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XPS MEASUREMENTS OF PASSIVE FILM FORMED ON AISI 316L SS AFTER ELECTROPOLISHING IN A MAGNETIC FIELD (MEP)

ABSTRACT

Electrochemical polishing of metals and alloys is one of the most currently used finishing treatments, covering metallic biomaterials with complicated shapes (coronary stents, prostheses, etc.). A standard electropolishing (EP) process has been recently modified by including a magnetic field, and called the magnetoelectropolishing (MEP). Many surface properties and even mechanical features may be modified and improved by MEP. The changes are concerned with the surface film composition which undergo a modification. For the present studies, X-ray Photoelectron Spectroscopy (XPS) analysis was applied to measure the surface film composition on AISI 316L stainless steel. In conclusion both Cr-X/Fe-X compounds ratio as well as Cr/Fe total ratio of the 316L steel after EP and MEP were calculated and compared to reveal the advantage of the magnetic field used.

Keywords: 316L SS, XPS results, Magnetoelectropolishing

INTRODUCTION

The process of a standard electropolishing (EP) is the controlled anodic dissolution of metals which considerably improves a variety of the surface properties. Electropolishing is often referred to as the electrochemical polishing, "reverse plating" or "super passivation" process. Commercial applications for electropolishing have been in use since the early 1950's [1-4]. The studies on electropolishing also allowed us to confirm the concept of microsmoothing in the EP process [2, 4] and formulate the enhanced oxidation-dissolution theory [5].

The EP process has been often used for the finishing treatments, specifically in case of metallic biomaterials with complicated shapes (coronary stents, prostheses, endodontic files, etc.) [3, 4, 6-10]. After the EP process, the reduced surface roughness, a high corrosion resistance and the lack of carcinogenic elements in the surface layer, are also desired [3, 4, 6-9]. Many of these properties appear to be improved and/or enhanced after introducing a magnetic field into the process called magnetoelectropolishing (MEP) [3, 4, 9-21].

In the literature, there is no studies found on the magnetic field effect on the chemical composition and corrosion resistance of the surface layers formed on the steels after magnetoelectropolishing (MEP), apart from the selective Authors' own results published [12-17, 19-21]. This study is to prove how the magnetic field applied to the electrochemical polishing may affect the composition of the 316L stainless steel surface film obtained after

the process. The comparison of the surface film content and Cr/Fe ratio obtained after different surface finishing operations, are revealed in the paper.

METHOD AND EXPERIMENTAL SET UP

Austenitic stainless steel of grade AISI 316L was used for the investigation. A detailed composition of the material used for the studies is presented in Table 1. All samples of dimensions $30 \times 5 \times 1$ mm were prepared by the abrasive mechanical polishing (MP) using SiC grit size up to 1000 and then treated by a standard electrochemical polishing (EP) and/or magnetoelectropolishing (MEP).

Table 1. Chemical composition of AISI 31L SS (wt%) used for the studies

Element	Content (wt%)
Cr	17.07
Ni	10.26
Mo	1.97
Mn	1.68
Si	0.64
Cu	0.19
V	0.11
Co	0.04
C	0.03
Ti	0.03
P	0.024
Al	0.011
W	0.01
Sn	0.009
B	0.0048
S	0.004
N ₂	0.0431
Fe	Balance

The experimental set up consisted with the stabilized power supply RNG-3010, cylindrical austenitic stainless steel cathode of the area over 100 times bigger than that of the tested sample-anode, which was placed inside the cathode, (the anode-cathode distance was about 4.5 cm), Hg/Hg₂SO₄ MSE reference electrode, heater, thermometer and a neodymium magnet (Fig. 1).

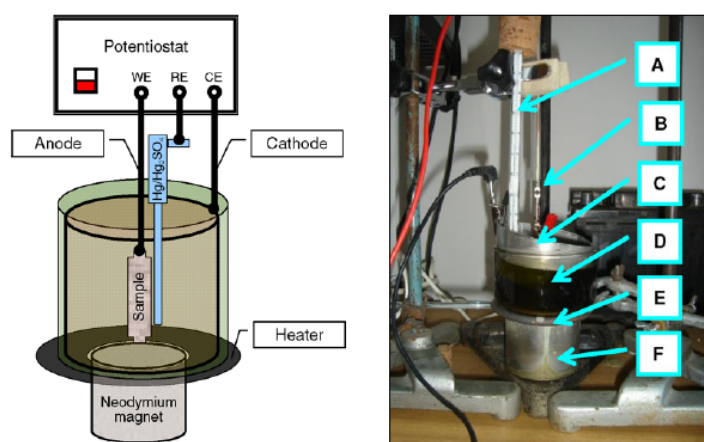


Fig. 1. Set up used for electrochemical polishing in the magnetic field: A – scheme of connections, B – photo (a – thermometer, b – anode, c – cathode, d – electrochemical cell, e – heater, f – neodymium magnet)

