic reactions are the same and were equal to 0.12 V.

The corrosion current density was calculated on the basis of the simplification i_{corr} = 0.026/R_p.

2.2. Chemical composition of the surface layer (XPS)

Chemical composition investigations of surface layers were realized with the use of the multifunctional electron spectrometer Physical Electronics PHI 5700/660. The X-ray photoelectron spectroscopy with monochromatic radiation AlKα of 1486.6 eV was applied.

The tests were carried out on the samples of polished as well as polished and passivated surfaces in the form of bar. The measurement of photoelectron spectrum in the wide range of binding energy from 0-1400 eV and precise measurements of the spectrum lines of elements from the surface layer were conducted. For the applied excitation energy, the mean free path of photoelectrons was in the range 5 Å-20 Å.

Chemical compositions obtained from the spectrums concern the surface layer of the given thickness. The chemical composition was calculated by integration of the appropriate photoemission lines with the use of the MULTIPAK (Physical Electronics) program.

Analysis of the individual elements spectra allowed to evaluate chemical composition of the passive layer of the alloy. The selected analysis area was a circle of diameter equal to 800 μm . Detection threshold of quantitative analysis was equal to 0.01 atomic %.

3. Results

3.1. Results of pitting corrosion resistance

Potentiodynamic tests carried out in artificial urine gave information about corrosion resistance of biomaterials with differentiated way of surface preparation - Figs. 1- 4, Table 6.

Anodic polarisation curves for steel samples with polished as well as polished and passivated surface were determined during the first stage of the tests. Created passive layer caused the shift of perforation potential in the anodic direction from the average value of $E_b = +350$ mV for polished surface to the average value of $E_b = +1203$ mV for polished and passivated surface - Tab. 6. Densities of corrosion current and polarisation resistance, determined for samples with polished surface did not differ significantly in relation to the values obtained for passivated surface - Tab. 6. Application of chemical passivation caused in this case only the increase in perforation potential, which is a favourable phenomenon. The course of changes of passivation current densities within anodic range was identical to both ways of surface preparation - Figs. 1 and 2 (curve 1).

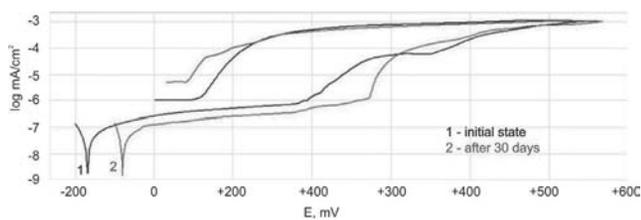


Fig. 1. Anodic polarisation curves determined for polished Cr-Ni-Mo stainless steel

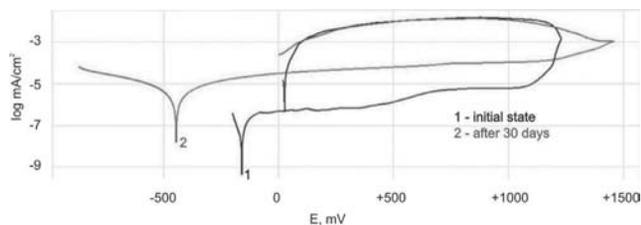


Fig. 2. Anodic polarisation curves determined for polished and passivated Cr-Ni-Mo stainless steel

Tests carried out on samples made of Co-Cr-W-Ni alloy with polished surface and polished and passivated surface showed practicability of the method of electrochemical polishing and passivation of alloy, proposed in the study, in order to improve its corrosion resistance. Creation of passive layer caused the increase in corrosion potential by the value of ca. +140 mV in relation to polished surface - Tab. 6. Applied chemical passivation process

also caused the increase in polarisation resistance R_p from the value of 1 320 $\text{k}\Omega\text{cm}^2$ to the value of 2 330 $\text{k}\Omega\text{cm}^2$ - Tab. 6. Favourable decrease of corrosion current density by half was also observed. However, transpassivation potential remained steady on the same level, adopting the values from within the range of $E_{np} = +820 - +853$ mV.

