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## Significant improvement of AISI 316L SS biomaterial surface after magnetoelectropolishing MEP: XPS measurements

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### Abstract

The main purpose of the work is to show a significant improvement of AISI 316L biomaterial after magnetoelectropolishing MEP. The studies were realized by taking XPS measurements on the steel samples after three surface treatments: abrasive polishing MP, standard electropolishing EP, and magnetoelectropolishing MEP to reveal the great advantage of magnetoelectropolished biomaterial over the 316L steel surface properties after other finishing operations. Moreover, a variety of electropolishing conditions (EP – without stirring, MIX – using electrolyte mixing) and parameters (current density from the plateau level EP, up to EP1000, meaning 1000 A/dm<sup>2</sup>) were considered and studied. Afterwards, basing on the XPS survey, the high resolution spectra were determined concerning three general elements of the 316L steel: iron, chromium, and oxygen. At the end, chromium compounds to iron compounds ratio (Cr-X/Fe-X) and Cr/Fe ratio could be calculated to reveal the optimum conditions of the studies. The main achievement of the work is proving the outstanding features of stainless steel biomaterial after MEP.

**Keywords:** AISI 316L SS; Magnetoelectropolishing MEP; XPS measurements; Cr-X/Fe-X ratio.

### Istotne polepszenie stali AISI 316L jako biomateriału po magnetoektopolerowaniu: pomiary XPS

#### Streszczenie

W artykule przedstawiono wyniki pomiarów składu chemicznego warstwy pasywnej wytworzonej na stali austenitycznej AISI 316L po polerowaniu elektrochemicznym w warunkach bez mieszania elektrolitu (EP), z mieszanym elektrolitem (MIX), oraz po magnetoektopolerowaniu (MEP). Wszystkie próby polerowania elektrochemicznego prowadzono w mieszaninie kwasów ortofosforowego i siarkowego o składzie objętościowym 6:4 w temperaturze (65±5) °C przy zastosowaniu gęstości prądu na poziomie plateau, 50 A/dm<sup>2</sup>, 200 A/dm<sup>2</sup>, i 1000 A/dm<sup>2</sup> oraz jednakowym czasie obróbki wynoszącym 3 minuty. Proces magnetoektopolerowania MEP prowadzono w stałym polu magnetycznym ( $B \approx 350$  mT). Dodatkowo, kilka prób MEP wykonano z parametrami  $i \approx 200$  A/dm<sup>2</sup>, w polu magnetycznym o natężeniu  $B \approx 420$  mT. Skład chemiczny warstwy wierzchniej stali AISI 316L zbadano przy użyciu fotoelektronowej spektroskopii promieniami Roentgena (XPS) po trzech obróbkach: polerowaniu ściernym MP, polerowaniu elektrolitycznym EP, oraz po MEP. Warunki elektropolerowania obejmowały mieszanie elektrolitu (MIX), lub jego brak (EP), oraz gęstość prądu od wartości plateau do 1000 A/dm<sup>2</sup> (EP1000). Po polerowaniu, w oparciu o pomiary XPS, uzyskano widma wysokiej rozdzielczości dotyczące trzech głównych pierwiastków stali 316L: żelaza, chromu i tlenu. Podstawowe zadanie polegało na wyznaczeniu zmian w stosunku zawartości chromu do żelaza w warstwie wierzchniej badanej stali austenitycznej AISI 316L, w zależności od warunków obróbki elektrochemicznej. Przedstawiono widma XPS wysokiej rozdzielczości chromu Cr 2p oraz żelaza Fe 2p badanej stali po poszczególnych obróbkach elektrochemicznych. Tabełarycznie przedstawiono analizę danych XPS przez dopasowanie jednopikowe O 1s. Następnie pokazano skład chemiczny warstwy wierzchniej obliczony w oparciu o trzy sygnały: Fe 2p, Cr 2p, O 1s oraz podano stosunki Cr-X/Fe-X i Cr/Fe. Metoda

badania XPS składu powierzchni została przedstawiona we wcześniejszych pracach Autorów, przy czym sposób podejścia do dwupikowej analizy zaprezentowano przykładowo na pierwszych dwu rysunkach niniejszej pracy. Badania XPS przeprowadzono na spektrometrze SCIENCE SES 2002. Widma rentgenowskie zapisywano przy normalnej emisji. W celu optymalizacji stosunku sygnału do szumu, jeden cykl pomiarowy XPS obejmował 10 przejść. Następnie wyznaczono stosunek Cr/Fe dla wszystkich wykonanych pomiarów. Do analizy danych XPS posłużono się programem Casa XPS 2.3.14. Wykorzystując program Casa XPS 2.3.14, zgodnie z zaproponowanym algorytmem, dokonano interpretacji wyników XPS. W końcu wyznaczono stosunki związków (Cr-X/Fe-X) i Cr/Fe celem pokazania optimum. Głównym osiągnięciem pracy jest pokazanie znacznej poprawy właściwości powierzchni stali 316L po MEP.

