XPS MEASUREMENTS OF AISI 316LVM SS BIOMATERIAL TUBES AFTER MAGNETOELECTROPOLISHING

Krzysztof Rokosz, Tadeusz Hryniewicz, Ryszard Rokicki

XPS (X-ray Photoelectron Spectroscopy) measurements were performed on AISI 316LVM stainless steel tubes of biomaterial samples, serving for stents, after a standard electropolishing (EP), and magnetoelectropolishing (MEP). After electropolishing operations, the samples were kept in a closed foil pack for about four years. The results of XPS analysis indicate a significant difference in the measurement and calculation values, dependent on surface treatment method: EP and/or MEP. The steel surface film composition and PREN (pitting resistance equivalent number) were calculated. The highest numbers of these values were obtained on samples after MEP where both chromium compounds (Cr 2p) and molybdenum (Mo 3d) increased over three times against these values after EP treatment. The calculated $PREN_{MEP}$ (Fe, Cr, Mo, Mn, Ni, P, S, O) = 16,37, with $PREN_{MEP}$ (Fe, Cr, Mo, Mn, Ni, P, S) = 36,89, versus $PREN_{EP}$ (Fe, Cr, Mo, Mn, Ni, P, S, O) = 3,12, with $PREN_{EP}$ (Fe, Cr, Mo, Mn, Ni, P, S) = 8,53. The results obtained point to an advantageous and unusual effect of the magnetic field action during MEP.

Keywords: magnetoelectropolishing (MEP), PREN (pitting resistance equivalent number), 316LVM SS tube biomaterial, XPS results comparison

XPS mjerenja cijevi od biomaterijala AISI 316LVM SS nakon magnetoelektropoliranja

Izvorni znanstveni članak

XPS (X-ray Photoelectron Spectroscopy) mjerenja obavljena su na uzorcima cijevi od biomaterijala AISI 316LVM nehrđajućeg čelika koji služi za stentove, nakon uobičajenog elektropoliranja (EP) i magnetoelektropoliranja (MEP). Nakon izvršenih operacija elektropoliranja, uzorci su se, zapakirani u foliji, držali otprilike četiri godine. Rezultati XPS analize pokazuju značajnu razliku u vrijednostima mjerenja i računanja, ovisno o metodi površinske obrade: EP i/ili MEP. Izračunat je sastav površinskog sloja čelika i PREN (ekvivalentni broj otpornosti na točkastu eroziju). Najveći su iznosi tih vrijednosti dobiveni na uzorcima poslije MEP-a kada su i vrijednosti spojeva kroma (Cr 2p) i molibdena (Mo 3d) porasle više od tri puta u odnosu na te vrijednosti nakon postupka EP. Izračunati $PREN_{MEP}$ (Fe, Cr, Mo, Mn, Ni, P, S, O) = 16,37, s $PREN_{MEP}$ (Fe, Cr, Mo, Mn, Ni, P, S) = 36,89, u odnosu na $PREN_{EP}$ (Fe, Cr, Mo, Mn, Ni, P, S, O) = 3,12, s $PREN_{EP}$ (Fe, Cr, Mo, Mn, Ni, P, S) = 8,53. Postignuti rezultati ukazuju na korisno i neobično djelovanje magnetskog polja tijekom MEP-a.

Ključne riječi: cijevi od biomaterijala 316LVM SS, magnetoelektropoliranje MEP, PREN (ekvivalentni broj otpornosti na točkastu eroziju), usporedba XPS rezultata