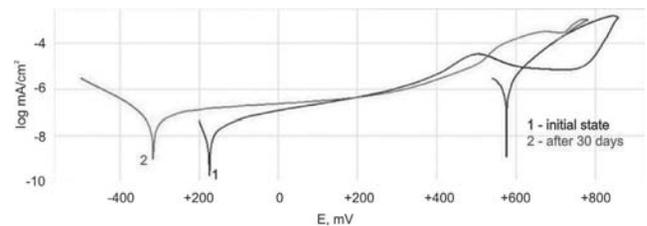


Fig. 3. Anodic polarisation curves determined for polished Co-Cr-W-Ni alloy

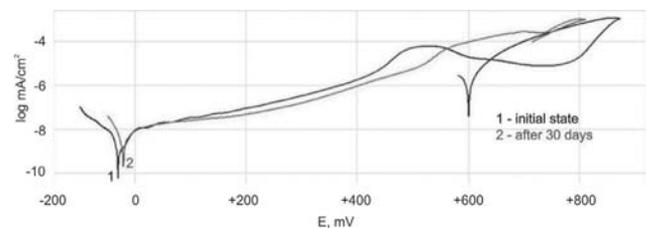


Fig. 4. Anodic polarisation curves determined for polished and passivated Co-Cr-W-Ni alloy

In the next stage of tests, anodic polarisation curves for steel samples after 30 days' exposure in artificial urine were determined. For samples with polished surface a slight increase in corrosion potential was observed, from the value $E_{kor} = -83$ mV to $E_{kor} = -39$ mV. Slight decrease in perforation potential E_b by ca. 100 mV and polarisation resistance R_p by the value of 64 $\text{k}\Omega\text{cm}^2$ was also demonstrated - Tab. 6. Substantial decrease in corrosion potential was observed for samples with polished and passivated surface. The period of 30 days' impact of artificial urine on the surface caused decrease in its value by ca. 300 mV. Huge decrease in polarisation resistance R_p from the value of 216 $\text{k}\Omega\text{cm}^2$ to 16 $\text{k}\Omega\text{cm}^2$ also took place - Tab. 6. Only the value of perforation potential E_b virtually remained on the same level.

In the last stage of corrosion tests, anodic polarisation curves were determined for samples made of Co-Cr-W-Ni alloy after 30 days' exposure in artificial urine. Pitting corrosion characteristics obtained in those tests showed that 30 days' exposure in artificial urine was favourable only for the alloy with surface that was polished and passivated. The fact that the values of corrosion potential E_{corr} , transpassivation potential E_{tr} , corrosion current density i_{corr} as well as polarisation resistance R_p remained at a similar level to the samples that had not been exposed to artificial urine, proves that passive layer protection was really beneficial.

Anodic polarisation curves determined for Cr-Ni-Mo steel - Figs. 1 and 2, featured the presence of hysteresis loop within the whole anodic range, which proves initiation of corrosion processes in artificial urine environment. For Co-Cr-W-Ni alloy, hysteresis loop in the limited range was present only for samples in the initial condition - Figs. 3 and 4.

Table 6. Results of pitting corrosion resistance

Time	Method of surface preparing	Corrosion potential E_{corr} , mV	Breakdown potential E_b , mV	Corrosion current density i_{corr} , nA/cm ²	Polarisation resistance R_p , kΩcm	Corrosion, μm/year
Cr-Ni-Mo steel						
Initial state (0 days)	polished	-86 - -80	+325 - +375	0.124 - 0.117	210 - 222	0.25 - 0.23
Initial state (0 days)	passivated	-167 - -147	+1195 - +1211	0.117 - 0.107	222 - 242	0.23 - 0.21
30 days	polished	-43 - -35	+270 - +278	0.162 - 0.148	160 - 176	0.33 - 0.30
30 days	passivated	-445 - -435	+1145 - +1153	2.167 - 1.444	12 - 18	4.35 - 2.89
Co-Cr-W-Ni alloy						
Initial state (0 days)	polished	-176 - -166	+820 - +840*	0.020 - 0.019	1 310 - 1 330	0.04 - 0.04
Initial state (0 days)	passivated	-33 - -27	+833 - +853*	0.011 - 0.011	2 325 - 2 335	0.02 - 0.02
30 days	polished	-322 - -302	+702 - +722*	0.064 - 0.061	403 - 423	0.13 - 0.12
30 days	passivated	-23 - -17	+738 - +758*	0.013 - 0.013	2 057 - 2 061	0.02 - 0.02

*Transpassivation potential E_{np} , mV

3.2. Results of chemical composition of the surface layer

Chemical composition of surface layers, created on the surface of samples made of Cr-Ni-Mo steel and Co-Cr-W-Ni alloy after 30 days' exposure in artificial urine solution was determined by means of XPS method.