**Słowa kluczowe:** pomiary XPS, stal austenityczna AISI 316L, magnetoektopolerowanie MEP.

### 1. Introduction

This work presents the research results on magnetoelectropolishing MEP of AISI 316L austenitic stainless steel used as a biomaterial. Within last few years we have noticed a great interest in our earlier works published in different journals [1-8]. It is known that the XPS is a powerful tool to measure and analyse the surface film composition [9-11]. Some of the readers, expressing their continuous interest in the MEP process would wish to see the XPS results *in extenso* [12]. Therefore, the work starts with the XPS high resolution spectra results obtained on 316L steel samples, presenting the way of approach to the spectra analysis. Next two basic elements of the steel, Fe and Cr, as well as oxygen are analysed using XPS high resolution spectra.

Afterwards, the chromium compounds to iron compounds ratio (Cr-X/Fe-X) and Cr/Fe ratio are calculated to reveal the fluctuations dependent on the conditions of the studies. The main achievement of the work is proving the outstanding features of the 316L stainless steel biomaterial after MEP. At the end the authors indicate that also other surface measurement techniques reveal the improvement of the surface layer formed after MEP.

### 2. The method

Samples of AISI 316L austenitic stainless steel, of characteristics and dimensions presented in [1], were used for the study. All the electrochemical treatments (EP, MIX, MEP) were conducted at (65±5) °C in phosphoric-sulfuric mixed acids (H<sub>3</sub>PO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub>) with the volume ratio of 6:4, at respective current densities, of the plateau level, 50 A/dm<sup>2</sup>, 200 A/dm<sup>2</sup>, and 1000 A/dm<sup>2</sup> in 3 minutes' time. For the MEP studies, a constant magnetic field was applied ( $B \approx 350$  mT). Besides, additional magnetoelectropolishing MEP experiments were carried out, by providing with new parameters covering both current density ( $i \approx 200$  A/dm<sup>2</sup>) and magnetic field intensity ( $B \approx 420$  mT).

The surface study method follows mostly the procedures described in our previous works [1,7,13] with a 2-peak approach to the analysis, as presented by examples given in Figs. 1 and 2.

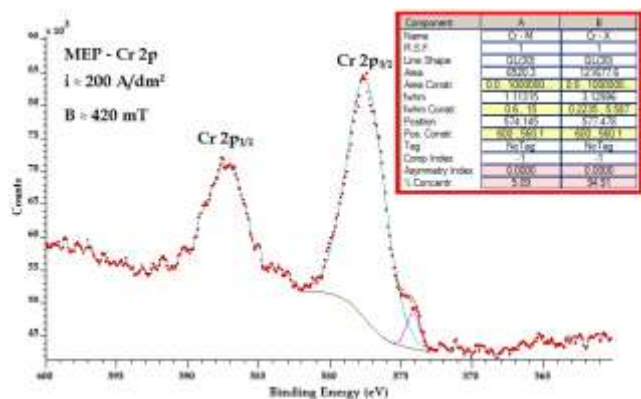


Fig. 1. XPS high resolution Cr 2p spectra: results with analysis in CasaXPS software [9] for AISI 316L SS surface after magnetoelectropolishing MEP200 ( $i \approx 200 \text{ A/dm}^2$ ,  $B \approx 420 \text{ mT}$ )

Rys. 1. Widma XPS wysokiej rozdzielczości dla chromu Cr 2p w stali AISI 316L po magnetoektopolerowaniu MEP200 ( $i \approx 200 \text{ A/dm}^2$ ,  $B \approx 420 \text{ mT}$ ): analiza w programie CasaXPS [9]

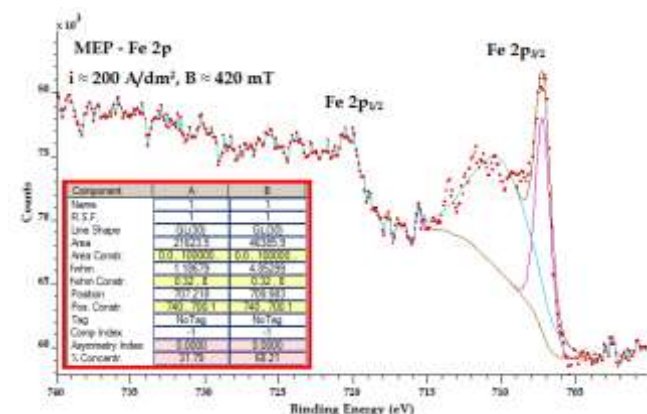


Fig. 2. XPS high resolution Fe 2p spectra: results with analysis in CasaXPS software [9] for AISI 316L SS surface after magnetoelectropolishing MEP200 ( $i \approx 200 \text{ A/dm}^2$ ,  $B \approx 420 \text{ mT}$ )

Rys. 2. Widma XPS wysokiej rozdzielczości dla żelaza Fe 2p w stali AISI 316L po magnetoektopolerowaniu MEP200 ( $i \approx 200 \text{ A/dm}^2$ ,  $B \approx 420 \text{ mT}$ ): analiza w programie CasaXPS [9]

The XPS measurements on electrochemically polished AISI 316L SS samples were performed using a SCIENCE SES 2002 instrument. The XP spectra were recorded in normal emission [1, 7]. A new approach to the XPS measurement [9-11] data was used to develop our study results presented mostly in the tabulated form (see the calculation results shown in Tables below) and Figures.