All the electrochemical polishing treatments (EP, MEP) were conducted at 65 ± 5 °C in the phosphoric-sulfuric mixture of acids ($\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4$) at the volume ratio of 4:6, with the current density of approximately 200 ± 10 A/dm² during 3 minutes. Stainless steel cathode plates were submerged into the bath and connected to the negative pole of the power source. A steel sample was fixed to a rack. That rack was connected to the positive pole of the power source. In case of the magnetoelectropolishing operation (MEP) the experiments were conducted for the following two magnetic field intensities: $B = 120 \pm 30$ mT, and $B = 420 \pm 30$ mT. The characteristic of the neodymium magnet used for the MEP system is shown in Figure 2.

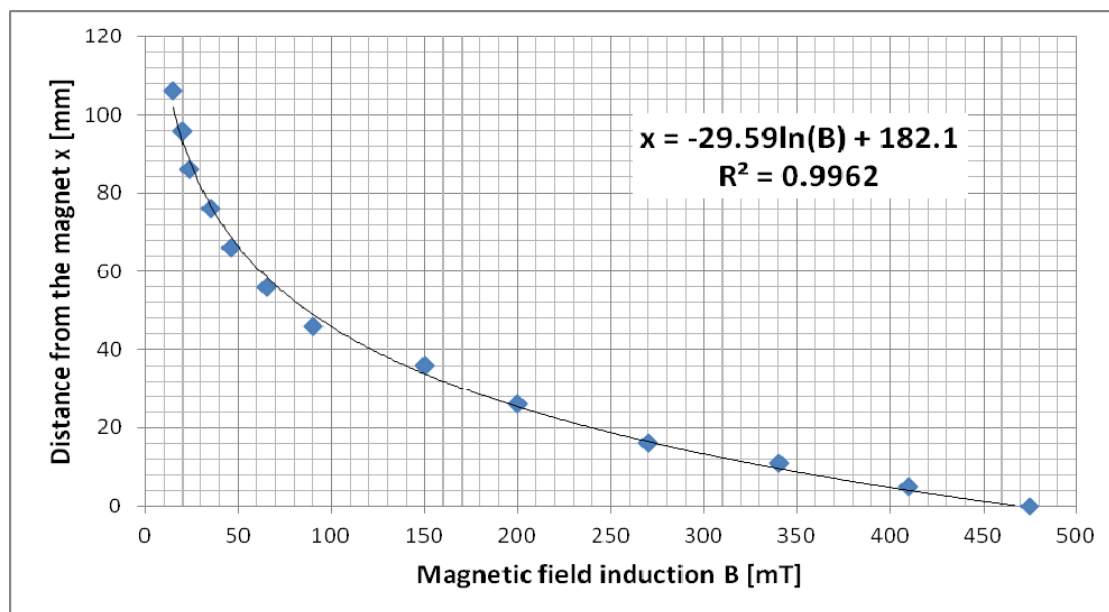


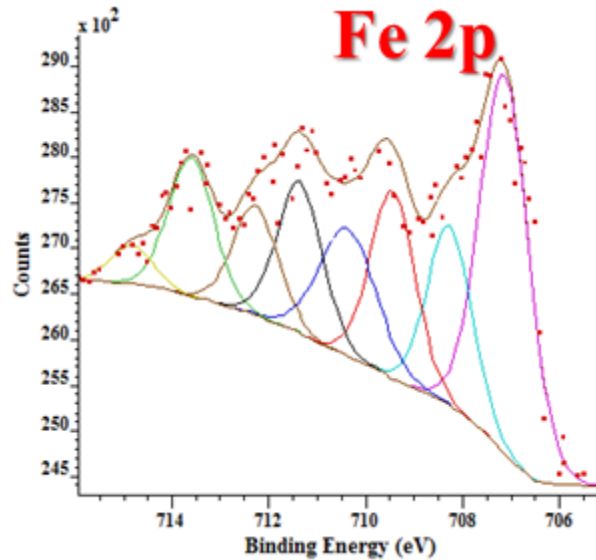
Fig. 2. Characteristic of neodymium magnet used for the studies

