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Chemical composition of passive layers formed on metallic biomaterials

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ABSTRACT

Purpose: In the paper the results of chemical composition investigations of passive layers formed on implants made of Cr-Ni-Mo steel, Co-Cr-W-Ni alloy and Ni-Ti alloy have been presented.

Design/methodology/approach: Chemical composition investigations of the passive layer have been carried out with the use of X-ray Photoelectron Spectroscopy (XPS). 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. 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.

Findings: The chemical composition analysis of passive layers on the Cr-Ni-Mo steel, the Co-Cr-W-Ni alloy and the Ni-Ti alloy has revealed the presence of the following elements: (C, N, O, Na, Mg, Ca, Cr, Fe, Ni), (C, O, N, Cr, Fe, Co, Ni, W) and (C, N, O, Na, Si, S, Cl, K, Ca, Ti, Ni) respectively.

Research limitations/implications: The research was carried out on samples, not on final parts. The tests were carried out in in vitro conditions. 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.

Originality/value: The obtained results show the usefulness of the applied surface treatment to refine surfaces of implants made of the Cr-Ni-Mo steel, the Co-Cr-W-Ni alloy and the Ni-Ti alloy.

Keywords: Metallic alloys; Biomaterials; XPS

MATERIALS

1. Introduction

Application of intravascular implants, called stents, is a common treatment method of many diseases causing a stenosis of tube-shape organs in a cardiovascular, digestive, respiratory and urinary system. Physiochemical properties of stents' surfaces should be characterized by a good biocompatibility. Stents' reactivity must be compatible with a reactivity of surrounding tissues and physiological fluids [9]. The latest literature data indicate that mechanical properties of stents and their physiochemical properties are of great, clinical importance. Therefore, the authors focused on these issues.

Application of stents became widespread mainly in a vascular surgery, but not only in treatment of advanced plaques, but also in treatment of aortic aneurysms or arteriostenosis. Nowadays, scientific research, in leading centers of biomedical engineering, is focused on reduction of postoperative complications by applying diverse surface treatment methods [1-4, 9].

Stainless steels are the most common metallic biomaterials used for vascular stents [5-7]. Almost 90% of these stents is made of steel [1, 8, 9]. Since many years this group of biomaterials is in common use mainly as short term implants, for example in orthopaedic surgery, dental surgery and thoracosurgery [10].

In recent years attempts to apply Co alloys and NiTi alloys for vascular stents are observed. For this reason the authors suggested the surface treatment method of Cr-Ni-Mo steel, Co-Cr-W-Ni alloy and Ni-Ti alloy, appropriate from a biocompatibility point of view, minimizing postoperative complications [7-16].

2. Materials and methods

Chemical composition investigations of passive 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 (∅ 6 mm). Chemical composition of the alloys has been shown in the table 1. 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.

Table 1.
Chemical composition of the investigated materials

Element	Cr-Ni-Mo steel	Co-Cr-W-Ni alloy	Ni-Ti alloy
		% mass.	
C	0,02	0,08	0,002
Cr	17,42	20,45	0,001
Fe	balance	1,88	0,01
Mn	1,81	1,24	-
N	0,07	0,019	-
Ni	14,15	10,16	55,5
P	0,016	0,002	-
S	0,001	0,001	-
Si	0,54	0,01	-
W	-	15,14	-
Co	-	balance	0,001
Cu	0,05	-	0,001
Mo	2,74	-	-
Ti	-	-	balance
Nb	-	-	0,004
O	-	-	0,004
H	-	-	0,0005

3. Results

For the electropolished and passivated samples of the Cr-Ni-Mo steel the presence of the following elements was revealed: C, N, O, Na, Mg, Ca, Cr, Fe, Ni. Furthermore, the general – fig. 1 and the detailed spectrums for the O1s, Mo3d, Cr2p, Fe2p3/2 lines – fig. 2 were recorded. Next, atomic concentrations of the individual elements were calculated – table 2.

Analysis of the obtained results show that the C1s carbon line (with the maximum reached for the energy E_b = 285,3 eV) corresponds with carbon compounds of C-C double bond – air origin impurities.