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 the measurements made. For the XPS analyses the CasaXPS 2.3.14 software was used [9]. Following the Casa XPS 2.3.14 software, the interpretation of XPS results was performed in accordance to the algorithm [9-11].

In Figs. 1 and 2 there are presented the methods of evaluating the fitting XPS spectra for iron (Fe 2p) and chromium (Cr 2p). There also GL(p) is the Gaussian/ Lorentzian product formula where the mixing, as determined by  $m = p/100$ , GL(100) is a pure Lorentzian while GL(0) is pure Gaussian [14].

### 3. Results

The main task solved was to reveal changes in the Cr/Fe ratio in the AISI 316L SS surface film studied, dependent on the surface treatment conditions. The high interest of readers forced the

authors to develop the results *in extenso*. Therefore, herewith we take the opportunity to present our results in detail with the form quite readable and clear.

In Figs. 3 and 4 there are shown XPS high resolution spectra for Fe 2p and Cr 2p performed on 316L SS surface after all electrochemical treatments (EP, MIX and MEP) in the plateau region. It appears, for iron (Fe 2p) spectra (Fig. 3) there are not noted big differences in the shape of the analyzed XPS data. However, one can easily notice that the minimum values of intensity are recorded for MEP and the maximum ones for the sample after a MIX operation. The other trend can be observed for chromium Cr 2p spectra (Fig. 4). In this case the maximum values of intensity are noted for MEP and MIX against EP sample, where the values are the smaller ones. The data visible suggest, that the maximum of Cr/Fe ratio should be reported for MEP, what was confirmed by the authors' studies [1, 13].

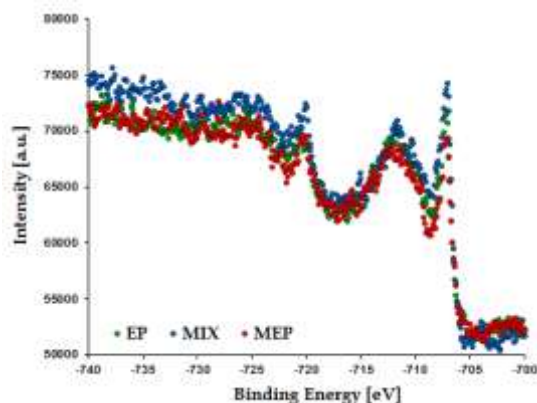


Fig. 3. XPS high resolution Fe 2p spectra: results for AISI 316L SS surface after electropolishing in the plateau region: EP, MIX, MEP

Rys. 3. Widma XPS wysokiej rozdzielczości dla żelaza Fe 2p w stali AISI 316L po elektropolerowaniu bez mieszania EP, elektropolerowaniu z mieszaniami MIX, oraz magnetoektopolerowaniu MEP (zakres plateau)

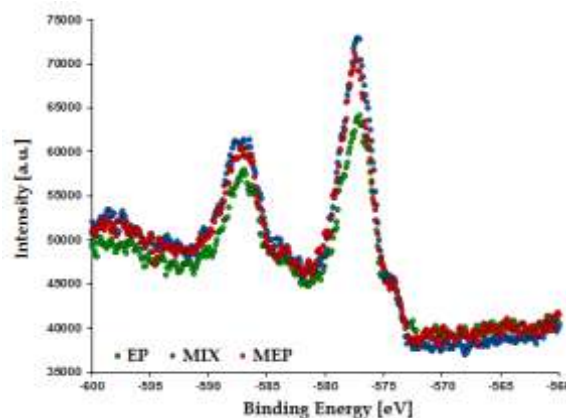


Fig. 4. XPS high resolution Cr 2p spectra for AISI 316L SS surface after electropolishing in the plateau region: EP, MIX, MEP

Rys. 4. Widma XPS wysokiej rozdzielczości dla chromu Cr 2p w stali AISI 316L po elektropolerowaniu bez mieszania EP, elektropolerowaniu z mieszaniami MIX, oraz magnetoektopolerowaniu MEP (zakres plateau)

In Figs. 5 and 6 there are shown the XPS spectra for Fe 2p and Cr 2p performed on 316L SS surface after EP50, EP200 and EP1000 electropolishing in a transpassive region, with 50, 200 and 1000 referred to the current density in  $\text{A/dm}^2$ , respectively. Here the differences are more pronounced in respect to the results of the plateau region. The minimum values of intensity of iron (Fe 2p) signal and simultaneously maximum of chromium (Cr 2p) are observed for a standard electrochemical polishing with current density  $i = 1000 \text{ A/dm}^2$ , which can suggest the highest Cr/Fe ratio out of EP50, EP200 and EP1000 samples. The opposite situation

is for EP50 and EP200, where more iron (Fe 2p) than chromium (Cr 2p) in the surface layer is detected.