1 Introduction

Recent publications on the use of metallic biomaterials [1 ÷ 5], show that apart from increasing interest in such materials like titanium and a variety of its alloys [6 ÷ 13], cobalt alloys [14], and others [15, 16], the AISI 316LVM stainless steel remains one of the least expensive biomaterial used both for a common purpose and for biomedical applications [1 ÷ 5, 17 ÷ 34]. The task with biomaterial improvement is worth undertaking in case of elimination or diminishing some of the alloying elements from the stainless steel surface and searching for an opportunity to increase the (Cr+Mo)/Fe ratio. One of commonly used technologies to reach this aim is electropolishing (EP) treatment, specifically enhanced by the magnetic field [33]. Magnetoelectropolishing (MEP) has become an interesting electrochemical technology in case of the need for both the finishing intricate shapes of parts and obtaining additional advantageous surface properties not known before [4 ÷ 31]. The studies are of special importance especially when the parts are provisioned for biomedical applications [5 ÷ 11, 16 ÷ 34]. Our recent works indicate also significant advantageous changes in mechanical properties of magnetoelectropolished samples [8 ÷ 12, 23], as well as improvement in dehydrogenation [6, 25] in comparison with the ones after a standard electropolishing.

The aim of the paper is to provide the evidence for a possibility to improve AISI 316LVM stainless steel biomaterial concerning its corrosion resistance and biocompatibility. The samples of this steel were kept in a closed foil pack for about for years and then examined by XPS (X-ray Photoelectron Spectroscopy).
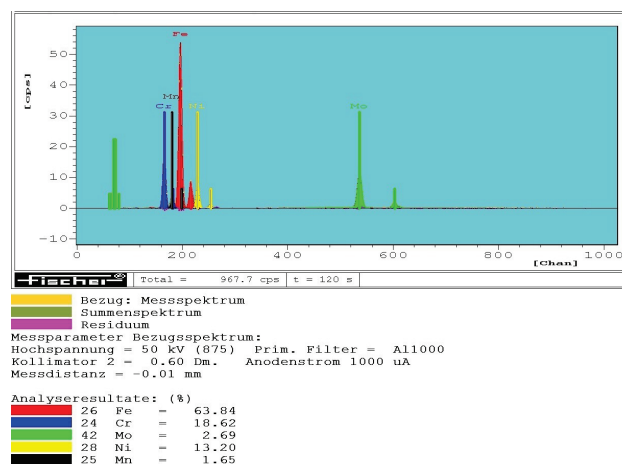

Figure 1 AISI 316LVM SS tubes composition measurement results by X-ray Fluorescence Material Analyser RFS with CCD-Spectrometer CDS

2 Method
2.1 Material

A set of AISI 316LVM SS biomaterial tubes, used for stents manufacture, was prepared for the studies. The thin-walled tubes of ∅1,50 mm (OD) × 0,14 mm wall thickness were cut into pieces 30 and 37 mm long, respectively (30 mm tubes destined for MEP, and 37 mm tubes destined for EP). The bulk material of the steel was

studied using X-ray Fluorescence Material Analyzer RFS with CCD-Spectrometer CDS. The results of the material composition, in wt. %, are presented in Fig. 1. The main elements of the stainless steel are as follows: Cr 18,62; Ni 13,20; Mo 2,69; Mn 1,65 and Fe balance (wt. %).

2.2 Set up and parameters

The steel samples were electropolished under a standard process (EP), and in the magnetic field (MEP). The electrolyte used consisted of concentrated acids of H_2SO_4 and H_3PO_4 in the volumetric proportion of 1:3. The electrolytic cell was filled with the electrolyte, and the stainless steel round cathode was applied. For electropolishing, the samples were placed in the centre of the cell in vertical position. The EP process parameters were as follows: electrolyte temperature about 60 °C, constant voltage of 10 V so that the process was carried out under oxygen evolution regime.

The experimental set-up used for both the standard electropolishing EP and for the magnetoelectropolishing MEP was presented elsewhere [27]. For each run, the electrolytic cell made of glass was used, containing up to 500 cm^3 of electrolyte.

