XPS SURFACE CHARACTERIZATION OF AISI 316L (EN 1.1404) SS ELECTROCHEMICALLY POLISHED IN THE MIXTURE OF H_3PO_4, H_2SO_4 AND HNO_3 ACIDS

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Abstract

In the paper, the chemical composition of the passive surface layer obtained on AISI 316L (EN 1.4404) austenitic stainless steel after electrochemical treatment at the current density of 50 A/dm^2 in the mixture of three acids H_3PO_4, H_2SO_4 and HNO_3, is presented. The obtained results have shown that mainly $Fe_2(SO_4)_3$, Cr_2O_3, $Cr_2(SO_4)_3$, $CrPO_4$, CrO_3 as well as ions CrO_4^{2-}, $Cr_2O_7^{2-}$, were detected. In total, however, phosphates form the passive layer. The calculated Pitting Resistance Equivalent Number (PREN) for this surface layer is equal over 20.

Keywords: electrochemical treatment; AISI 316L stainless steel; H_3PO_4+H_2SO_4+HNO_3 mixture; XPS results

1. INTRODUCTION

Electropolishing is an important electrochemical treatment enabling to obtain the specific surface properties of many metals and alloys [1-8]. A significant modification of surface layer is achieved after magnetoelectropolishing, the process developed in recent years [9-25]. Stainless steels are the most popular materials undergoing continuous research and development concerning their surface properties and modification of surface layers formed after these electrochemical processes [2,3,9-22]. Moreover, besides corrosion resistance improvement [1-3, 8-13, 18-23] as the main effect of these processes, the modification and enhancement of mechanical properties has been also gained [24,25]. The electrolyte used in these processes consists mainly of orthophosphoric and sulfuric acids. This present study includes the mixture of three acids H_3PO_4, H_2SO_4 and HNO_3, used for electropolishing of austenitic AISI 316L stainless steel. After this process the XPS characterization of surface layer was done.

2. METHOD

2.1 Material

The AISI 316L (EN 1.440) stainless steel samples served for the study, with the material composition presented in the paper [11]. The samples were cut off a cold-rolled metal sheet after plate rolling so that the austenitic structure of the 316L SS was retained. They were prepared in the form of rectangular specimens of dimensions 5×30 mm cut off the metal sheet 1 mm thick.

2.2 Set up and parameters

The electrolytic treatment was performed at the current density of 50 ± 0.1 A/dm^2. The main elements of the set-up were: a processing cell, a dc power supply, the electrodes and connecting wiring. The studies were carried out in the electrolyte of initial temperature of 60 ± 2 °C. For each run, the electrolytic cell made of glass was used, containing up to 500 cm^3 of electrolyte of H_3PO_4, H_2SO_4, HNO_3 in proportions 1 : 1 : 1.

2.3 XPS studies

The XPS measurements were performed using the SCIENCE SES 2002 instrument with a monochromatic (Gammadata-Scienta) Al K(alpha) (*hv* = 1486.6 eV) X-ray source (18.7 mA, 13.02 kV). Scans analyses were carried out with an analysis area of 1×3 mm and a pass energy of 500 eV with the energy step of 0.2 eV and a step time 200 ms. The binding energy of the spectrometer has been calibrated by the position of the Fermi level on a clean metallic sample. The power supplies were stable and of high accuracy. The experiments were carried out in an ultra-high-vacuum system with a base pressure of about 6×10^{-10} Pa. The XPS spectra were recorded in normal emission. In view of optimizing the signal-to-noise ratio to about 3.2, one the XPS measurement cycle covered 10 sweeps. For the XPS analyses the CasaXPS 2.3.14 software with Shirley background type was applied [26].

