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Corrosion resistance and chemical composition investigations of passive layer on the implants surface of Co-Cr-W-Ni alloy

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Properties

ABSTRACT

Purpose: The paper presents results of corrosion resistance and surface properties of Co-Cr-W-Ni alloy used in interventional cardiology.
Design/methodology/approach: The tests were carried out on grinded, electropolished and passivated samples. The pitting corrosion tests were realized by recording of anodic polarization curves with the use of the potentiodynamic method. The saturated calomel electrode (SCE) of KP-113 type was applied as the reference electrode. The tests were carried out in electrolyte simulating human blood environment (artificial plasma). Crevice corrosion resistance was carried out in accordance to the ASTM F-746-81:1999 standard. Chemical composition investigations of the passive layer were realized with the use of multifunctional electron spectrometer Physical Electronics PHI 5700/660. The X-ray photoelectron spectroscopy with monochromatic radiation AlKα of 1486,6 eV was applied.
Findings: Results of electrochemical tests have revealed the influence of surface preparation of the Co-Cr-W-Ni alloy on the corrosion resistance. The tests carried out in the artificial plasma for the grinded, the electropolished and the chemically passivated samples have showed that Co-Cr-W-Ni alloy is resistant to both crevice and pitting corrosion. The chemical composition analysis of the passive layer on Co-Cr-W-Ni alloy has revealed the presence of the following elements: C, O, N, Cr, Fe, Co, Ni and W.
Research limitations/implications: The research was carried out on samples, not on final elements. The tests were carried out in in vitro conditions.
Practical implications: The suggested surface treatment can be used for implants made of the Co-Cr-W-Ni alloy.
Originality/value: The proposed surface treatment ensures the increase of the corrosion resistance in the blood environment that increases biocompatibility.
Keywords: Biomaterials; Vascular stent; Passive layer; Surface chemical composition; Corrosion resistance

1. Introduction

The epidemiological assessment of the cardiovascular diseases reveals that morbid states of this system take the lead in the statistics of diseases and deaths. Heart diseases, and especially the ischaemic heart disease cause yearly deaths of about 180,000 people in UK and of more than 500.000 in USA. They are the main reason of the premature death of 40% middle-aged men (45÷54 years of age), and for women they feature the second, after neoplasms, cause of the premature deaths. This disease can

be the reason of the 10 times larger death rate than the neoplastic one in certain age groups [1÷3, 18÷21].

Dilating of the artery lumen by means of the percutaneous transluminal coronary angioplasty (PTCA) is one of the basic methods of the coronary artery disease treatment, apart from the coronary artery bypass grafting (CABG). This method, introduced by A. Gruentzig in 1977, featured the turning point in the ischaemic heart disease therapy [1, 3].

One of the most important achievements of the last years in the area of the interventional cardiology in treatment of the ischaemic heart disease is employment of the intravascular implants, called stents. Stents are a kind of metal elastic frames with spatial cyllindrical structure and of millimetre sizes that are implanted into a critically stenosed section of the coronary vessel to support its walls and to dilate its lumen. They are used for the percutaneous treatment of the ischaemic heart disease in all haemodynamic laboratories being engaged in the interventional cardiology.

Portion of operations in which stents are implanted reaches even 80% in USA [4÷11].

The initial experiences connected with implanting of stents were not too encouraging, as blood thrombosis used to occur often, closing the artery lumen and causing severe complications, leading in consequence to cardiac infarction or death of the patient. Year 1993 was the turning point when Antonio Colombo introduced the high-pressure method of stent deployment (16÷20 atmospheres), verifying the results with the intravascular ultrasonography (IVUS) [2, 3]. It was the high-pressure deployment and introducing the antithrombotic treatment that significantly lowered the frequency of thrombosis incidences. This lead to wide use of stents and after several years long investigation they turned out to be the nearly ideal solution for the ischaemic heart disease. The implantation operations carried out reduced nearly by half the incidences of restenosis (secondary coronary vascular stenosis) with patients that were subjected to the balloon angioplasty operation [10, 11, 18÷21].