2.3 XPS studies

After electropolishing operations, both EP and MEP, the tube samples were kept closed in the foil at a room temperature (of about 25 °C) for a long time, about 4 years, and then underwent X-ray Photoelectron Spectroscopy (XPS) studies. The XPS measurements on electrochemically polished AISI 316LVM SS samples were performed using KRATOS Analytical AXIS ULTRA instrument [35]. The XPS apparatus with the sample/tube under measurements is presented in Fig. 2. Detailed description of the XPS measurements was given elsewhere [28]. The XP spectra were recorded in normal emission.
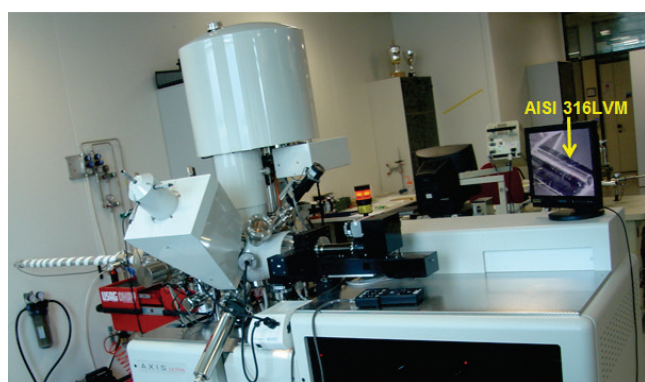

Figure 2 A view on XPS apparatus with the AISI 316LVM SS sample measured

In view of optimizing the signal-to-noise ratio, one XPS measurement cycle covered 10 sweeps. Next the Cr/Fe ratio was determined for all measurements done. For the XPS analyses the CasaXPS 2.3.14 software was used. Following the CasaXPS 2.3.14 software, the interpretation of XPS results was performed in accordance to the algorithm [36 ÷ 38].

3 Study results

Primary results of XPS survey spectra for essential elements of the studied AISI 316LVM SS tube samples are presented in Fig. 3. Main alloy's high resolution XPS spectra after EP and MEP by elements are given in Fig. 4, concerning: (a) chromium (Cr 2p), (b) iron (Fe 2p), (c) molybdenum (Mo 3d), (d) manganese (Mn 2p), and (e) nickel (Ni 2p). In Fig. 5 there are high resolution XPS spectra of main elements coming from the environment/electrolyte, concerning: (a) phosphorus (P 2p), (b) sulphur (S 2p). Then the high resolution XPS spectra by fitting were performed with some exemplary analyses, presented in Figs. 6 and 7, and Tabs. 1 and 2, respectively. The contents of elements and compounds are given in Tab. 3, with the passive film conditions placed in Tab. 4.
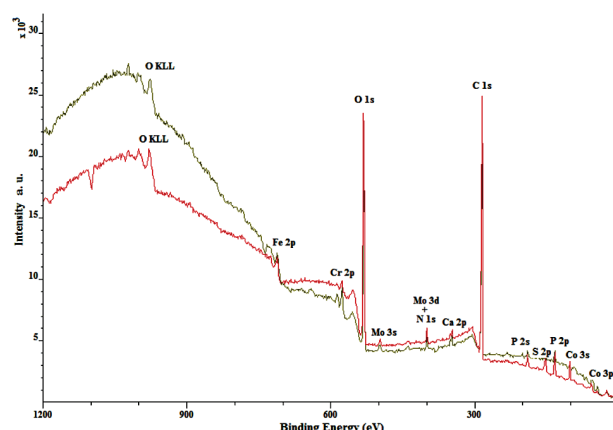

Figure 3 XPS survey of AISI 316LVM SS after EP & MEP; red - EP, green - MEP

Fig. 3 presents XPS survey of AISI 316LVM SS after EP and MEP in the whole range of binding energy applied. One may easily notice a big difference in the curve courses depending on the steel treatment process, if the magnetic field was used to electropolishing (MEP), or not (EP). Two sharp and high peaks are visible, O 1s, and C 1s, with the first one, oxygen, coming from the electropolishing process, and the second one, carbon, coming typically from the sample preparation for the XPS measurements.