3. RESULTS

In **Fig. 1**, the XPS results of iron (Fe 2p), chromium (Cr 2p), manganese (Mn 2p), molybdenum (Mo 3d, Mo 3s), nickel (Ni 2p), carbon (C 1s), oxygen (O 1s, O KLL), phosphorus (P 2s, P 2p), sulfur (S 2s, S 2p), nitrogen (N 1s) as well as calcium (Ca 2p) spectra of AISI 316L surface electrochemically treated at 50 A/dm^2 in the electrolyte consisting of H_3PO_4, H_2SO_4, HNO_3, are presented. Based on the results, it can be concluded, that the passive layer consists mainly of chromium, iron, molybdenum and oxygen bonded with phosphorus and/or sulfur, forming together most likely phosphates and sulfates. The carbon, a part of oxygen and part of nitrogen, should be treated as contaminations.

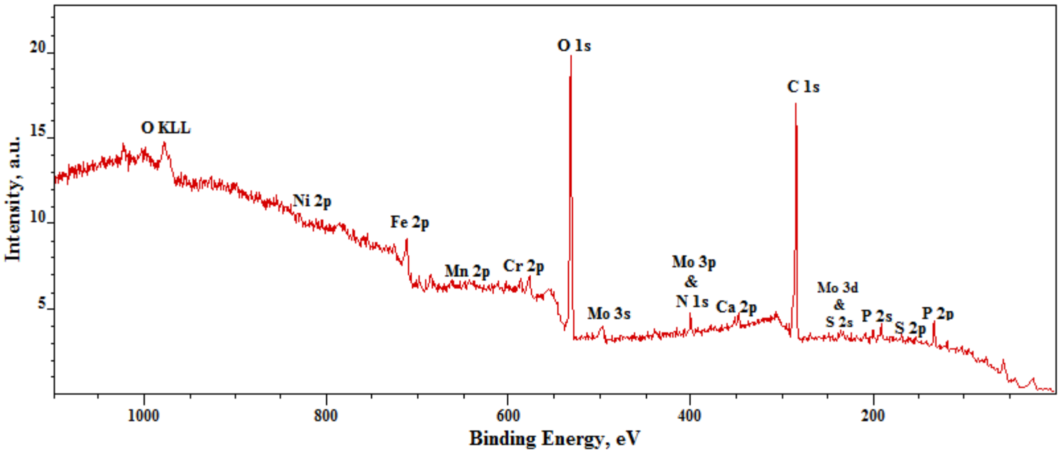


Fig. 1. XPS survey spectrum of both, passive carbon and contamination layers of AISI 316L surface electrochemically treated at 50 A/dm^2 in H_3PO_4, H_2SO_4, HNO_3 electrolyte mixture

Based on the survey XPS measurements, the high resolution XPS spectra were performed that is shown in **Fig. 2**. First analysis of the obtained spectra leads to the conclusion that there are mainly phosphates and sulfates in the surface passive layers, as indicated by the bond energies of phosphorus (P 2p) and sulfur (S 2p), which are equal to 133.6 eV and 169.2 eV, respectively. In the case of manganese (Mn 2p), the binding energy equaling to about 643 eV suggests a dominance of manganese compounds on the fourth state of oxidation. The maximum of binding energy for nickel (BE=856.3 eV) can be interpreted as $NiSO_4$ (856.8 eV [26-31]). More difficult situation is in the case of Mo 3d and N 1s overlapping spectra, where maximum binding energy at 400.5 eV was found, that regarding nitrogen can be interpreted as an organic contamination [26-31]. The main iron, chromium and molybdenum oxidation states, on the basis of main maximum signal in the spectrum, can suggest that Fe^{3+}, Cr^{3+}, Mo^{6+} ions were found in the passive surface layer. In order to propose specific chemical compounds which could be interpreted with a high probability, the fitting of high resolution Fe $2p_{3/2}$ and Cr $2p_{3/2}$ spectra were performed, as presented in **Figs. 3** and **4**. In **Table 1**, the chemical composition of passive layer formed on AISI 316L SS after the electrochemical treatment at 50 A/dm^2 in H_3PO_4, H_2SO_4, HNO_3 electrolyte, is given. There is visible the dominance of phosphorus (56.2 at%), which is most likely bonded with oxygen to form phosphates ($PO_4^{3\square}$). The Pitting Resistance Equivalent Number (PREN) for the obtained passive layer is above 20, that is a good achievement of the study.