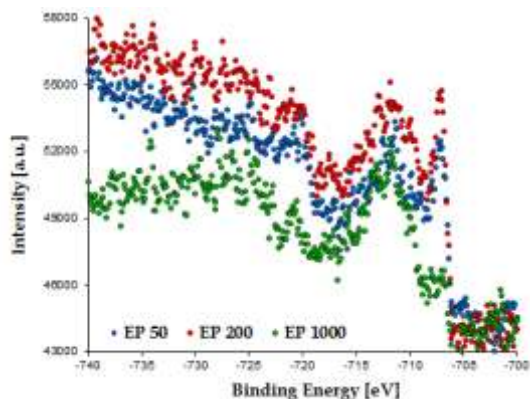


Fig. 5. XPS high resolution Fe 2p spectra: results for AISI 316L SS surface after a standard electropolishing EP50, EP200, EP 900 in a transpassive region (still electrolyte)

Rys. 5. Widma XPS wysokiej rozdzielczości dla żelaza Fe 2p w stali AISI 316L po elektropolerowaniu EP50, EP200, EP 900 w zakresie trans pasywnym (bez mieszania elektrolitu)

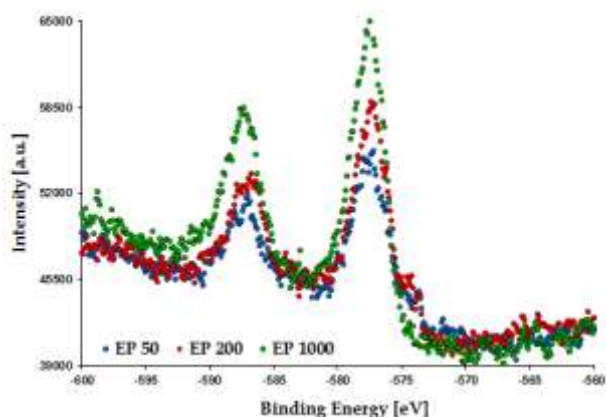


Fig. 6. XPS high resolution Cr 2p spectra for AISI 316L SS surface after electropolishing EP50, EP200, EP 1000 in a transpassive region (still electrolyte)

Rys. 6. Widma XPS wysokiej rozdzielczości dla chromu Cr 2p w stali AISI 316L po elektropolerowaniu EP50, EP200, EP 1000 w zakresie transpasywnym (bez mieszania elektrolitu)

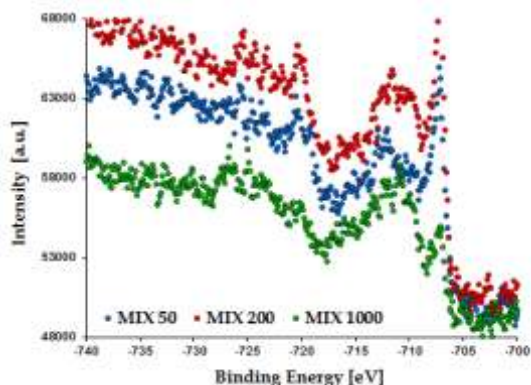


Fig. 7. XPS high resolution Fe 2p spectra: results for AISI 316L SS surface after a standard electropolishing MIX50, MIX200, MIX 1000 in a transpassive region (electrolyte stirring included)

Rys. 7. Widma XPS wysokiej rozdzielczości dla żelaza Fe 2p w stali AISI 316L po elektropolerowaniu MIX50, MIX200, MIX 1000 w zakresie transpasywnym (z mieszaniem elektrolitu)

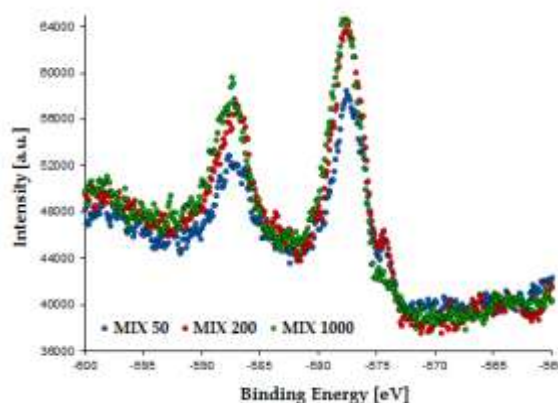


Fig. 8. XPS high resolution Cr 2p spectra for AISI 316L SS surface after electropolishing MIX50, MIX200, and MIX1000 in a transpassive region (electrolyte stirring included)