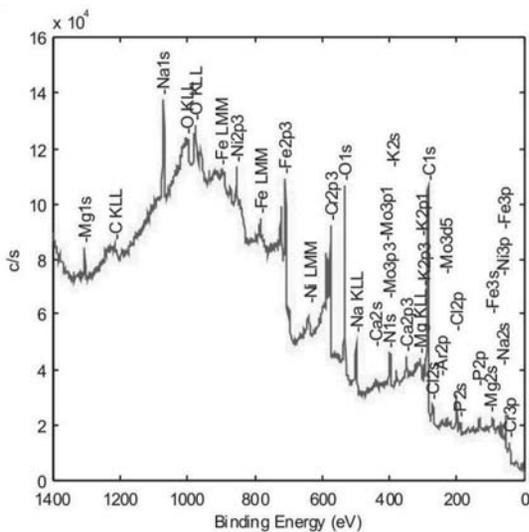


Fig. 5. XPS spectrums of Cr-Ni-Mo steel samples of electro-polished surface after 30 days in artificial urine

In surface layer of steel samples after polishing and exposure in artificial urine, presence of such elements as: C, N, O, Na, Mg, Si, P, Cl, K, S, Ca, Ni, Cr, Fe was discovered. For the sample surface prepared in such a way, also its overview spectrum was registered – Fig. 5 as well as detailed spectra for the line Fe2p_{3/2}, Cr2p, Ni2p_{3/2}, C1s, O1s, N1s, – Fig. 5.

On the spectrum presented in Fig. 5 one can see the lines showing electron states of the respective chemical elements, as well as lines of Auger's electrons, marked as KLL or LMM.

Production of detailed spectra enabled to identify chemical compounds in relation to the respective elements and their quantity in the layer – Tab. 7, Fig. 5. Iron was present in two chemical states: main line Fe2p_{3/2} came from metallic state (706.8 eV), and adjacent energy line of ca 710.0 eV probably from oxidised ferrum Fe₂O₃. The situation was inverse for chromium. Oxidised state was dominant; line Cr2p_{3/2} with energy of 576.7 eV was emitted by Cr₂O₃, whereas light line with energy of 574.4 eV by metallic chromium. Nickel was present in metallic state – Ni2p_{3/2} line with energy of 852.8 eV and in oxidised state Ni₂O₃ – line 855.9 eV. However, presence of molybdenum in the surface layer was not observed. The position of nitrogen line corresponded to compounds containing groups: NH₃ or -NH₂. In addition, presence of phosphates (Na1s – 1071.2 eV) and sulphates (S2p – 169.0 eV) was observed. For line Ca2p_{3/2} with energy of ca. 347.5 eV, chemical compositions such as CaSO₄, CaCl₂ were assigned. Increased content of sodium, magnesium and calcium was also discovered, and decreased content of nitrogen, carbon and phosphorus.

Table 7.
Chemical composition of layer formed on the Cr-Ni-Mo steel

Element	C	N	O	Na	Mg	P	Cl	K	Ca	Cr	Fe	Ni	Mo
(electrochemically polished and after 30 days)													
% at. (survey spectrum)	59.35	7.22	26.46	1.67	0.21	1.53	1.63	0.18	0.40	0.66	0.28	0.08	-
% at. (detailed spectrum)	-	17.77	65.09	4.11	0.51	3.76	4.00	0.45	0.97	1.63	0.68	0.19	-
(electrochemically polished and passivated and after 30 days)													
% at. (survey spectrum)	45.42	5.59	36.83	1.28	0.33	3.08	1.00	0.42	0.41	3.71	1.26	0.29	0.15
% at. (detailed spectrum)	-	8.63	62.16	2.51	0.65	6.79	1.29	2.11	1.02	8.26	4.60	0.69	0.23

Table 8
Chemical composition of layer formed on the Co-Cr-W-Ni alloy

Element	C	O	N	Na	Si	Cl	Ca	Cr	Co	Ni	W
(electrochemically polished and after 30 days)											
% at. (survey spectrum)	60.05	20.89	4.59	1.08	0.81	6.57	2.52	2.02	0.59	0.44	0.45
% at. (detailed spectrum)	-	50.90	11.83	2.46	-	17.72	7.23	5.21	1.79	1.17	1.69
(electrochemically polished and passivated and after 30 days)											
% at. (survey spectrum)	60.18	25.50	-	0.29	0.90	5.17	2.85	2.93	1.15	0.31	0.71
% at. (detailed spectrum)	-	55.01	10.55	1.05	-	12.58	6.87	7.69	2.75	1.51	1.99

For steel sample with polished and passivated surface after 30 days' exposure in artificial urine, presence of the following elements in the surface layer was discovered: C, N, O, Na, Mg, Si, P, Cl, K, S, Ca, Ni, Cr, Fe, Mo – Fig. 6, Tab. 7.