Stainless steels are the most common metallic biomaterials used for vascular stents [19÷21]. Almost 90% of these stents is made of steel [1, 2, 6, 11]. Since many years this group of biomaterials is in common use mainly as short term implants, for example in an orthopaedic surgery, a dental surgery and a thoracosurgery [2, 6]. In recent years attempts to apply Co alloys for vascular stents are observed. For this reason a surface treatment of that alloy is presented in this work. The surface treatment is important because of corrosion resistance minimizing reactions and postoperative complications [14÷21] .

2. Material and methods

The investigations were carried out on Co-Cr-W-Ni alloy. The samples in the form of rod of diameter d = 5mm and length l = 10 mm were used for tests. Chemical composition of the alloy has been shown in the table 1.

The tests were carried out on grinded, electropolished and passivated samples in conditions worked out by the authors. 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 [12] – fig. 1.

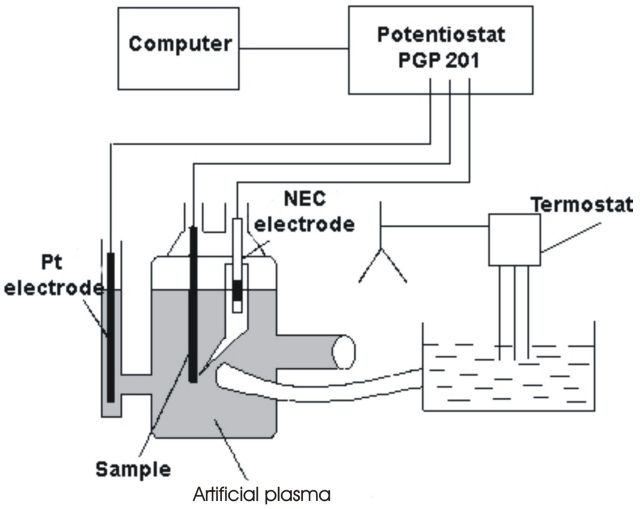

Fig.1. Diagram of the corrosion resistance set

Table 1.
Chemical composition of Co-Cr-W-Ni alloy

Elements concentration, %	Ladle analysis	Acc. to ISO 5832-6
C	0,08	<0,15
Cr	20,45	19,0 ÷ 21,0
Fe	1,88	<3,0
Mn	1,24	<2,0
N	0,019	-
Ni	10,16	9,0 ÷ 11,0
P	0,002	<0,04
S	0,001	<0,03
Si	0,01	<1,0
W	15,14	14,0 ÷ 16,0
Co	balance	balance

Table 2.
Chemical composition of the artificial plasma according to PN – EN ISO 10993-15 standard

Ingredients	Ingredients concentration, g/l distilled water
NaCl	6,8
$CaCl_2$	0,2
KCl	0,4
$MgSO_4$	0,1
$NaHCO_3$	2,2
Na_2HPO_4	0,126
NaH_2PO_4	0,026

The saturated calomel electrode (SCE) of KP-113 type was applied as the reference electrode. The tests were carried out in electrolyte simulating human blood environment (artificial

plasma) at the temperature of 37±1 °C and pH = 7,2 – table 2. Owing to the implantation technique of vascular stents, a deformability of a passive layer was also evaluated with the use of the bend test. Bend angles were equal to 30°, 60° and 90°.

Crevice corrosion resistance was carried out in accordance to the standard [13]. The samples were polarized in the potential of +0,8 V for 900 seconds and the dependence of anodic current intensity versus time was recorded.

Chemical composition investigations of the passive layer were realized with the use of 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 polished and passivated surfaces. 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.

3. Results

Results of electrochemical tests have revealed the influence of surface preparation of the Co-Cr-W-Ni alloy on the corrosion resistance – fig. 2, 3 and table 3. For grinded samples, the corrosion potential was in the range E_{cor} = -211 ÷ -173 mV – fig. 2a and table 3.

Table 3.
Pitting corrosion resistance of Co-Cr-W-Ni alloy

Surface preparation method	Corrosion potential E_{cor}, mV	Transpassivation potential E_{tr}, mV	Polarization resistance R_p, MΩcm^2
Grinded	-211 ÷ -173	+780 ÷ +800	0,4
Electropolished	-66 ÷ -55	+815 ÷ +825	0,9
Electropolished and passivated	+51 ÷ +57	+825 ÷ +835	2,1

Polarization of samples caused the increase of anodic current for potentials in the range E_{tr} = +780 ÷ +800 mV – fig. 3a. Polarization resistance of the samples was equal to R_p = 0,4 MΩcm^2.