The XPS experiments were performed in an ultra-high-vacuum system with a base pressure of about 10^{-8} Pa. XPS measurements were performed using a SES2002 electron energy analyzer in conjunction with a monochromatized Al K α ($h\nu = 1486.6$ eV) X-ray source (Gammadata-Scienta). A total resolution of about 0.7 eV was obtained for the presented spectra. The binding energies (BE) for the XPS survey spectra were in the range of 0-1100 eV: for the XPS spectra of iron Fe 2p in the range of 700-730 eV; and for chromium Cr 2p in the range of 560-600 eV. The spectra were recorded in normal emission. The binding energy of the spectrometer was calibrated by the position of the Fermi level on a clean metallic sample. The Fermi level is determined by the work function of the electron energy analyzer and does not vary from sample to sample. CasaXPS Software was used for the evaluation and fitting of the XPS spectra [22, 25]. The tabulated data used to interpret the peaks were obtained from the literature on XPS [23-27].

RESULTS

In Figure 3, there are shown the high resolution XPS spectra of Fe 2p of AISI 316L SS after MEP carried out at a low magnetic induction ($i \approx 200$ A/dm², $B \approx 120$ mT). The peak of metal iron (Fe-M) at the binding energy of 707.1376 eV is clearly noticed. There are also other peaks

observed at the binding energies 708.2613 eV (Fe^{2+}) and 710.3669 eV (Fe^{3+}), which correspond to Fe_3O_4 . The binding energies of 709.4406 eV, 711.3637 eV, 712.2757 eV, and 713.6044 eV correspond with the following compounds: FeO (Fe^{2+}), FeOOH (Fe^{3+}), FeSO_4 (Fe^{2+}), $\text{Fe}_2(\text{SO}_4)_3$ (Fe^{3+}), respectively.



BE [eV]	FWHM	Area	Fe – X	at%
707.1376	1.18121	5345.1	Fe – M	30
708.2613	1.09061	2330.2	Fe_3O_4 , Fe^{2+}	13
709.4406	1.09061	2444.3	FeO	13.7
710.3669	1.37918	2088.5	Fe_3O_4 , Fe^{3+}	11.7
711.3637	1.09061	1972.5	FeO-OH	11
712.2757	1.09061	1412.4	FeSO_4	7.9
713.6044	1.09061	1804.6	$\text{Fe}_2(\text{SO}_4)_3$	10.1
714.8361	1	466.7	sat Fe^{2+}	2.6

Fig. 3. Results of XPS for Fe 2p_{3/2} spectra of AISI 316L SS surface after MEP at $i \approx 200 \text{ A/dm}^2$, $B \approx 120 \text{ mT}$

In Figure 4, there are given the high resolution XPS spectra of Cr 2p of AISI 316L SS after MEP performed at a low magnetic induction ($i \approx 200 \text{ A/dm}^2$, $B \approx 120 \text{ mT}$). The peak of metal chromium (Cr-M) at the binding energy of 574.2495 eV is clearly visible. There are other peaks observed at the binding energies of 576.3294 eV and 777.2762 eV which correspond to CrO_2 and $\text{Cr}(\text{OH})_3$, respectively. The binding energies of 578.0447 eV and 579.1780 eV correspond with the compounds of $\text{Cr}_2(\text{SO}_4)_3$ and/or CrPO_4 and $(\text{CrO}_4)^{2-}$, respectively.