Rys. 8. Widma XPS wysokiej rozdzielczości dla chromu Cr 2p w stali AISI 316L po elektropolerowaniu MIX50, MIX200, MIX 1000 w zakresie transpasywnym (z mieszaniem elektrolitu)

In Figs. 7 and 8 there are visible XPS spectra for iron (Fe 2p) and chromium (Cr 2p) performed on 316L SS surface after MIX50, MIX200 and MIX1000 electropolishing in the transpassive region. The minimum values of intensity of iron (Fe 2p) signal and simultaneously the maximum of chromium (Cr 2p) are observed for electrochemical polishing with stirring with current density  $i = 1000 \text{ A/dm}^2$ , which can suggest the highest Cr/Fe ratio out of MIX50, MIXP200 and MIX1000. The opposite situation is noted for MIX50 and MIX200, where more iron (Fe 2p) than chromium (Cr 2p) is detected in the surface layer.

In Figs. 9 and 10 there are visible XPS spectra for iron (Fe 2p) and chromium (Cr 2p) performed on 316L SS surface after MEP (plateau level), MEP50 and MEP200 polishing in the transpassive region. The maximum values of intensity both for iron (Fe 2p) as well as for chromium (Cr 2p) are observed after electrochemical polishing in the magnetic field in the plateau region of polarization curve. The interesting finding is the MEP200 sample, where the magnitude of iron signal (Fe 2p) is quite small in reference to the chromium signal (Cr 2p), which can suggest a high value of Cr/Fe ratio.

The graphical findings can only suggest the chemical composition of the surface layer and, hence, also Cr/Fe ratio value. In the next part of the paper the detailed analysis results are presented in the form of Tables. To estimate the amount of chromium and iron compounds, the minimum number of peaks will be used to avoid coarse errors (outlier values) in determining the significant differences.

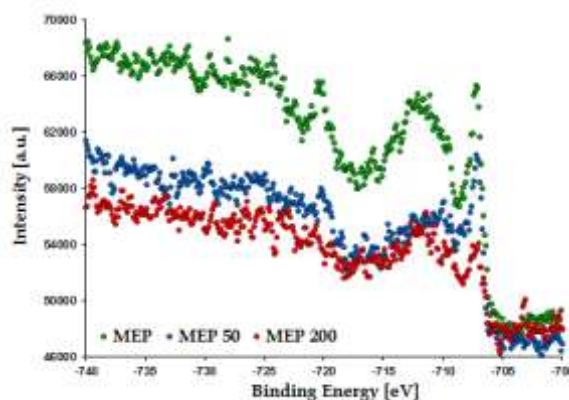


Fig. 9. XPS high resolution Fe 2p spectra: results for AISI 316L SS surface after magnetoelectropolishing MEP, MEP50, and MEP200

Rys. 9. Widma XPS wysokiej rozdzielczości dla żelaza Fe 2p w stali AISI 316L po magneto elektropolerowaniu MEP, MEP50, i MEP200

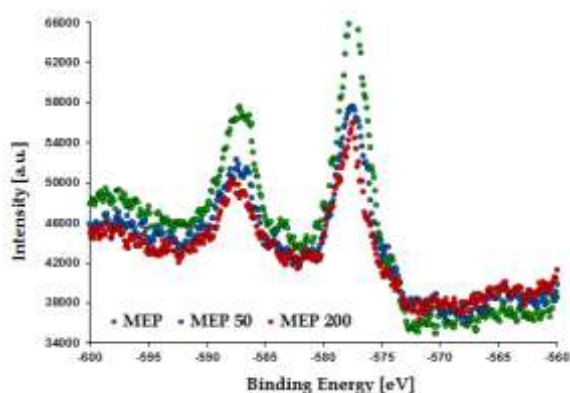


Fig. 10. XPS high resolution Cr 2p spectra for AISI 316L SS surface after magnetoelectropolishing MEP, MEP50, and MEP200

Rys. 10. Widma XPS wysokiej rozdzielczości dla chromu Cr 2p w stali AISI 316L po magnetoektopolerowaniu MEP, MEP50, and MEP200

First, we made the analysis as one-peak fitting (see Table 1). One may easily notice in Table 1 that there is a big difference between the XPS data obtained after a standard electropolishing on the plateau level (EP, MIX, MEP) and those obtained in the transpassive regions of the electrochemical treatments (EP50, EP200, EP1000; MIX50, MIX200, MIX1000; MEP50, MEP200), with the numbers 50, 200, 1000 referred to the respective current densities, in A/dm<sup>2</sup>.

In the surface layers formed on AISI 316L SS surface after electropolishing in the plateau region, the oxides and hydroxides of iron and chromium dominate. In the case of electropolishing in the transpassive region there are phosphates and sulfates of iron and chromium noted. That way the provided in Table 1 results have been completed.