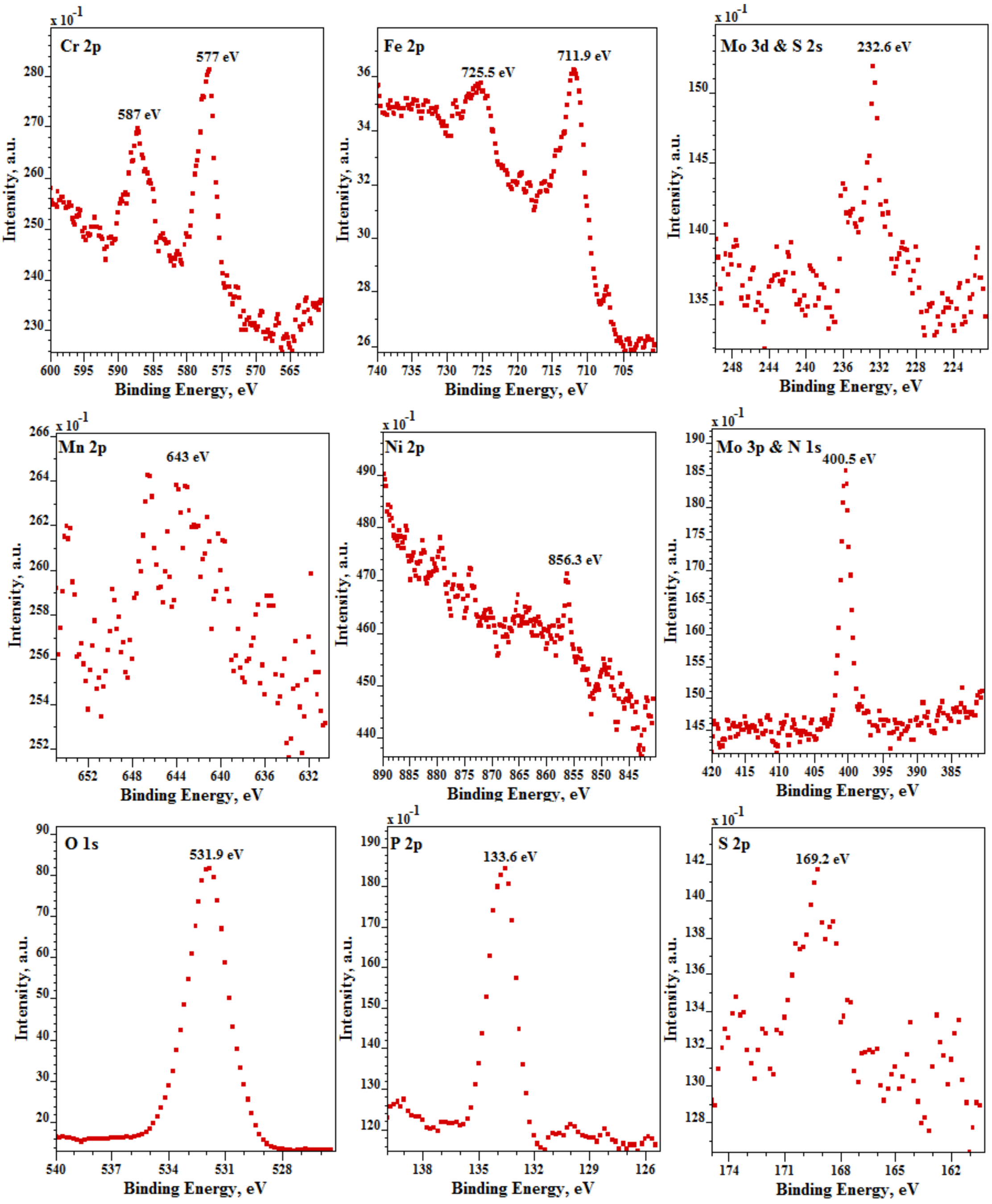
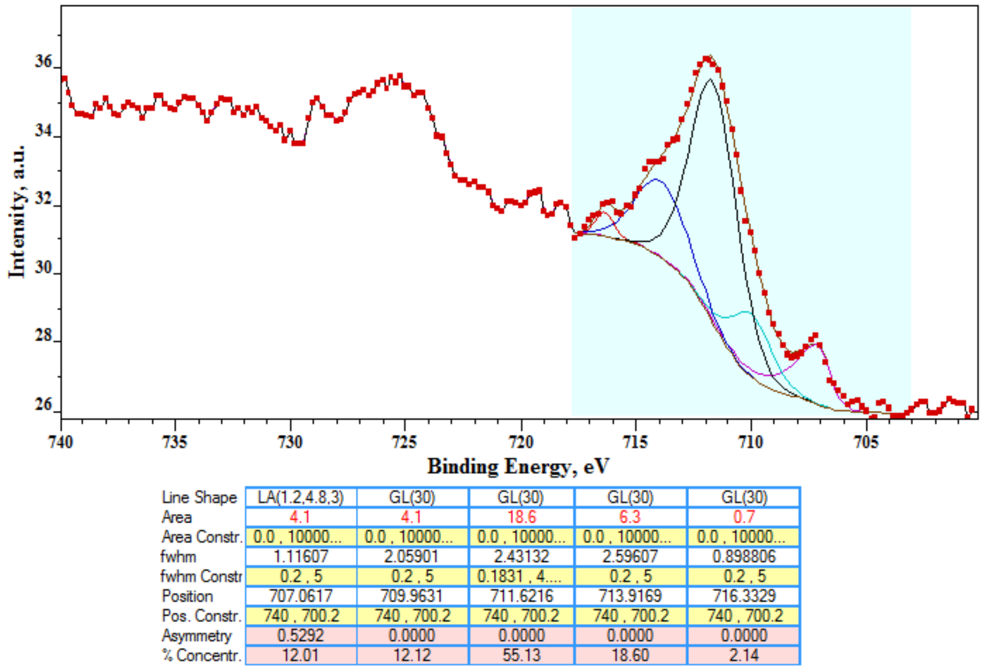