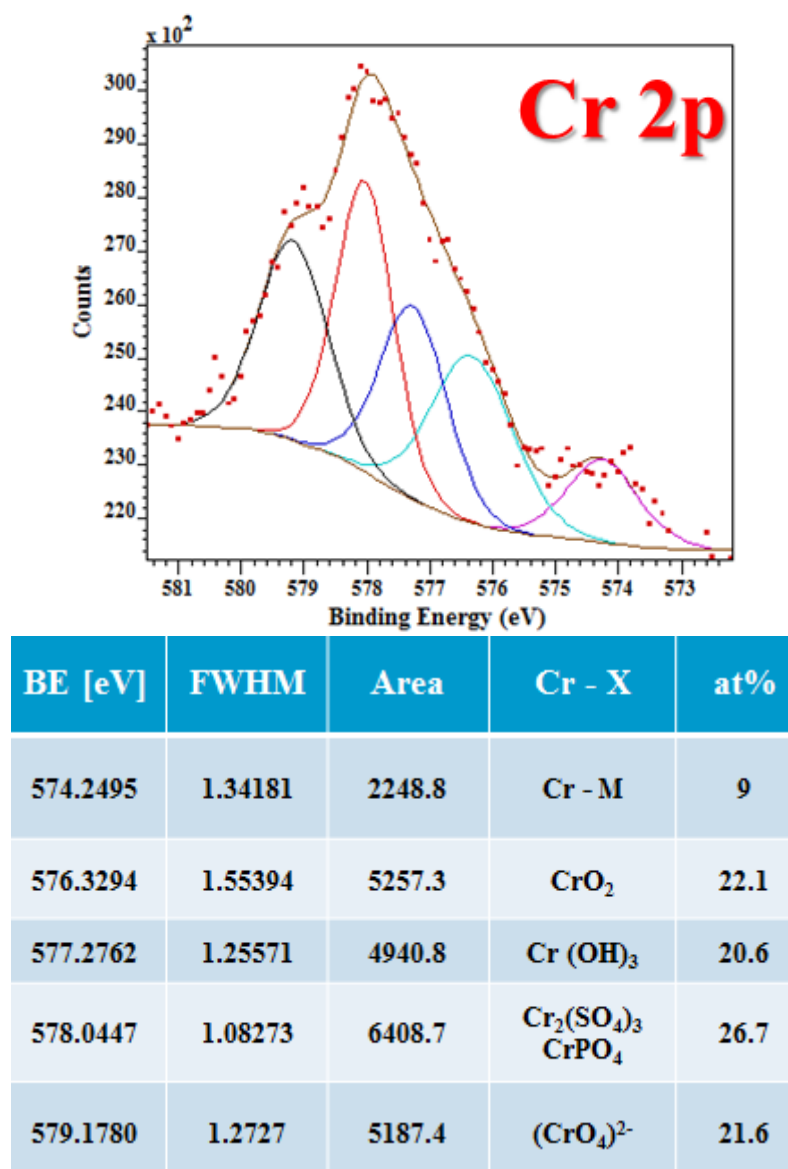


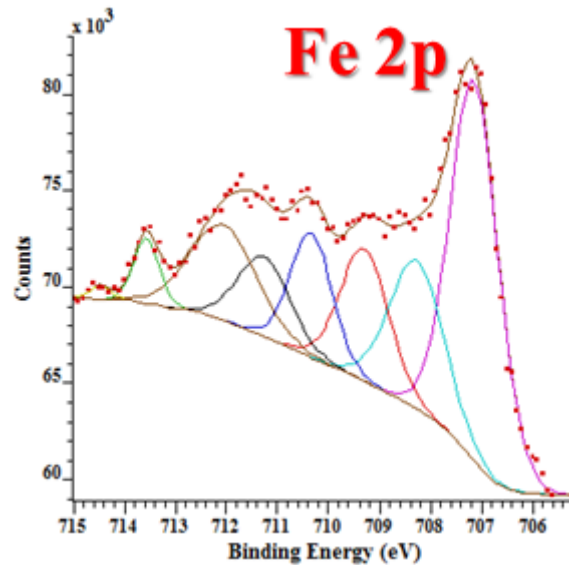
Fig. 4. Results of XPS for Cr 2p_{3/2} spectra of AISI 316L SS surface after MEP at $i \approx 200 \text{ A/dm}^2$, $B \approx 120 \text{ mT}$

On the basis of data given in Tables inserted in Figures 3 and 4, it is possible to calculate the Cr-X/Fe-X compounds ratio and Cr/Fe total ratio by including the sensitivity factor of chromium-to-iron ratio as 1.37 [22, 25]. Therefore

$$\frac{Cr-X}{Fe-X} = 1.37 \cdot \frac{5257.3 + 4940.8 + 6408.7 + 5187.4}{2330.2 + 2444.3 + 2088.5 + 1972.5 + 1412.4 + 1804.6 + 466.7} = 1.37 \cdot \frac{21794.2}{12519.2} = 2.38$$

$$\frac{Cr}{Fe} = 1.37 \cdot \frac{2248.8 + 5257.3 + 4940.8 + 6408.7 + 5187.4}{5345.1 + 2330.2 + 2444.3 + 2088.5 + 1972.5 + 1412.4 + 1804.6 + 466.7} = 1.37 \cdot \frac{24043}{17864.3} = 1.84$$