Fig. 4 presents high resolution XPS spectra of all main elements of the studied steel samples: Fe, Cr, Ni, Mo, and Mn. Fig. 4a shows the XPS spectra of chromium (Cr 2p) of AISI 316LVM steel. A big difference amongst the spectra obtained on the steel tubes after EP and MEP are visible with dominating peaks of MEP sample.

Next, in Fig. 4b, the high resolution XPS spectra of iron (Fe 2p) are given with big differences amongst the curves visible. Two additional peaks differentiating the MEP sample in comparison with EP sample are visible: one sharp peak observed at about 707 eV (metallic iron: Fe^0) on the sample after MEP, and the second additional one noticed at about 719,5 eV (mixture of phosphate and sulphate of iron: $FeSO_4$, $Fe_2(SO_4)_3$, $FePO_4$, $Fe_3(PO_4)_2$).
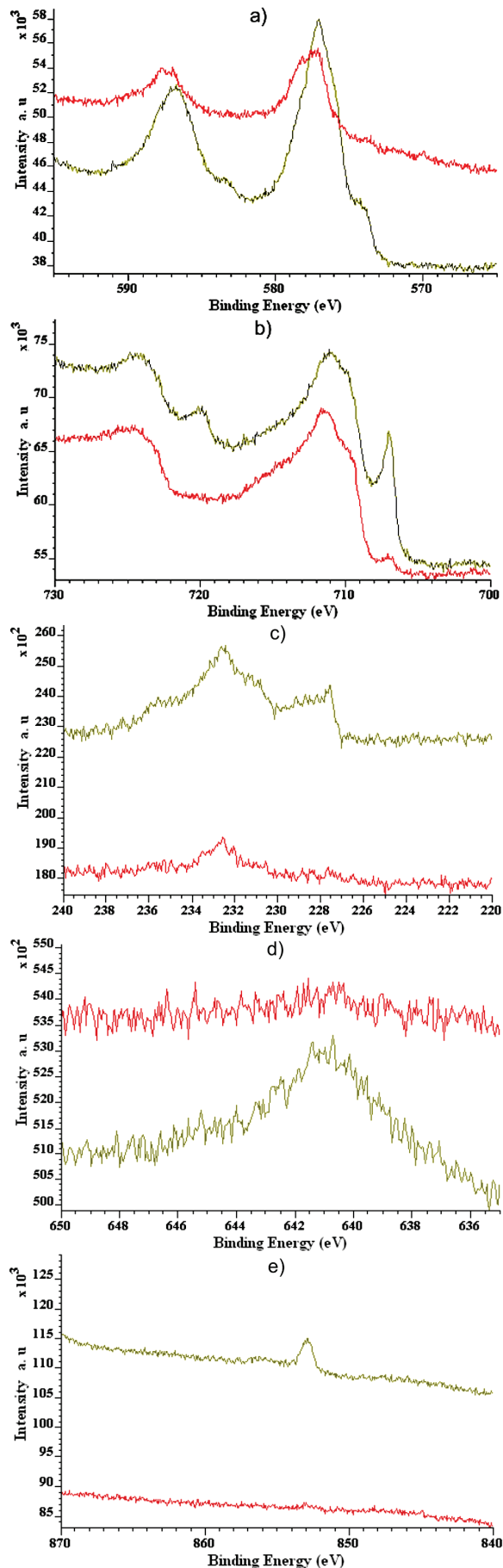
Figure 4 High resolution XPS spectra of AISI 316LVM surface after EP and MEP of: (a) chromium (Cr 2p), (b) iron (Fe 2p), (c) molybdenum (Mo 3d), (d) manganese (Mn 2p), (e) nickel (Ni 2p); red - EP, green - MEP

In Fig. 4c, the high resolution XPS spectra of molybdenum (Mo 3d) of the steel are shown. A big difference exists between the courses amongst the EP and MEP samples with much more distinct peaks of Mo after MEP, first of all at about 228 eV (metallic molybdenum Mo^0) and higher at about 232,6 eV (Mo^{x+}, $x > 2$).