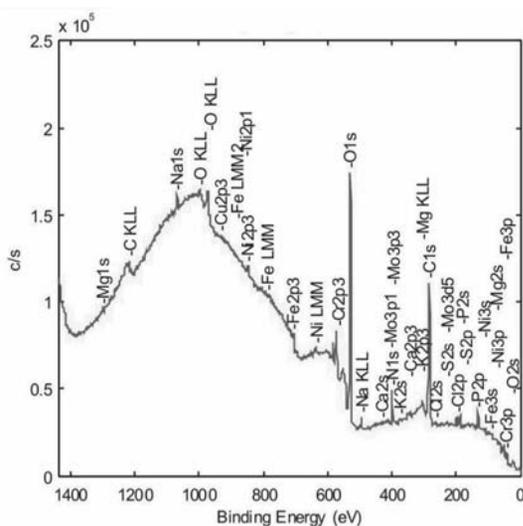


Fig. 6. XPS spectrums of Cr-Ni-Mo steel samples of electro-polished and chemically passivated surface after 30 days in artificial urine

Determination of detailed spectra enabled to identify chemical compounds and determine their respective elements as well as their quantitative participation in the layer – Tab. 7. The number of individual elements, place they can be located at and compounds made by them, which are included in the surface layer were analogical to steel sample with polished surface. It must be stated, though, that on the surface of passivated sample molybdenum in metallic state was also observed (line – Mo3d_{5/2} with energy 228.1 eV). Performed analysis of detailed spectra for this sample showed specific presence of huge amount of chromium (as oxide Cr₂O₃) in the surface layer.

Next, analysis of chemical composition of Co-Cr-W-Ni alloy samples, polished as well as polished and passivated, after exposure in artificial urine solution, was made. Figs. 7 and 8 present overview spectra obtained for cobalt alloy after 30 days' exposure in artificial urine. Performed detailed spectra measurement showed presence of the following elements in the surface layer: C, O, N, Na, Cl, Ca, Cr, Co, Ni and W – Tab. 8. Cobalt was present in two chemical states: main line Co2p_{3/2} originated in metallic state (778.1 eV), and adjacent energy line ca. 780.4 eV probably from CoO. For chromium, the situation was inverse. Oxidised state was dominant; line Cr2p_{3/2} with energy 577.0 eV was emitted by Cr₂O₃, whereas light line with energy 574.4 eV by metallic chromium. Nickel was in metallic state. For the line 4f of tungsten, two doublets shifted by several eV could be seen. The first one, with smaller intensity originated in metallic state, the other one could be attributed to oxide WO₃ (energy line 35.6 eV). Oxygen line included various chemical states. The component with bond energy of ca. 532.5 eV, that could originate from hydroxides and from adsorbed on the surface

OH groups, was dominant. Changing its intensity line at 531.5 originates from chromium oxide. Strong contribution with energy 530.4 eV may come from tungsten oxide WO_2 . After longer etching, line with energy ca. 530 eV, which could be attributed to cobalt oxides of Co_2O_3 or Co_3O_4 , was dominant.

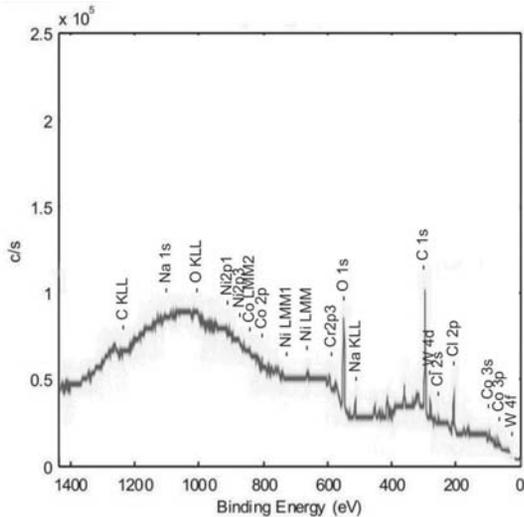


Fig. 7. XPS spectrums of Co-Cr-W-Ni alloy samples of electro-polished surface after 30 days in artificial urine