The following important results were obtained on the same 316L stainless steel samples treated by MEP under higher magnetic field intensity and the same current density. In Figure 5, there are the high resolution XPS spectra of Fe 2p of AISI 316L SS obtained on the samples after MEP at a high magnetic induction ($i \approx 200 \text{ A/dm}^2$, $B \approx 420 \text{ mT}$). There are clearly visible peaks of the metal iron (Fe-M) obtained at the binding energy of 707.1449 eV. The following consecutive peaks are also observed at the binding energies of 708.2735 eV (Fe^{2+}) and 710.3385 eV (Fe^{3+}), which correspond to Fe_3O_4 . The binding energies 709.296 eV, 711.2606 eV, 712.0603 eV, and 713.5667 eV may be referred to the following compounds: FeO (Fe^{2+}), FeOOH (Fe^{3+}), FeSO_4 (Fe^{2+}), and $\text{Fe}_2(\text{SO}_4)_3$ (Fe^{3+}), respectively.

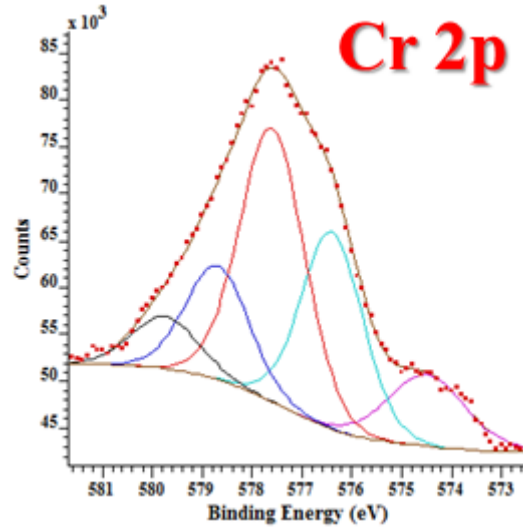


BE [eV]	FWHM	Area	Fe - X	at%
707.1449	1.1142	23783.9	Fe - M	36.38
708.2735	1.25009	10479.8	Fe_3O_4 , Fe^{2+}	16.04
709.2960	1.10981	8320.7	FeO	12.73
710.3385	0.952936	6701.0	Fe_3O_4 , Fe^{3+}	10.25
711.2606	1.18769	5388.0	FeO-OH	8.24
712.0603	1.54031	8231.1	FeSO_4	12.59
713.5667	0.577421	2116.4	$\text{Fe}_2(\text{SO}_4)_3$	3.24
714.4875	0.46261	348.6	sat Fe^{2+}	0.53

Fig. 5. Results of XPS for Fe 2p_{3/2} spectra of AISI 316L steel surface after MEP at $i \approx 200 \text{ A/dm}^2$, $B \approx 420 \text{ mT}$

In Figure 6, there are the high resolution XPS spectra of Cr 2p of AISI 316L SS after MEP at a high magnetic induction ($i \approx 200 \text{ A/dm}^2$, $B \approx 420 \text{ mT}$). There are clearly visible peaks of metal chromium (Cr-M) obtained at the binding energy of 574.5021 eV. The peaks obtained at the

binding energies of 576.401 eV and 777.592 eV correspond with CrO_2 and $\text{Cr}(\text{OH})_3$, respectively. The binding energies of 578.6961 eV and 579.6965 eV correspond with the following compounds: $\text{Cr}_2(\text{SO}_4)_3$ and/or CrPO_4 and $(\text{CrO}_4)^{2-}$, respectively.



BE [eV]	FWHM	Area	Cr - X	at%
574.5021	1.81808	14957.3	Cr - M	12
576.4010	1.45858	33240.4	CrO_2	26.5
577.5972	1.53286	48464.5	$\text{Cr}(\text{OH})_3$	38.6
578.6961	1.49136	19630.8	$\text{Cr}_2(\text{SO}_4)_3$ CrPO_4	15.6
579.7565	1.54558	9316.4	$(\text{CrO}_4)^{2-}$	7.3

Fig. 6. Results of XPS for Cr $2p_{3/2}$ spectra of AISI 316L steel surface after MEP at $i \approx 200 \text{ A/dm}^2$, $B \approx 420 \text{ mT}$