Very interesting are the high resolution XPS spectra of manganese (Mn 2p), given in Fig. 4d. The spectrum of EP sample does not present a noticeable peak of manganese whereas it is very distinct on the MEP sample at about 641 eV (MnO: Mn^{2+}).

In Fig. 4e, the high resolution XPS spectra of nickel (Ni 2p) are shown. They both, related to EP and MEP treatments, run nearly alike with some small peak of MEP sample visible at about 852,8 eV and with this differentiating from the EP sample. It corresponds with metallic nickel Ni^0.
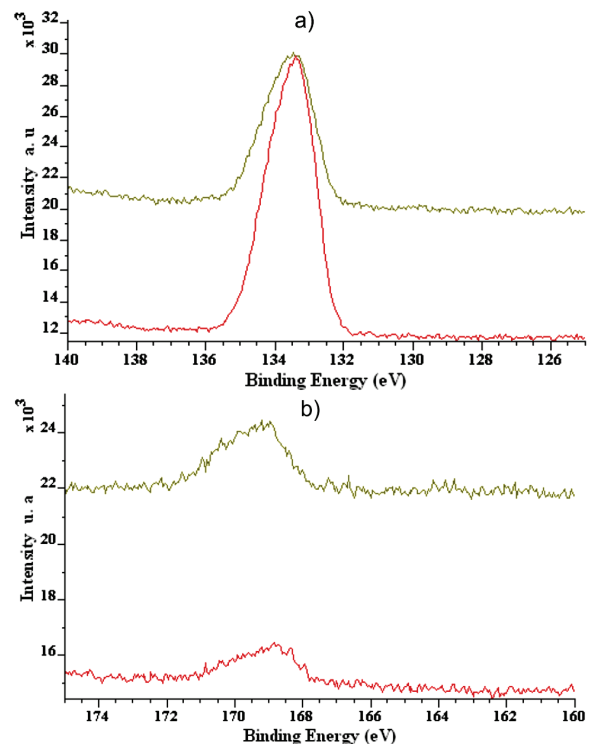

Figure 5 High resolution XPS spectra of AISI 316LVM surface after EP and MEP of: (a) phosphorus (P 2p), (b) sulphur (S 2p); red - EP, green - MEP

In Fig. 5 the high resolution XPS spectra of phosphorus (P 2p) and sulphur (S 2p) coming from the electrolyte, as detected on AISI 316LVM sample surface, are visible. These peaks correspond to phosphate (Fig. 5a) and sulphate (Fig. 5b) of iron and/or chromium and/or molybdenum. The phosphorus (P 2p) peak of the sample after EP treatment is much higher than that after MEP (Fig. 5a). There is also some difference in the high resolution XPS spectra of sulphur (S 2p) of the steel (Fig. 5b). Here a little higher peak of the sample plot after MEP is noticed.

Next two illustrations (Figs. 6 and 7) show the high resolution XPS spectra with the fitting results of chromium and oxygen. Figure 6 presents the high resolution XPS spectra of Cr 2p and O 1s related to EP sample. In Fig. 7 the two high resolution XPS spectra related to MEP sample are given.
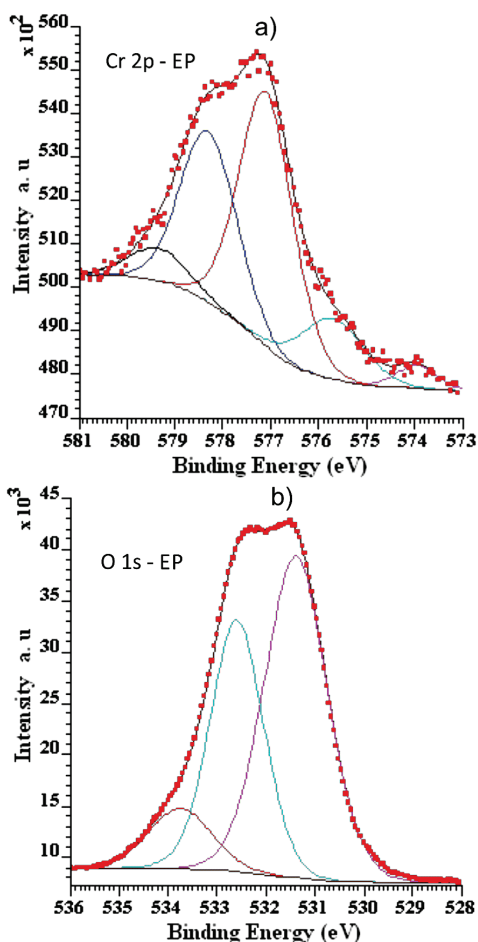
Figure 6 High resolution XPS results of AISI 316LVM after EP by fitting: (a) Cr 2p, (b) O 1s