Fig. 2. High resolution XPS spectra of iron (Fe 2p), chromium (Cr 2p), molybdenum (Mo 3d), manganese (Mn 2p), nickel (Ni 2p), nitrogen (N 1s), oxygen (O1s), phosphorus (P 2p) and sulfur (S 2p) spectra of AISI 316L surface after electrochemical treatment at 50 A/dm^2 in H_3PO_4, H_2SO_4, HNO_3 electrolyte

Table 1 Chemical composition of the passive surface layer after electrochemical treatment at 50 A/dm² in H_3PO_4, H_2SO_4, HNO_3 electrolyte, in at%

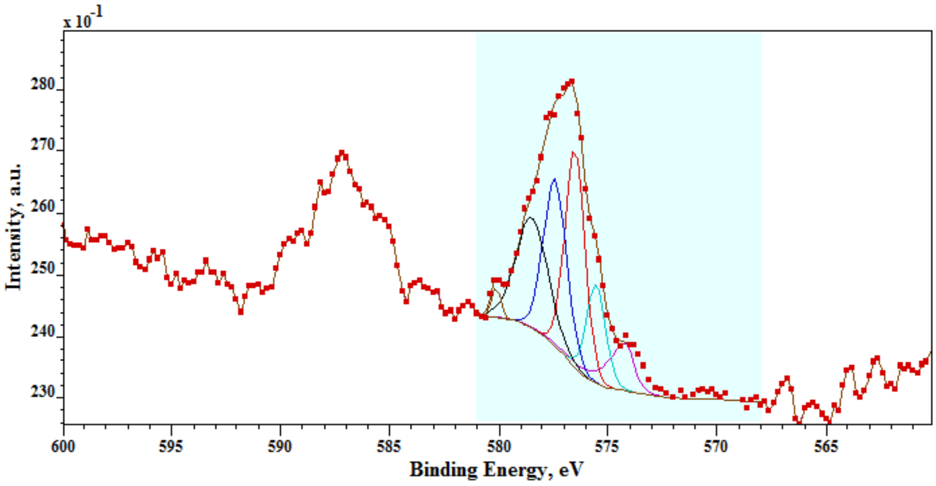
Fe	Cr	Mo	Ni	Mn	P	S
13.5	12.0	2.5	3.2	3.4	56.2	9.3