Tab. 1. Data analysis by one-peak fitting of O 1s

Tab. 1. Analiza danych XPS przez dopasowanie jednopikowe O 1s

O 1s	BE, eV	FWHM	Area
EP	531.7	2.67	159141.6
MIX	531.8	2.61	200540.2
MEP	531.8	2.52	206679.9
EP50	532.1	2.75	126260.7
EP200	532.1	2.66	163436.5
EP1000	532.1	2.50	191811.8
MIX50	532.2	2.67	171068.8
MIX200	532.1	2.74	163227.5
MIX1000	532.3	2.77	179091.8
MEP50	532.2	2.74	154981.8
MEP200	532.3	2.65	167974.6

The studies of the experimental results were calculated and given in the numerical form below (see the consecutive Tables 2, 3, 4). In Table 2, the Fe-M and Cr-M notations refer to the metallic part (Fe<sup>0</sup> and Cr<sup>0</sup>, respectively), whereas Fe-X and Cr-X – to the compounds. Next the results are presented in Tables 3 and 4, by two-peak fitting for Cr 2p<sub>3/2</sub> and Fe 2p<sub>3/2</sub> data, respectively. In Tables 1, 3, and 4, BE [eV] refers to the binding energy; FWHM (Full Width at Half Maximum) is an expression of the extent of a function, given by the difference between the two extreme values of the independent variable at which the dependent variable is equal to half of its maximum value; AREA is in square units under the distribution curve against the Shirley background. In Tables 3, 4 the last column provides the content in atomic per cent (at.%).

Tab. 2. Chemical composition of the surface layer based on three signals (Fe 2p, Cr 2p, O 1s) with Cr-X/Fe-X and Cr/Fe ratios

Tab. 2. Skład chemiczny warstwy wierzchniej obliczony w oparciu o trzy sygnały (Fe 2p, Cr 2p, O 1s); podano stosunki Cr-X/Fe-X i Cr/Fe

	Cr-M, %	Cr-X, %	Fe-M, %	Fe-X, %	Oxygen, %	Cr-X/Fe-X	Cr/Fe
MP	0.9	8.1	3.3	8.3	79.4	1.0	0.8
EP	0.7	11.2	2	5.9	80.2	2.0	1.5
MIX	0.8	12	2.1	4.9	80.2	2.5	1.9
MEP	0.9	10.7	1.5	4.1	82.8	2.7	2.1
EP50	0.4	7.9	1.2	4.4	86.0	1.8	1.5
EP200	0.7	8	1.2	4.1	86.0	2.0	1.7
EP1000	0.0	9.7	0.2	3.1	87.0	3.2	3.0
MIX50	0.8	8	1.6	4.1	85.5	2.0	1.6
MIX200	1.2	11.7	1.8	5.5	79.9	2.2	1.8
MIX1000	0.5	10.7	0.4	3.4	84.9	3.2	3.0
MEP50	1.0	9.7	1.3	3.4	84.6	2.9	2.3
MEP200	0.7	7.6	0.7	2.4	88.6	3.2	2.7

Tab. 3. Results of fitting Cr 2p<sub>3/2</sub> data by two peaks

Tab. 3. Wyniki dopasowania danych Cr 2p<sub>3/2</sub> na podstawie analizy 2-pikowej

Cr 2p <sub>3/2</sub>	METAL				COMPOUNDS			
	BE, eV	FWHM	AREA	at. %	BE, eV	FWHM	AREA	at. %
MP	574.1	1.06	12874.0	10.10	576.6	3.09	114600.3	89.90
EP	574.1	1.04	4209.2	5.51	577.1	3.14	72230.6	94.49
MIX	574	1.30	6571.5	6.34	577.2	3.06	97173.6	93.66
MEP	574	1.39	7163.2	7.6	577.3	3.014	87028.6	92.40
EP50	574	1.07	2115.6	5.33	577.4	3.13	37552.5	94.67
EP200	574.1	1.21	4339.1	8.09	577.2	3.01	49297.0	91.91
EP1000	-	-	-	0.00	577.5	2.92	69178.7	100.00
MIX50	574.1	1.14	5259.7	9.19	577.2	3.10	51983.2	90.81
MIX200	574.1	1.09	5955.0	7.25	577.4	3.20	76154.5	92.75
MIX1000	573.8	1.45	3248.1	4.23	577.6	3.02	73505.5	95.77
MEP50	574.2	1.52	5813.4	9.15	577.4	3.06	57743.3	90.85
MEP200	574.3	1.81	4572.7	8.97	577.5	2.91	46381.3	91.03

Tab. 4. Results of fitting Fe 2p<sub>3/2</sub> data by two peaks

Tab. 4. Wyniki dopasowania danych Fe 2p<sub>3/2</sub> na podstawie analizy 2-pikowej