The electropolishing process caused the increase of the corrosion potential up to E_{cor} = -66 ÷ -55 mV – fig. 2b and polarization resistance up to R_p = 0,9 MΩcm^2 – fig. 3b, table 3. The recorded curves of the anodic polarization were mainly characterized by the decrease of the anodic current density in the passive range with reference to the grinded samples – fig. 3. The increase of the anodic current intensity was observed for potentials in the range E_{tr} = +815 ÷ +825 mV.

The tests have revealed for electropolished and chemically passivated samples the corrosion potential was in the range of E_{cor} = +51 ÷ +57 mV – fig. 2c and the average value of the polarization resistance was equal R_p = 2,1 MΩcm^2 – table 3.

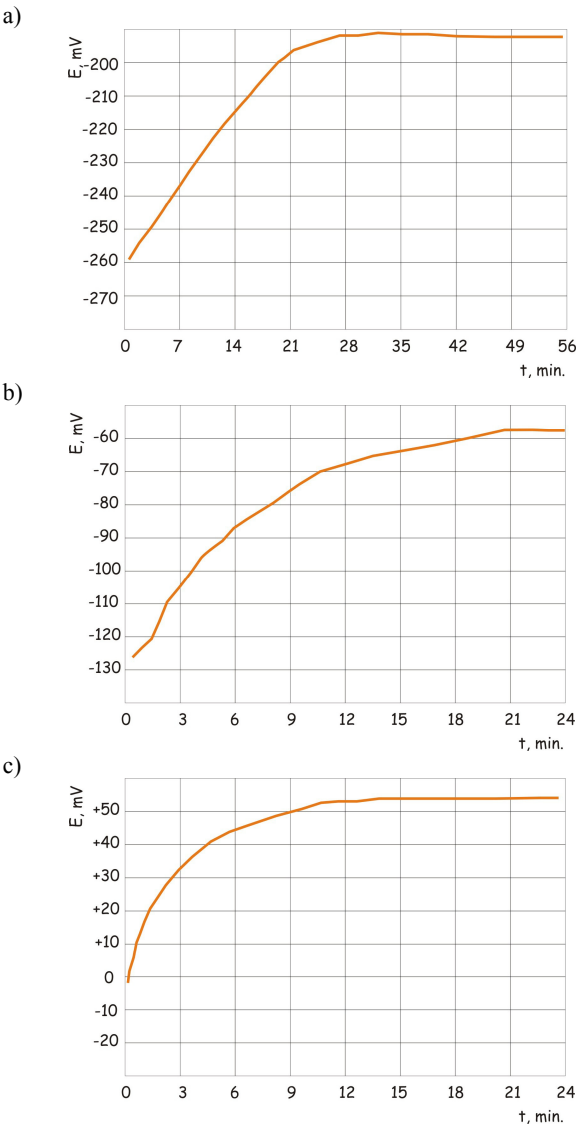

Fig. 2. Change of corrosion potential E_{cor} in a function of time for Co-Cr-W-Ni samples after different surface preparation: a) grinded surface, b) electropolished surface, c) electropolished and chemically passivated surface

The recorded curves of the anodic polarization were characterized by the further decrease of the anodic current density in the passive range – fig. 3. Polarization of the samples in direction of positive values of the potential caused the increase of the current density for potentials in the range E_{tr} = +825 ÷ +835 mV.

Corrosion resistance of the electropolished and the chemically passivated samples, deformed in the bend test (for the given bend angles α was comparable – table 4.

No tendency to decrease the value of corrosion and transpassivation potential with reference to the non-deformed samples was observed.