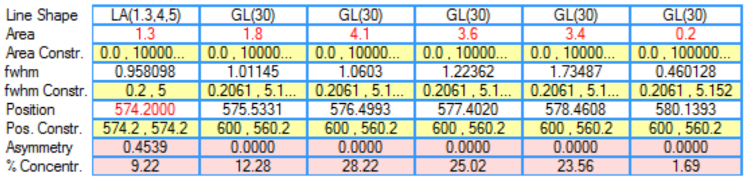


Line Shape	LA(1.2,4.8,3)	GL(30)	GL(30)	GL(30)	GL(30)
Area	4.1	4.1	18.6	6.3	0.7
Area Constr.	0.0 , 10000...	0.0 , 10000...	0.0 , 10000...	0.0 , 10000...	0.0 , 10000...
fwhm	1.11607	2.05901	2.43132	2.59607	0.898806
fwhm Constr	0.2 , 5	0.2 , 5	0.1831 , 4....	0.2 , 5	0.2 , 5
Position	707.0617	709.9631	711.6216	713.9169	716.3329
Pos. Constr.	740 , 700.2	740 , 700.2	740 , 700.2	740 , 700.2	740 , 700.2
Asymmetry	0.5292	0.0000	0.0000	0.0000	0.0000
% Concentr.	12.01	12.12	55.13	18.60	2.14

Fig. 3 Fitting of Fe $2p_{3/2}$ spectrum of AISI 316L passive layer formed after electrochemical treatment

In **Fig. 3**, the fitting of iron Fe $2p_{3/2}$ spectrum of AISI 316L passive layer formed after electrochemical treatment at 50 A/dm² in H_3PO_4, H_2SO_4, HNO_3 electrolyte, is presented. The peak at binding energy (BE) equaling 707 eV represents the metal iron (Fe^0). The peaks 709.96 eV and 716.3 eV can suggest, that the iron bonded with oxygen has a second oxidation state (Fe^{2+}). The next peak, *i.e.* 711.6 eV, which is a maximum of that spectrum, and 713.9 eV, can be interpreted most likely as $Fe_2(SO_4)_3$, that matches with the previous two peaks.





Line Shape	LA(1.3,4,5)	GL(30)	GL(30)	GL(30)	GL(30)	GL(30)
Area	1.3	1.8	4.1	3.6	3.4	0.2
Area Constr.	0.0 , 10000...	0.0 , 10000...	0.0 , 10000...	0.0 , 10000...	0.0 , 10000...	0.0 , 100000...
fwhm	0.958098	1.01145	1.0603	1.22362	1.73487	0.460128
fwhm Constr.	0.2 , 5	0.2061 , 5.1...	0.2061 , 5.1...	0.2061 , 5.1...	0.2061 , 5.1...	0.2061 , 5.152
Position	574.2000	575.5331	576.4993	577.4020	578.4608	580.1393
Pos. Constr.	574.2 , 574.2	600 , 560.2	600 , 560.2	600 , 560.2	600 , 560.2	600 , 560.2
Asymmetry	0.4539	0.0000	0.0000	0.0000	0.0000	0.0000
% Concentr.	9.22	12.28	28.22	25.02	23.56	1.69

Fig. 4. Fitting of Cr $2p_{3/2}$ spectrum of AISI 316L passive layer formed after electrochemical treatment

In **Fig. 4** the fitting of iron Cr $2p_{3/2}$ spectrum of AISI 316L passive layer formed after electrochemical treatment at 50 A/dm^2 in H_3PO_4, H_2SO_4, HNO_3 electrolyte, is presented. The peak at binding energy (BE) equaling 574.2 eV represents the metal chromium (Cr^0). The peaks 575.5 eV, 576.49 eV, 577.4 eV and 578.46 eV can suggest that the chromium bound with oxygen has a third oxidation state (Cr^{3+}). The most likely chromium compounds on the base of those peaks can be a mixture of Cr_2O_3, $Cr_2(SO_4)_3$ and $CrPO_4$. The next peak, *i.e.* 580.1 eV, can be interpreted as Cr^{6+} (CrO_3, CrO_4^{2-}, $Cr_2O_7^{2-}$).