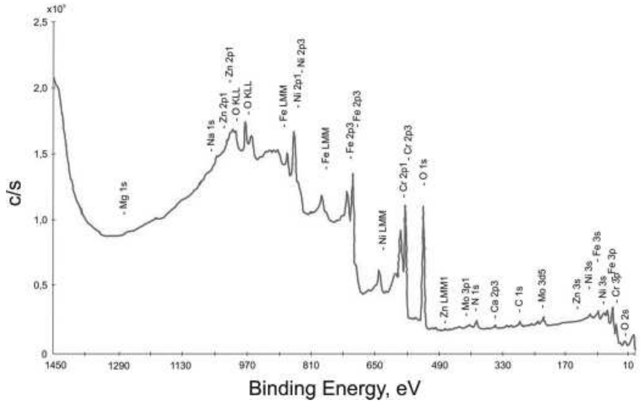

Fig. 1. XPS spectrums of Cr-Ni-Mo steel samples of electro-polished and chemically passivated surface

Wide oxygen line with the peak of E_b = 530,5 eV corresponds to metal oxides (Fe, Mo, Zn). The Mo3d5/2 line (the maximum for the energy E_b = 228,1 eV) confirms the presence of metallic Mo. The asymmetry of line in the direction of higher energy shows the influence of molybdenum oxide. The Cr2p3/2 line refers to three chemical states of chromium – metallic, CrO_2 and Cr_2O_3. The 852,8 eV binding energy (Ni2p3/2 line) relates to metallic Ni. The recorded Fe2p3/2 line (with the maximum reached for the energy E_b = 706,9 eV) shows dominant, metallic state of iron. Deformation of the line observed for higher energy indicates that iron is also present in the form of the Fe_2O_3 oxide – fig. 2.

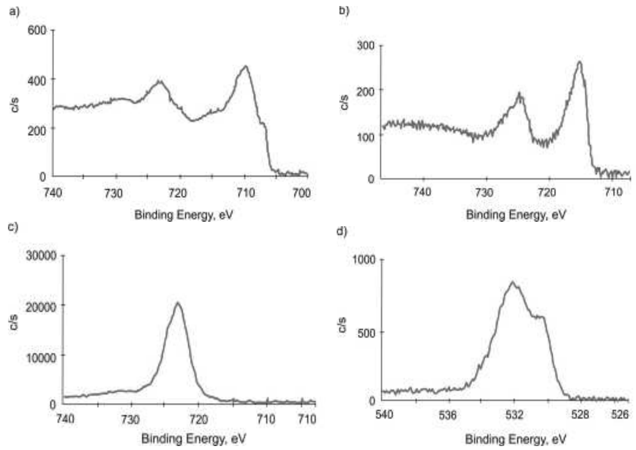

Fig. 2. XPS spectrums of Cr-Ni-Mo steel samples of electro-polished and chemically passivated surface for lines: a) Cr2p, b) Fe2p, c) O1s, d) Mo3d

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. 3. The detailed spectrums of Cr2p, Co2p, Ni2p3/2, W4f lines - fig. 4, and also the C1s, O1s, N1s, Fe2p3/2 lines have been also recorded. Next the atomic concentrations of the particular elements have been determined – table 2.

Table 2.
Chemical composition of passive layers formed on the alloys

Material	Elements concentration, %														
	C	N	O	Na	Mg	Ca	Cr	Fe	Ni	Zn	Mo	Co	W	Si	Ti
Cr-Ni-Mo steel	6,92	3,44	41,4	0,29	0,45	0,81	21,6	17,0	6,07	0,52	1,49	-	-	-	-
Co-Cr-W-Ni	44,2	1,09	36,7	-	-	-	9,54	0,04	0,87	-	-	5,48	2,05	-	-
Ni-Ti	72,3	3,6	20,4	0,31	-	0,19	-	-	0,03	-	-	-	-	1,37	1,51

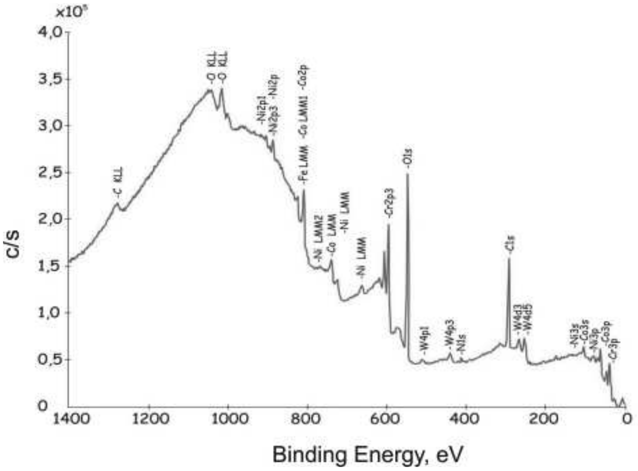

Fig. 3. XPS spectrums of Co-Cr-W-Ni alloy samples of electro-polished and chemically passivated surface

Cobalt was in two energy states: main line Co2p3/2 derived from the metallic state (778,1 eV) and the adjacent line of energy about 780,4 eV derived probably from CoO – fig. 4. Concerning chromium the situation was reverse. The presence of oxides was dominating: Cr2p3/2 line 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.