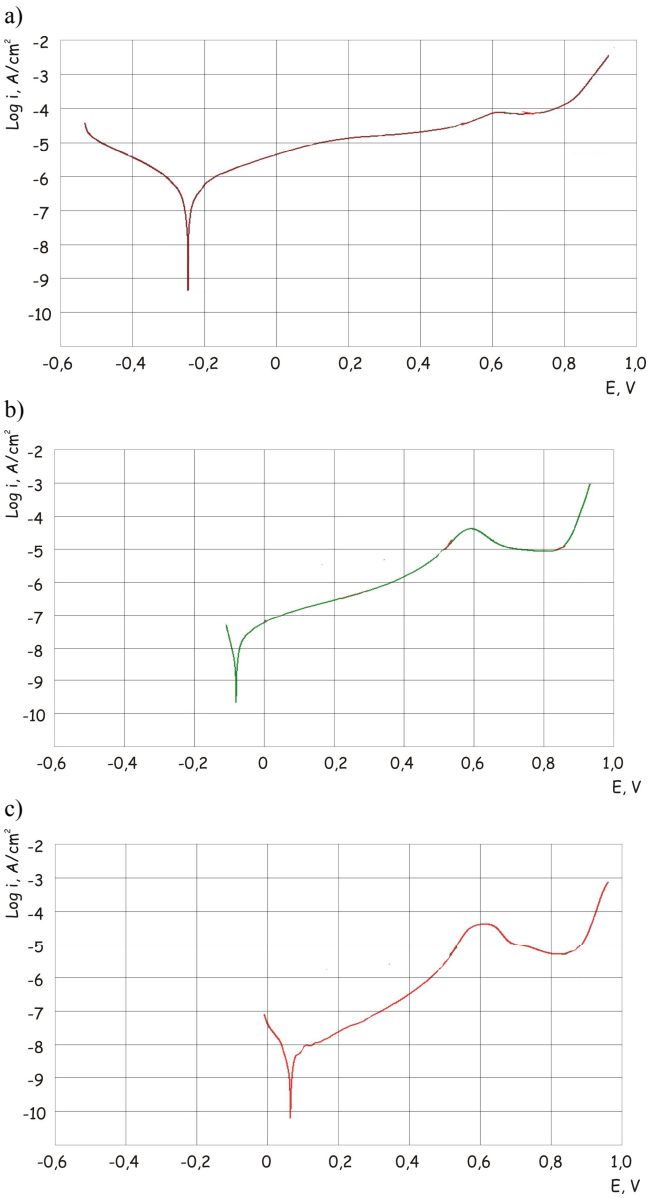

Fig. 3. Anodic polarization curves of Co-Cr-W-Ni samples after different surface preparation: a) grinded surface, b) electropolished surface, c) electropolished and chemically passivated surface

Table 4.
Corrosion resistance of deformed Co-Cr-W-Ni samples of electropolished and chemically passivated surface

Bend angle α, °	Corrosion potential E_{cor}, mV	Transpassivation potential E_{tr}, mV
30	+46 ÷ +50	+810 ÷ +825
60	+58 ÷ +52	+815 ÷ +820
90	+44 ÷ +48	+810 ÷ +820

The tests carried out in the artificial plasma for the grinded, the electropolished and the chemically passivated samples have showed that Co-Cr-W-Ni alloy is resistant on the crevice corrosion. The increase of anodic current intensity wasn't observed for the all samples tested at the potential of +800 mV in time of 900s – fig.4.

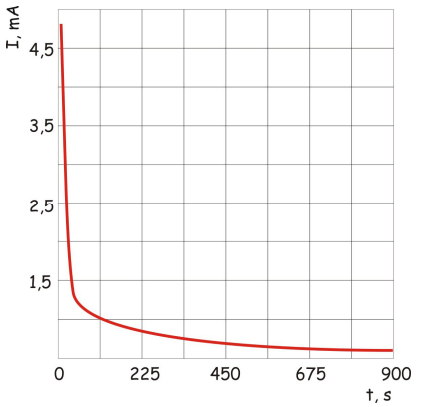

Fig. 4. Change of anodic current intensity in a function of time for Co-Cr-W-Ni samples of electropolished and chemically passivated surface (potential +800 mV)