4. CONCLUSIONS

After electrochemical treatment of austenitic AISI 316L (EN 1.4404) stainless steel at current density of 50 A/dm^2 in H_3PO_4, H_2SO_4, HNO_3 electrolyte iron, chromium, molybdenum, manganese, nickel, oxygen, phosphorus, sulfur, were detected in the passive layer. Additional elements found in the passive layer may be treated as contamination consisting of carbon, nitrogen, and calcium. On the basis of the binding energies of analyzed peaks it can be concluded that in the passive layer there is mainly a mixture of $Fe_2(SO_4)_3$, Cr_2O_3, $Cr_2(SO_4)_3$, $CrPO_4$, CrO_3 as well as ions CrO_4^{2-}, $Cr_2O_7^{2-}$. Pitting Resistance Equivalent Number (PREN) of the passive layer, consisting mainly of phosphates, equals over 20.

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REFERENCES

[1] DETTNER P. *Electrolytic and Chemical Polishing of Metals*. 2nd ed. Tel Aviv: Ordentlich Publishers, Express-SDAR Ltd., Needar Press, 1988, 340 p.

[2] BARON A. , SIMKA W., NAWRAT G., SZEWIECZEK D., KRZYZAK A. *Influence of electrolytic polishing on electrochemical behavior of austenitic steel*. J. Achiev. Mater. Manuf. Eng., 2006, 18(1–2), pp. 55–58.

[3] ROKOSZ K. *Polerowanie elektrochemiczne stali w polu magnetycznym (Electrochemical polishing of steel in the magnetic field) (in Polish).* Monograph no 219, Koszalin : Edit. Office of Politechnika Koszalińska, 2012, 211 pages.

[4] DIEPERS H., SCHMIDT O., MARTENS H., SUN F.S. *A new method of electropolishing niobium*. Phys. Letters, 1971, 37A (2), pp. 139–140.

[5] HRYNIEWICZ T., ROKOSZ K., ZSCHOMMLER S.H.R. *SEM/EDX and XPS studies of niobium after electropolishing.* Applied Surface Science, 2012, 263, pp. 357–361.

[6] 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]*. Applied Surface Science, 2013, 265, pp. 931-934.

[7] ROKICKI R., HRYNIEWICZ T. *Enhanced oxidation-dissolution theory of electropolishing*, Transactions of the Institute of Metal Finishing, 2012, 90(4), pp. 188-196.

[8] KUHN A. *The electropolishing of titanium and its alloys*, Metal Finish., 2006, 102(6), pp. 80–86.

[9] HRYNIEWICZ T., ROKICKI R., ROKOSZ K. *Magnetoelectropolishing Process Improves Characteristics of Finished Metal Surfaces.* Metal Finishing, 2006, 104(12), pp. 26-33.

[10] HRYNIEWICZ T. *Introduction to Surface Finishing of Metallic Biomaterials (in Polish)*, Koszalin: Edit. Office of Politechnika Koszalińska, 2007, 155 pages.

[11] HRYNIEWICZ T., ROKICKI R., ROKOSZ K. *Magnetoelectropolishing for metal surface modification.* Transactions of the Institute of Metal Finishing, 2007, 85(6), pp. 325-332.

[12] HRYNIEWICZ T., ROKICKI R., ROKOSZ K. *Corrosion Characteristics of Medical Grade AISI 316L Stainless Steel Surface after Electropolishing in a Magnetic Field.* CORROSION (The Journal of Science and Engineering), 2008, 64(8), pp. 660-665.

[13] HRYNIEWICZ T., ROKOSZ K., ROKICKI R. *Electrochemical and XPS Studies of AISI 316L Stainless Steel after Electropolishing in a Magnetic Field.* Corrosion Science, 2008, 50(9), pp. 2676-2681.