In Tab. 1 the share of chromium and its compounds in AISI 316LVM SS surface after EP and MEP treatments are given. A big difference is noticed on Cr 2p (at. %) concerning EP and MEP samples and chromium share: Cr^0 equals 3 at. % after EP, and 14 at. % after MEP. A 5 at. % difference in advantage of MEP sample is noticed in CrO_2 oxide, no difference with $Cr(OH)_3$ hydroxide, 10 at. % less $CrPO_4$ phosphate, and, what is most important, only 1 at. % of Cr^{6+} is noted in comparison with 6 at. % of this ionic chromium which occurred in EP sample.

Table 1 Share of chromium and its compounds in AISI 316LVM SS surface film after EP and MEP treatments

		Cr^0	CrO_2	$Cr(OH)_3$	$CrPO_4$	$(CrO_4)^{2-}$
EP	BE / eV	573,95	575,707	577,1	578,293	579,346
	FWHM	0,964	1,508	1,322	1,367	1,447
	Cr 2p / at. %	3	13	46	32	6
MEP	BE / eV	574,221	575,814	576,977	578,313	579,865
	FWHM	1,617	1,192	1,594	1,803	1,062
	Cr 2p / at. %	14	18	45	22	1

Tab. 2 covers data of oxygen share resulting from metallic compounds and water in AISI 316LVM SS surface film after EP and MEP treatments. The result of 11 at. % oxygen coming of M-O oxide as calculated after MEP, in relation to zero oxygen after EP treatment, makes a fundamental difference in the steel surface film composition between these two surface finishing methods. The oxygen coming from hydroxides M-OH remains nearly the same in each studied sample, with much less value noted in phosphates M-PO_4 (13 at. %

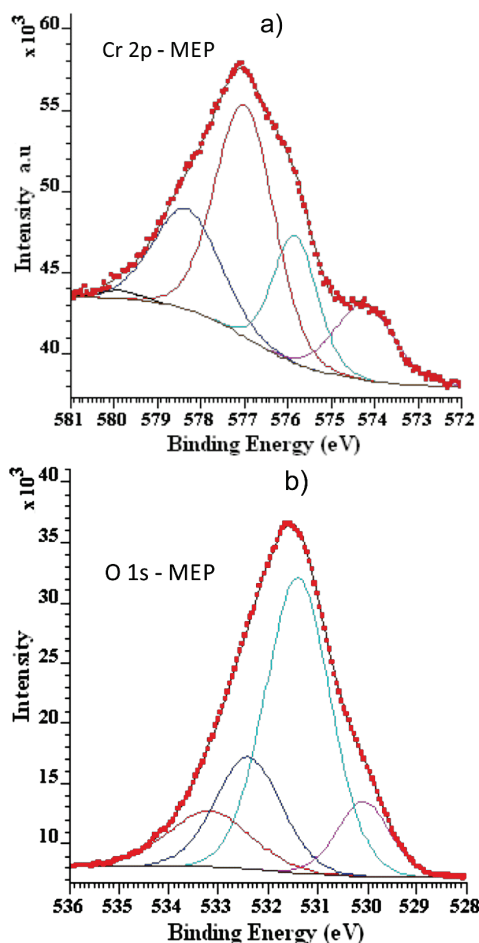after MEP, and 36 at. % after EP), and a higher amount of oxygen (21 at. %) coming from water, in MEP sample.