Fe 2p <sub>3/2</sub>	METAL				COMPOUNDS			
	BE, eV	FWHM	AREA	at. %	BE, eV	FWHM	AREA	at. %
MP	707.1	1.30	64758.6	27.86	710.5	4.91	167660.2	72.14
EP	707.2	1.13	17917.2	25.74	710.9	4.89	51693.2	74.26
MIX	707.2	1.22	23256.3	30.02	710.5	4.98	54218.2	69.98
MEP	707.2	1.18	16921.9	27.19	710.8	4.97	45315.2	72.81
EP50	707.1	1.20	7984.7	21.64	710.9	5.91	28908.9	78.36
EP200	707.2	1.12	10287.9	23.12	710.8	5.27	34200.9	76.88
EP1000	707.1	0.93	2213.4	6.76	711.7	4.96	30520.0	93.24
MIX50	707.3	1.22	13866.3	27.49	710.6	6.24	36582.0	72.51
MIX200	707.2	1.06	15956.1	24.29	710.4	5.57	49743.6	75.71
MIX1000	707.2	0.93	3910.3	10.82	710.9	5.08	32235.3	89.18
MEP50	707.1	0.96	10185.2	26.86	709.9	5.14	27727.7	73.14
MEP200	707.2	1.12	5487.4	21.07	710.9	4.68	20550.8	78.93

In case of the oxygen (O 1s) data analysis it should be noted that the analyzed surface layers consist of the carbon-oxygen film and passive film of the chromium-iron-molybdenum-oxygen compounds.

The carbon-oxide film should be considered as contamination, which has been frequently noted by other authors [15, 16]. It is important to note, that the percentage of oxygen in the surface layer belongs partly to the carbon compounds (C-O, C=O, C-O-H). The rest of the oxygen in the surface layer is a part of the passive layer (chromium, iron, molybdenum, manganese, and/or nickel compounds with oxygen).

At the end of the result presentation it is worth noting that our findings in magnetoelectropolishing of stainless steels [17, 18] very well correlate with our earlier results concerning the increase in corrosion resistance [18, 19], considerable changes in nanoindentation results [20, 21], and dehydrogenation effect [6, 22] reported. It appears that the magnetoelectropolishing affects also basic mechanical properties of the materials treated [23-25].

#### 4. Conclusions

In conclusions it is worth noting that the detailed XPS results were obtained on AISI 316L SS samples after finishing processes (MP, EP, MIX, MEP) concerning the main elements (Fe, Cr, and oxygen). The fitting of XPS analysis shows, that the best Cr/Fe ratio is obtained after electrochemical polishing operations EP1000 and MIX1000 as well after MEP200. The treatments with and without stirring at high current density (about 1000 A/dm<sup>2</sup>) were unpredictable due to the significant and rapid increase in the temperature of solution as well as safety of the experiment. On the other hand, the shape of the machined workpiece was losing its geometry during some seconds of the operation which was indicated by dissolving sharp edges. In addition, under extreme experimental conditions, there was obtained a non-uniform surface after EP1000 and MIX 1000 due to the unexpected roughness obtained. For this reason, it was decided to qualify the surface after MEP200 as the best in terms of a high ratio of Cr/Fe and appearance, which was confirmed by other authors' studies [4, 18, 19].

We hope this work confirms a significant meaning of the magnetoelectropolishing MEP process, proving considerable advantages of the study results and the process development.