[14] HRYNIEWICZ T., ROKOSZ K., FILIPPI M. *Biomaterial Studies on AISI 316L Stainless Steel after Magnetoelectropolishing*. Materials, 2009, 2(1), pp. 129-145.

[15] HRYNIEWICZ T., ROKOSZ K. *Polarization Characteristics of Magnetoelectropolishing Stainless Steels*. Materials Chemistry and Physics, 2010, 122 (1), pp. 169-174.

[16] HRYNIEWICZ T., ROKOSZ K. *Analysis of XPS results of AISI 316L SS electropolished and magnetoelectropolished at varying conditions.* Surface and Coatings Technology, 2010, 204(16-17), pp. 2583-2592.

[17] 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 and Coatings Technology, 2011, 205, pp. 4228–4236.

[18] ROKOSZ K., HRYNIEWICZ T. *Pitting corrosion resistance of AISI 316L SS in Ringer's solution after magnetoelectrochemical polishing*. CORROSION – The Journal of Science and Engineering, 2010, 66(3), pp. 035004-1…11.

[19] ROKOSZ K., HRYNIEWICZ T. *Investigation of selected surface properties of AISI 316L SS after magnetoelectropolishing.* Materials Chemistry and Physics, 2010, 123, pp. 47-55.

[20] 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, 83(9), pp. 910-918.

[21] ROKOSZ K., HRYNIEWICZ T. *XPS measurements of LDX 2101 duplex steel surface after magnetoelectropolishing.* International Journal of Materials Research (former: Zeitschrift für Metallkunde), 2013, 104(12), pp. 1223-1232.

[22] ROKOSZ K., HRYNIEWICZ T. *Cr/Fe Ratio by XPS Spectra of Magnetoelectropolished AISI 316L SS using Linear, Shirley and Tougaard Method of Background Subtraction*. Advances in Materials Science, 2013, 13(1), pp. 11-20.

[23] HRYNIEWICZ T., ROKICKI R., ROKOSZ K. *Co-Cr alloy corrosion behaviour after electropolishing and “magnetoelectropolishing” treatments.* Materials Letters, 2008, 62, pp. 3073-3076.

[24] HRYNIEWICZ T., ROKOSZ K., VALÍČEK J., ROKICKI R. *Effect of magnetoelectropolishing on nanohardness and Young's modulus of titanium biomaterial.* Materials Letters, 2012, 83, pp. 69-72.

[25] HRYNIEWICZ T., ROKOSZ K., ROKICKI R., PRIMA F. *Nanoindentation and XPS studies of titanium TNZ alloy after electrochemical polishing in a magnetic field*, Materials, 2015, 8, pp. 205-215; DOI:10.3390/ma8010205

[26] CasaXPS 2.3.14 software, Casa Software Ltd., Devon, UK.

[27] WAGNER C.D., RIGGS W.M., DAVIS L.E., MOUELER J. E., MULLENBERG G.E. (Eds.). *Handbook of X-Ray Photoelectron Spectroscopy*, Minnesota: Perkin-Elmer, 1979, 190 pages.

[28] CRIST B. V. *PDF Handbook of The Elements and Native Oxides - The Elements and Native Oxides*, Mountain View, California: XPS International, LLC, 2005, 419 pages.

[29] BIESINGER M.C., BROWN C., MYCROFT J.R., DAWIDSON R.D., MCINTYRE N.S. *X-ray photoelectron spectroscopy studies of chromium compounds.* Surface and Interface Analysis, 2004, 36, pp. 1550-1563.

[30] GROSVENOR A., KOBE B. A., BIESINGER M.C., MCINTYRE N.S. *Investigation of multiplet splitting of Fe 2p XPS spectra and bonding in iron compounds.* Surface and Interface Analysis, 2004, 36(12), pp. 1564-1574.

[31] WAGNER C.D., NAUMKIN A.V., KRAUT-VASS A., ALLISON J.W., POWELL C.J., RUMBLE J.R.Jr. NIST Standard Reference Database 20, Version 3.4 (web version) (http:/srdata.nist.gov/xps/) 2003.