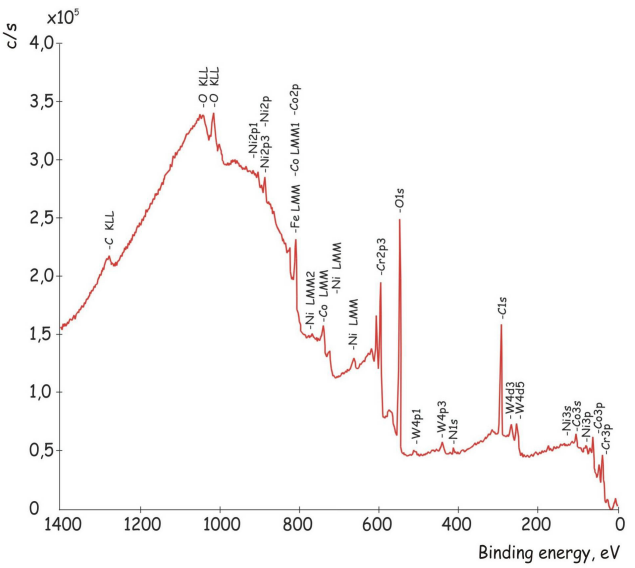

Fig. 5. The survey spectrum made for Co-Cr-W-Ni specimens of electropolished and chemically passivated surface

The chemical composition analysis of the passive layer on Co-Cr-W-Ni alloy has revealed the presence of the following elements: C, O, N, Cr, Fe, Co, Ni and W – fig. 5. The detailed spectrums for lines of Cr2p, Co2p, Ni2$p_{3/2}$, W4f, C1s, O1s, N1s, Fe2$p_{3/2}$ have been also recorded – fig. 6. Next the atomic concentrations of the particular elements have been determined – table 5.