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#### 5. References

- [1] Hryniewicz T., Rokosz K.: Analysis of XPS results of AISI 316L SS electropolished and magnetoelectropolished at varying conditions, *Surface & Coatings Technology*, 2010, 204(16-17), 2583-2592.
- [2] Hryniewicz T., Rokosz K., Filippi M.: Biomaterial Studies on AISI 316L Stainless Steel after Magnetoelectropolishing. *Materials*, 2009, 2(1), 129-145.
- [3] Hryniewicz T., Rokicki R., Rokosz K.: Magnetoelectropolishing for metal surface modification. *Trans. Inst. Metal Finish.*, 2007, 85(6), 325-332.
- [4] Hryniewicz T., Rokosz K.: Polarization Characteristics of Magnetoelectropolishing Stainless Steels. *Materials Chemistry and Physics*, 2010, 122, 169-174. DOI: 10.1016/j.matchemphys.2010.02.055
- [5] Rokosz K., Hryniewicz T., Valíček J., Harničárová M., Vyležik M.: Nanoindentation measurements of AISI 316L biomaterial samples after annual immersion in Ringer's solution followed by electrochemical polishing in a magnetic field. *PAK (Measurement Automation and Monitoring)*, 2012, 58(5), 460-463.
- [6] Hryniewicz T., Konarski P., Rokosz K., Rokicki R.: SIMS analysis of hydrogen content in near surface layers of AISI 316L SS after electrolytic polishing under different conditions. *Surface & Coatings Technology*, 2011, 205, 4228-4236, DOI: 10.1016/j.surfcoat.2011.03.024.
- [7] Hryniewicz T., Rokosz K.: Investigation of selected surface properties of AISI 316L SS after magnetoelectropolishing. *Materials Chemistry and Physics*, 2010, 123, 47-55, DOI: 10.1016/j.matchemphys.2010.03.060.
- [8] Hryniewicz T., Rokicki R., Rokosz K.: Surface characterization of AISI 316L biomaterials obtained by electropolishing in a magnetic field. *Surface and Coatings Technology*, 2008, 202(9), 1668-1673.
- [9] CasaXPS Version 2.3.16 (Pre-rel 1.4)
- [10] Crist B. V.: *Handbook of Monochromatic XPS Spectra. The elements and Native Spectra Oxide*. John Wiley & Sons Ltd., Chichester, New York, Weinheim, Brisbane, Singapore, Toronto, 2000.
- [11] Grosvenor A. P., Kobe B. A., McIntyre N. S., Tougaard S., Lennard W. N.: Use of QUASES/XPS measurements to determine the oxide composition and thickness on an iron substrate. *Surf. Interface Anal.*, 2004, 36, 632-639.
- [12] Baron A., Simka W., Nawrat G., Szewieczek D., Krzyżak A.: Influence of electrolytic polishing on electrochemical behavior of austenitic steel, *J. Achiev. Mater. Manuf. Eng.*, 2006, 18(1-2), 55-58.
- [13] Rokosz K., Hryniewicz T., Raaen S.: Characterization of Passive Film Formed on AISI 316L Stainless Steel after Magnetoelectropolishing in a Broad Range of Polarization Parameters, *Steel Research International*, 2012, DOI: 10.1002/srin.201200046.
- [14] Hryniewicz T., Rokosz K.: Corrigendum to "SEM/EDX and XPS studies of niobium after electropolishing" by T. Hryniewicz, K. Rokosz, H.R. Zschommler Sandim [Appl. Surf. Sci., yyy (2012) xxx], <http://dx.doi.org/10.1016/j.apsusc.2012.09.060>, *Appl. Surf. Sci.*, 2013, 265, 931-934.
- [15] Flori M., Gruzza B., Bideux L., Monier G., Robert-Goumet C.: A study of steel surface contamination by XPS electron spectroscopy, *Annals of the Faculty of Engineering Hunedoara – Journal of Engineering*, 2007, 5(1), 165-170.
- [16] Vêgh J.: The "carbon contamination" rule set implemented in an "embedded expert system", *Journal of Electron Spectroscopy and Related Phenomena*, 2003, 133, 87-101.
- [17] Rokosz K.: Electrochemical polishing of steel in the magnetic field (in Polish), *Monograph*, ed. by Politechnika Koszalińska, Koszalin 2012, (211 pages).
- [18] Rokosz K., Hryniewicz T.: Pitting corrosion resistance of AISI 316L SS in Ringer's solution after magnetoelectrochemical polishing, *Corrosion (J. Sci. Eng.)*, 2010, 66 (3), 035004-1 to 11 (11 pages).
- [19] Hryniewicz T., Rokosz K.: Theoretical basics and practical aspects of corrosion (in Polish), ed. Politechnika Koszalin, Koszalin 2010 (112 pages).
- [20] Rokosz K., Hryniewicz T., Valíček J., Harničárová M., Vyležik M.: Nanoindentation measurements of AISI 316L biomaterial samples after annual immersion in Ringer's solution followed by electrochemical polishing in a magnetic field. *PAK (Measurement Automation and Monitoring)*, 2012, 58(5), 460-463.
- [21] Hryniewicz T., Rokosz K., Valíček J., Rokicki R.: Effect of magnetoelectropolishing on nanohardness and Young's modulus of titanium biomaterial, *Materials Letters*, 2012, 83, 69-72 DOI: 10.1016/j.matlet.2012.06.010.
- [22] Hryniewicz T., Konarski P., Rokicki R., Valíček J.: SIMS studies of titanium biomaterial hydrogenation after magnetoelectropolishing, *Surface & Coatings Technology*, 2012, 206, 4027-4031, DOI: 10.1016/j.surfcoat.2012.03.083.
- [23] Rokicki R., Hryniewicz T., Rokosz K.: Modifying Metallic Implants with Magnetoelectropolishing, *Medical Device and Diagnostic Industry*, 2008, 30(1), 102-111 (Invited paper).
- [24] Hryniewicz T., Rokicki R., Rokosz K.: Corrosion and surface characterization of titanium biomaterial after magnetoelectropolishing, *Surface & Coatings Technology*, 2009, 203(10-11), 1508-1515, DOI: 10.1016/j.surfcoat.2008.11.028.
- [25] Praisarnti C., Chang J.W.W., Cheung G.S.P.: Electropolishing enhances the resistance of nickel-titanium rotary files to corrosion-fatigue failure in hypochlorite, *J. Endodontics*, 2010, 36(8), 1354-1357.