Figure 7 High resolution XPS results of AISI 316LVM after MEP by fitting: (a) Cr 2p, (b) O 1s

Table 2 Share of oxygen in metallic compounds and water in AISI 316LVM SS surface film after EP and MEP treatments

		M-O	M-OH	M-PO_4 C-O, C=O	H_2O
EP	BE / eV	-	531,385	532,587	533,741
	FWHM	-	1,512	1,277	1,503
	O 1s / at. %	0	54	36	10
MEP	BE / eV	530,074	531,392	533,175	532,391
	FWHM	1,251	1,546	1,938	1,558
	O 1s / at. %	11	55	13	21

Table 3 Analysis of high resolution XPS C1s data

			EP	MEP
C 1s	C-C	BE / eV	285,1	285,2
		FWHM	1,09589	1,08978
		Area	19703,8	15393,9
		at. %	71	69
	C-O	BE / eV	286,1081	286,0
		FWHM	2,11249	1,80104
		Area	5817,1	5097,8
		at. %	21	23
	C=O	BE / eV	288,7882	288,6
		FWHM	1,93833	1,77459
		Area	2121,4	1795,2
		at. %	8	8

In Tab. 3, the XPS analysis of C 1s high resolution spectra is given, and Tab. 4 presents the surface film composition of the 316LVM surfaces after EP and MEP. Columns marked as 1 (100 %), both after EP and MEP, in

Tab. 4 refer to the surface film composition assuming carbon layer (contamination) plus passive layer resulting in 100 %. Columns marked as 2 (200 %), both after EP and MEP, in Tab. 4 refer to the separated layers, one of them being carbon layer (100 %), and the second one as passive layer (another 100 %).

Table 4 Surface film composition (at. %) in AISI 316LVM SS after EP and MEP treatments

		EP		MEP	
		at. %	at. %	at. %	at. %
		1	2	1	2
SURFACE LAYER	Carbon	59,6	77,5	60,5	76,3
	Oxygen	17,3	22,5	18,8	23,7
	Iron	4,2	15,4	2,0	9,7
	Chromium	0,5	1,8	2,1	10,1
	Nickel	0,0	0,0	0,1	0,5
	Molybdenum	0,1	0,4	0,4	1,9
	Manganese	0,0	0,2	0,4	1,9
	Phosphorus	4,7	17,2	3,4	16,4
	Sulphur	0,4	1,5	0,8	3,9
	Oxygen	13,2	63,5	11,5	55,6

Based on the type of carbon compounds, C-C, C-O, or C=O (see Tab. 3) authors separated carbon layer from passive layer (columns 2 in Tab. 4). In columns 1 of Tab. 4 the surface layer as passive layer with contaminations (carbon layer) is shown. In columns noted as 2 of Tab. 4 authors separated the carbon layer from passive layer.

For the surface after EP there is observed $(0,21+0,08)\cdot59,6 \% \approx 17,3 \%$ carbon-oxygen compounds (C 1s), where 1 atom of carbon corresponds with 1 atom of oxygen (C-O, C=O). Therefore the amount of oxygen bound with carbon (O 1 s) also equals 17,3 %. Hence, the oxygen in passive layer is the whole amount of oxygen (30,5 %) minus amount of oxygen bound with carbon (17,3 %): 30,5 %–17,3 % ≈ 13,2 %.

The same reasoning applies to MEP data with the amount of oxygen in the passive layer (without carbon layer) calculated as: $30,2 \%–(0,23+0,08)\cdot60,5 \% \approx 11,5 \%$.