On the basis of data placed in Tables inserted in Figures 5 and 6, one may calculate the Cr-X/Fe-X compounds ratio and Cr/Fe total ratio by including the sensitivity factor of chromium-to-iron ratio as 1.37 [22, 25]. Therefore

$$\frac{\text{Cr} - X}{\text{Fe} - X} = 1.37 \cdot \frac{33240.4 + 48464.5 + 19630.8 + 9316.4}{10479.8 + 8320.7 + 6701 + 5388 + 8231.1 + 2116.4 + 348.6} = 1.37 \cdot \frac{110652.1}{41585.6} = 3.65$$

$$\frac{\text{Cr}}{\text{Fe}} = 1.37 \cdot \frac{14957.3 + 33240.4 + 48464.5 + 19630.8 + 9316.4}{23783.9 + 10479.8 + 8320.7 + 6701 + 5388 + 8231.1 + 2116.4 + 348.6} = 1.37 \cdot \frac{125609.4}{65369.5} = 2.63$$

The results obtained in the XPS studies and the calculations performed may be compared. In Figure 7, there are the results of chromium-to-iron compounds (Cr/Fe) obtained on the samples after the mechanical polishing MP [10], the standard electrochemical polishing EP ($i = 50 \text{ A/dm}^2$) and magnetoelectropolishing MEP 200 ($i = 200 \text{ A/dm}^2$, $B = 120 \text{ mT}$ and/or $B = 420 \text{ mT}$). One may notice that after MEP with the current density $i = 200 \text{ A/dm}^2$ and the magnetic field induction of $B = 420 \text{ mT}$, the Cr/Fe ratio is four times higher than that after MP, and over 1.6 times higher than that after EP. On the other hand, the low magnetic field of the induction of about 120 mT resulted in the insignificant increase of the Cr/Fe ratio up to 2.38, much lower than that obtained after MEP at $B = 420 \text{ mT}$, and equaling 3.65 (Fig. 7).

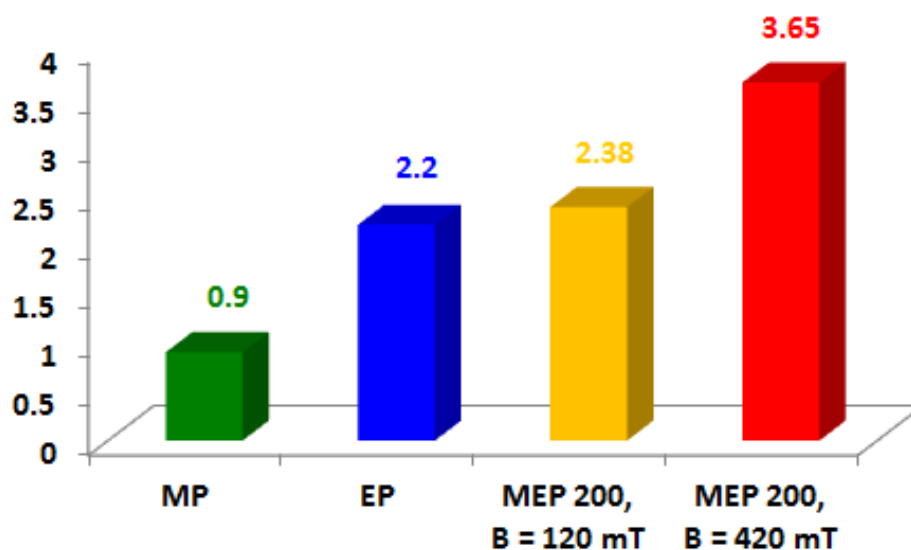


Fig. 7. Cr-X/Fe-X compounds ratio of the 316L SS surface film studied after MP, EP and MEP

CONCLUSIONS

Based on the XPS study results and the calculations performed, the following conclusions may be formulated:

1. Magnetic field induction has influenced the surface film composition obtained
2. Magnetic field induction changes the Cr/Fe compound ratio after MEP vs. EP
3. Cr-X/Fe-X compounds ratio after MEP ($i = 200 \text{ A/dm}^2$, $B = 420 \text{ mT}$) amounts 3.65, whereas the analogous compounds ratio after MEP ($i = 200 \text{ A/dm}^2$, $B = 120 \text{ mT}$) amounts 2.38
4. Cr/Fe total ratio after MEP ($i = 200 \text{ A/dm}^2$, $B = 420 \text{ mT}$) amounts 2.63, whereas the analogous total ratio after MEP ($i = 200 \text{ A/dm}^2$, $B = 120 \text{ mT}$) amounts 1.84
5. Cr-X/Fe-X compounds ratio is over 4 times higher than that after MP
6. Cr-X/Fe-X compounds ratio is and over 1.6 times higher than that measured after EP.

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