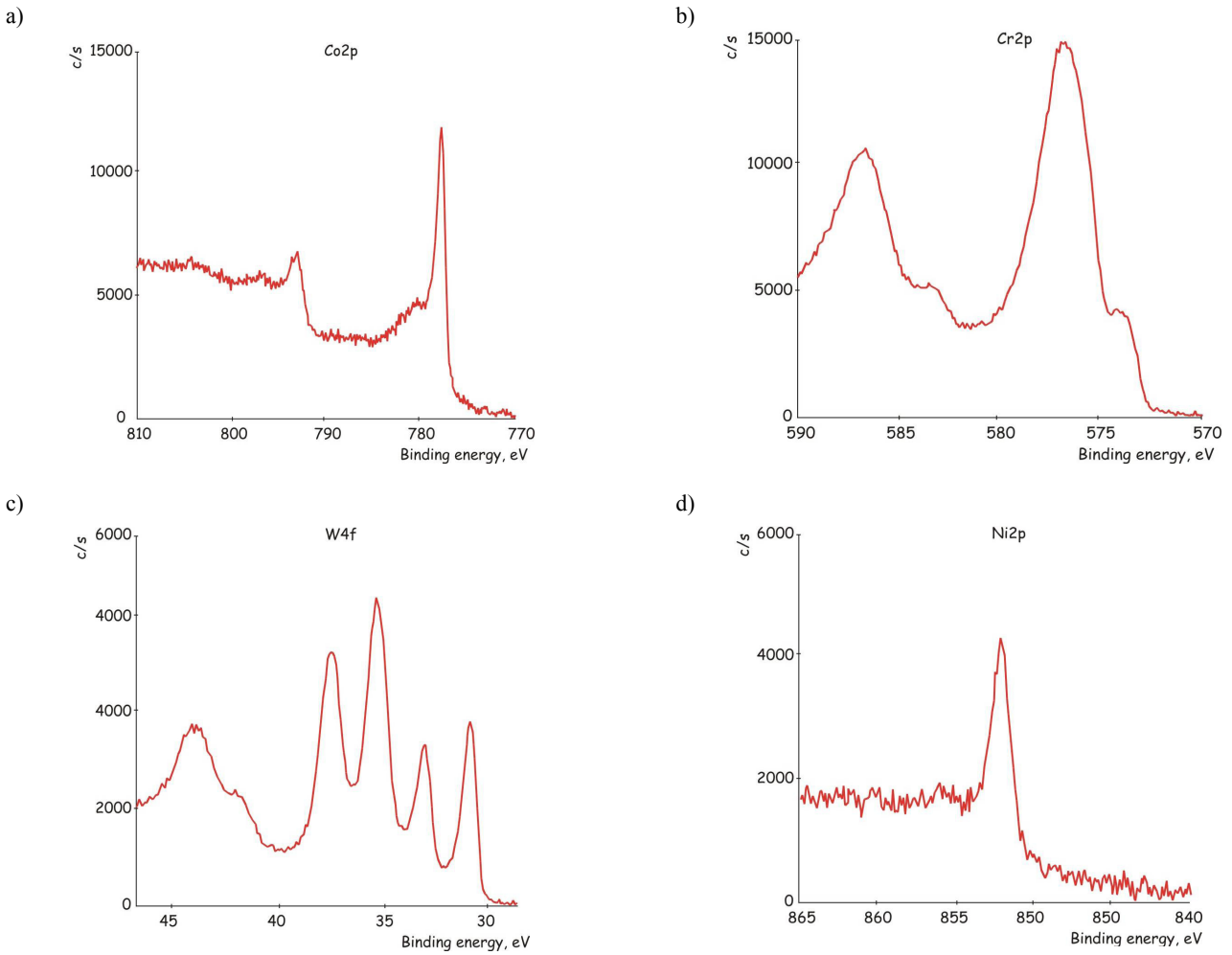

Fig. 6. XPS spectrums of Co-Cr-W-Ni specimens of electro-polished and chemically passivated surface for lines: a) Co2p, b) Cr2p, c) W4f, d) $Ni2p_{3/2}$

Cobalt was in two energy states: main line $Co2p_{3/2}$ derived from the metallic state (778,1 eV) and the adjacent line of energy about 780,4 eV derived probably from CoO – fig. 6. Concerning chromium the situation was reverse. The presence of oxides was dominating: line $Cr2p_{3/2}$ of 577,0 eV energy was emitted by Cr_2O_3 and weak line of 574,4 eV energy concerned the metallic chromium. Nickel was in the metallic state.

Two doublets displaced about few eV were visible for tungsten 4f line. The first one, of lower intensity, was from the metallic state, the second one was referred to the WO_3 oxide. Different chemical states were observed for oxygen line. Dominating was line of about 530,7 eV energy which can be assigned to the oxides of different metals for example to WO_3. Line of about 531,6 eV energy could be referred to Cr_2O_3.

The recorded line of C1s could be referred to several chemical states. The main line of energy equal to 285,29 eV could be assigned to hydrocarbons always present on the surface. Weak line with the maximum energy at 283,50 eV was derived from carbides, for example WC or Cr_3C_2.

Table 5.
Elements atomic concentration in passive layer of Co-Cr-W-Ni alloy determined in XPS method

Element	% at. (survey spectrum)	% at. (detailed spectrum)	% at.*
C	42,12	44,19	0,79
N	1,13	1,09	1,74
O	36,39	36,71	64,27
Cr	8,60	9,54	17,39
Fe	3,95	0,04	0,05
Co	4,61	5,48	9,55
Ni	1,52	0,87	2,23
W	1,67	2,25	2,21

** chemical composition takes into consideration the carbon originating only from the carbides*

Other weak lines in maximum corresponding to only slightly higher energy then 285,30 eV could be referred to organic compounds which contain oxygen or, to carbonate formed during the process of surface treatment. The line defined as $Fe2p_{3/2}$ was dominated by Co Auger peak in fact. Weak signal of energy binding of 707 eV was from the iron. Nitrogen demonstrated the line of energy of about 400,03 eV. This line can be connected with many compounds, for example with the organic containing groups of NH_3.

4. Conclusions

The carried out tests have shown favorable influence of the applied surface treatment process on the corrosion resistance of samples made of the Co-Cr-W-Ni alloy. The tests have revealed that the passive layer created in the electropolishing and the chemical passivation process improves the corrosion resistance of the investigated alloy.

To simulate stresses and strains occurring during implantation of a stent in a blood vessel, a plastic strain was applied.

Results of the corrosion resistance tests have shown that the applied plastic strain didn't change significantly the corrosion characteristic of the investigated material.

Chemical composition of passive layer decides considerably about its usefulness for stents' surface improvement. On the basis of carried out measurements with the use of XPS method it can be stated that all elements were present mainly in the oxides compounds. These compounds have higher biotolerance in environment of human physiological liquids.

Presented investigations are preliminary and need to be continued. The obtained results are promising however further studies, in particular in blood environment, will determine a usefulness of the suggested technique of stents' surface improvement.

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