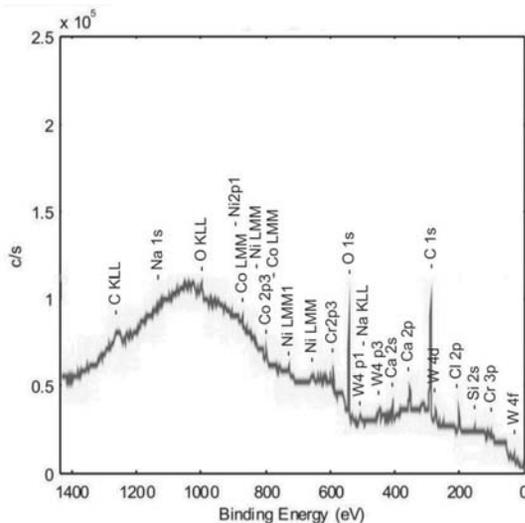


Fig. 8. XPS spectrums of Co-Cr-W-Ni alloy samples of electro-polished and chemically passivated surface after 30 days in artificial urine

4. Conclusions

A significant problem in the process of formation of urological implants application properties is the selection of mechanical characteristics of metallic biomaterial and its physical and chemical characteristics.

Potentiodynamic tests performed in artificial urine provided information about corrosion resistance of the selected metallic biomaterials with various ways of surface preparation. Performed chemical passivation process for steel samples did not cause the change of polarisation resistance value and corrosion current density – Tab. 6. Corrosion rate also remained at the same level. Created passive layer only caused the increase in perforation potential value from $E_b = +350$ mV (polished surface) to $E_b = +1203$ mV. Test performed on samples made of cobalt alloy with diversified way of surface preparation showed applicability of the developed method of electrochemical polishing and passivation of alloy for the improvement of its corrosion resistance. Creation of passive layer on the surface caused increase in corrosion potential by the value of ca. +140 mV in relation to the sample with surface that was only polished – Tab. 6. Carried out passivation process caused substantial decrease in corrosion current value by half and double increase in polarisation resistance R_p from the value of $1320 \text{ k}\Omega\text{cm}^2$ for samples with polished surface to the value of $2330 \text{ k}\Omega\text{cm}^2$ for samples with polished and passivated surface. Corrosion rate for cobalt samples after passivation process also decreased – Tab. 6. Generally it was found that chemical passivation process improved favourably corrosion resistance of steel and cobalt alloy in relation to samples with surface that was only polished.

Tests performed after 30 days' influence of artificial urine on the surface of steel and cobalt samples showed that passive layer fully protects only Co-Cr-W-Ni alloy. It can be proved by obtained values of corrosion potential, polarisation resistance and corrosion current density, which remained at the same level in relation to samples that had not been subject to exposure – Tab. 6. Determined anodic polarisation curved for samples made of Co-Cr-W-Ni alloy after exposure in artificial urine featured the absence of hysteresis loop, which means perfect passivation within anodic range to the value of transpassivation potential. This fact shall be accounted as extremely favourable for the improvement of biocompatibility of the alloy.

Applicability of proposed passive layers for the refinement of surface of urological implants is also determined to a great extent by their chemical composition [19]. Therefore, in the next stage of work, analysis of chemical composition of surface layer of steel and cobalt alloy (polished as well as polished and passivated surface) after 30 days' of exposure in artificial urine was made by means of XPS method. Obtained detailed spectra of the respective elements showed that the process of passivation caused increase in oxygen concentration connected mainly with cobalt into oxide CoO (for Co-Cr-W-Ni alloy) and into ferrum oxide Fe_2O_3 and chromium oxide Cr_2O_3 (for Cr-Ni-Mo steel). Concentration of the respected alloy elements (Co, Cr, W, Ni – alloy of cobalt, Fe, Cr, Ni, Mo – austenitic steel) in relation to chemical composition of the substrate was substantially decreased – Tab. 7 and 8, which must be seen as really favourable for biocompatibility. All elements were in oxidised state. Only such elements as cobalt, nickel and ferrum were partially in metallic state. The analysis also showed that passive layer on Cr-Ni-Mo steel is more prone to deposition of ions of elements coming from the solution. A positive feature of this layer was small number of Cl ions (coming from physiological solution) that was incorporated into its structure. It testifies about relatively coating density of created passive layer, which was also shown

in corrosion tests ($E_b = +1145 - +1211$ mV). Vast majority of chlorine ions was observed on the surface of Co-Cr-W-Ni alloy after exposure in artificial urine. It influenced slight decrease in the value of transpassivation potential from $E_{tr} = +833 - +853$ mV to $E_{tr} = +738 - +758$ mV – Tab. 6.

Generally, it was determined that passive layer created on the surface of Co-Cr-W-Ni alloy has better combination of physical and chemical properties in comparison with passive layer created on steel after 30 days' exposure in artificial urine solution.

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