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 Fe2p3/2 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.

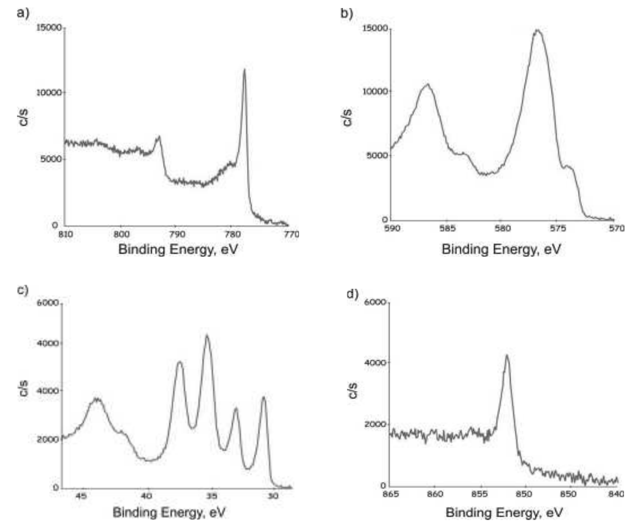

Fig. 4. XPS spectrums of Co-Cr-W-Ni alloy samples of electro-polished and chemically passivated surface for lines: a) Co2p, b) Cr2p, c) W4f, d) Ni2p3/2

In the research on passive layer of the NiTi alloy the presence of the following elements was revealed: C, N, O, Na, Si, S, Cl, K, Ca, Ti, Ni. For the prepared surface, the general – Fig. 5 and the detailed spectrums for the C1s, O1s Ti2p3 and Ni2p3 line were recorded. Furthermore, atomic concentrations of the individual elements present in the passive layer were calculated – table 2. Titanium was present in form of TiO_2 oxide (Ti2p line; binding energy E_b = 459,4 eV). The analysis of the Ni2p line revealed no nickel on the surface. The C1s line of the E_b = 286 eV can be connected with the present hydrocarbons. Generally, large amount of carbon of C-C single bond indicates air origin impurities. Oxygen on the sample' surface was generally present in the form of TiO_2 (the line of the binding energy equal to E_b = 531 eV). Furthermore, the hydroxide groups were observed (energy E_b = 533,3 eV). The N1s line indicate the presence of TiN nitrides (E_b = 401 eV).

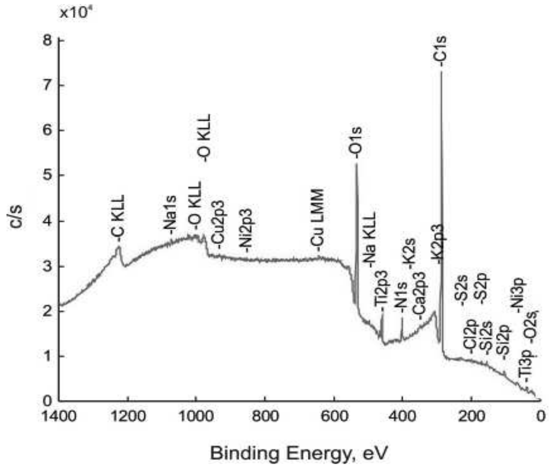

Fig. 5. XPS spectrums of Ni-Ti alloy samples of electro-polished and chemically passivated surface

4. Conclusions

Previous research carried out by the authors [4, 10, 14] had shown favorable influence of the applied surface treatment process on the corrosion resistance of samples made of the Cr-Ni-Mo steel, Co-Cr-W-Ni alloy and Ni-Ti alloy. The tests have revealed that the passive layers formed in the electropolishing and the chemical passivation process improve the corrosion resistance of the investigated alloys.

Chemical composition of passive layers indicates their usefulness for stents' surface improvement. On the basis of the carried out investigations 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 fluids.

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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