In Tab. 4, a comparison of data on surface film composition, in at. %, is presented for the tube samples treated by EP and MEP. The most important results are related to the change in contents of main alloying elements of the steel, in its passive film such as: iron, chromium, molybdenum, and manganese. Although some amount of metallic chromium was found after MEP, interesting is over five times higher amount of chromium (Cr 2p: 10,1 at. % against 1,8 at. % after EP), as well as over four times higher amount of molybdenum (Mo 3d: 1,9 at. % against 0,4 at. % after EP). On the other hand, iron amount (Fe 2p: 15,4 at. % after EP) contents are much lower after MEP Fe 2p: (9,7 at. %), respectively. Sulphur (S 2p) amount is over 2 times higher, and phosphorus (P 2p) is about 0,8 at. % less after MEP (16,4 at. % against 17,2 at. % after EP).

In Tab. 5, both PREN (Pitting Resistance Equilibrium Number) and the ratio of Cr and Mo to Fe are presented. It appears the Cr plus Mo to Fe ratio is almost eight times higher on samples after MEP than that on EP sample. Also PREN after MEP is several times higher than that after EP.

Table 5 Passive film conditions after EP and MEP treatments

	EP	MEP
(Cr + 3,3·Mo) / Fe (at. %)	0,21	1,62
PREN (Fe, Cr, Mo, Mn, Ni, P, S, O)	3,12	16,37
PREN (Fe, Cr, Mo, Mn, Ni, P, S)	8,53	36,89
Where: PREN = Cr + 3,3·Mo (at. %)		

4   Discussion

In this work the tube samples of AISI 316LVM stainless steel biomaterial after magnetoelectropolishing MEP, with the control group of samples after a standard electropolishing EP were studied. The material examination and XPS measurements were carried out concerning all basic elements of the steel, such as iron, chromium, nickel, molybdenum and manganese, together with oxygen, sulphur and phosphorus as the elements coming from the electrolyte. The XPS results have been documented in the form of ten figures and four tables.

After XPS examinations both the surface film composition and PREN (pitting resistance equivalent number) were calculated. Such calculated numbers appear to be strictly dependent on the type of treatment: EP and MEP (see Tabs. 1 through 4). The results of the steel passive film composition and PREN are well correlated with each other.

Some amount of metallic chromium (Cr 2p) and nickel (Ni 2p) detected by XPS measurements on MEP sample may be the proof of reaching core material under the surface layer studied. The amount of chromium oxide, which is responsible for corrosion resistance, is three times higher after MEP compared with that on EP sample. On the other hand iron oxide is significantly diminished in the passive layer after MEP process in comparison with EP. The results of PREN calculated for MEP sample in relation to those obtained for EP sample are very substantial. $PREN_{MEP}$ calculated by (Fe, Cr, Mo, Mn, Ni, P, S, O) is over four times higher than that referred to EP sample. By excluding oxygen, $PREN_{MEP}$ calculated by (Fe, Cr, Mo, Mn, Ni, P, S) appears to be 4,3 times higher than that of EP sample.

5   Conclusion

The work presents the study results of the AISI 316LVM SS tube biomaterial surface after magneto-electropolishing MEP in comparison with those obtained after a standard electropolishing EP. The XPS examinations have clearly shown the influence of magnetic field superimposed on electropolishing process on composition of passive film of the steel.

The results indicate over three-time increase in both chromium compounds and total molybdenum contents in the surface film studied. The composition differences of passive film of EP and MEP steel samples fundamentally influence the PREN (Pitting Resistance Equivalent Number) values. The calculated values of PREN, both including oxygen and without it, show these of the magnetoelectropolished biomaterial were much higher than those obtained on the samples after a standard EP. The calculated $PREN_{MEP}$ (Fe, Cr, Mo, Mn, Ni, P, S, O) = 16,37, with $PREN_{MEP}$ (Fe, Cr, Mo, Mn, Ni, P, S) = 36,89, and $PREN_{EP}$ (Fe, Cr, Mo, Mn, Ni, P, S, O) = 3,12, with $PREN_{EP}$ (Fe, Cr, Mo, Mn, Ni, P, S) = 8,53.

Acknowledgment

6   References

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