



XPS Analysis of nanolayers obtained on AISI 316L SS after Magneto-electropolishing

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ABSTRACT

In the present paper, the passive layers' chemical compositions of AISI 316L austenitic stainless steel samples after three treatments, such as mechanical/abrasive polishing (MP), standard electropolishing (EP) and magneto-electropolishing (MEP) are displayed. For the surface studies after each treatment, XPS analysis was performed. It has been noted that after MP treatment the Cr/Fe ratio in the passive layer is the lowest and equals to about 1, whereas after the MEP it is close to 3. Additionally, it has to be reported that the passive layers after MP consist mainly of Cr₂O₃ and Fe₂O₃, after a standard EP treatment – of CrOOH and FeOOH, and after MEP – of Cr(OH)₃ and FeOOH compounds. Concerning the surface layer compositions, in the passive layer formed after MP the detected iron consisted partly of Fe⁰ (46.5 at %) and partly of iron compounds Fe²⁺ and Fe³⁺ (53.5 at %), whereas the detected chromium consisted of Cr⁰ (16.5 at %) and mostly of chromium compounds Cr³⁺ (80.8 at%), with a small amount of Cr⁶⁺ (2.7 at %). In case of the nanolayer after EP treatment, the detected iron consisted of Fe⁰ (39.5 at %) and iron compounds Fe²⁺ and Fe³⁺ (60.5 at %), whereas the detected chromium consisted in a small amount of Cr⁰ (6.6 at %), and mostly chromium compounds Cr³⁺ (83.8 at %) with some Cr⁶⁺ (9.6 at %). The XPS analysis of nanolayer formed on AISI 316L after MEP indicates that the detected iron consisted partly of Fe⁰ (27.1 at %) and mostly of iron compounds Fe²⁺ and Fe³⁺ (72.9 at %) whereas the detected chromium contained Cr⁰ (18 at %) and chromium compounds of Cr³⁺ (76 at %) and Cr⁶⁺ (6 at %).

Keywords: XPS Analysis; Magneto-electropolishing (MEP); AISI 316L SS; Nanolayers

1. INTRODUCTION

Nowadays, the modification of surface layers of metals and alloys is equally important as finding of new materials. The mechanical and electrochemical properties of new surface layers, obtained under a variety of surface treatment processes, are totally different than those ones of matrices. The modification of surface layer up to a few millimeters is observed in the case of mechanical treatment such as burnishing rolling [1-11]. Generally the increase of hardness and toughness are gained after that operation. On the other hand, for specific medical applications, a porous surface layer enriched in a number of elements such as silver, copper, zinc, magnesium, calcium or phosphorus are expected to be inserted into the porous layer structure. In such cases, the Plasma Electrolytic Oxidation (PEO) known also as Micro Arc Oxidation [23] is used to obtain the coating of up to about ten micrometers thick [23-26]. Parts and devices coated with the porous layer during the PEO operations are prepared to be biocompatible and may serve for the metallic biomaterials. In case of smooth, inert and clean surfaces, the nano-layers may be formed by a standard electropolishing (EP) [26-34], magneto-electropolishing (MEP) [27-32, 36-50] and High-Current Density Electropolishing (HDEP) [51-54]. The standard EP has been known for about a century and developed continually. The MEP process has been under study for about a decade now, with a potential development and industrial use expected, whereas HDEP process may find its application for specific purposes.

The aim of this work is to present the composition of nanolayers formed on austenitic AISI 316L stainless steel after three basic surface treatments: MP, EP, and MEP. The surface studies were performed using X-ray Photoelectron Spectroscopy (XPS). The comparison of the results gained concerning the passive layer compositions, obtained after each of the processes is displayed.

2. METHOD

2. 1. Material

The new AISI 316L stainless steel samples after mechanical/abrasive polishing (MP), electrochemical polishing (EP) and magneto-electropolishing (MEP) for the XPS studies were used. The samples were prepared in the form of rectangular plates of dimensions $25 \times 5 \times 1$ mm. The chemical composition of the studied AISI 316L SS is shown in **Table 1**.

Table 1. Chemical composition of AISI 316L (wt %).

ELEMENT	wt %
Carbon	0.03
Silicon	0.64
Manganese	1.68
Phosphorus	0.024
Sufur	0.004

Chromium	17.07
Molybdenum	2.02
Nickel	10.26
Aluminum	0.011
Cobalt	0.04
Copper	0.19
Vanadium	0.11
Tungsten	0.01
Tin	0.009
Titanium	0.03
Nitrogen	0.0431
Boron	0.0048
Iron	balance

2. 2. Set up and parameters

The Standard Electropolishing (EP) and Magneto-electropolishing (MEP) were performed at the current densities of 50 A/dm^2 and 300 A/dm^2 , respectively, during 3 minutes of treatment. The studies were carried out in the electrolyte of initial temperature of $60 \pm 5 \text{ }^\circ\text{C}$. For the studies, the electrolyte composed of concentrated (85%) orthophosphoric and (95%) sulfuric acid in the proportion of 3 : 2, was used. For each run, the electrolytic cell made of glass was used, containing up to 500 ml of the electrolyte (**Fig. 1**).

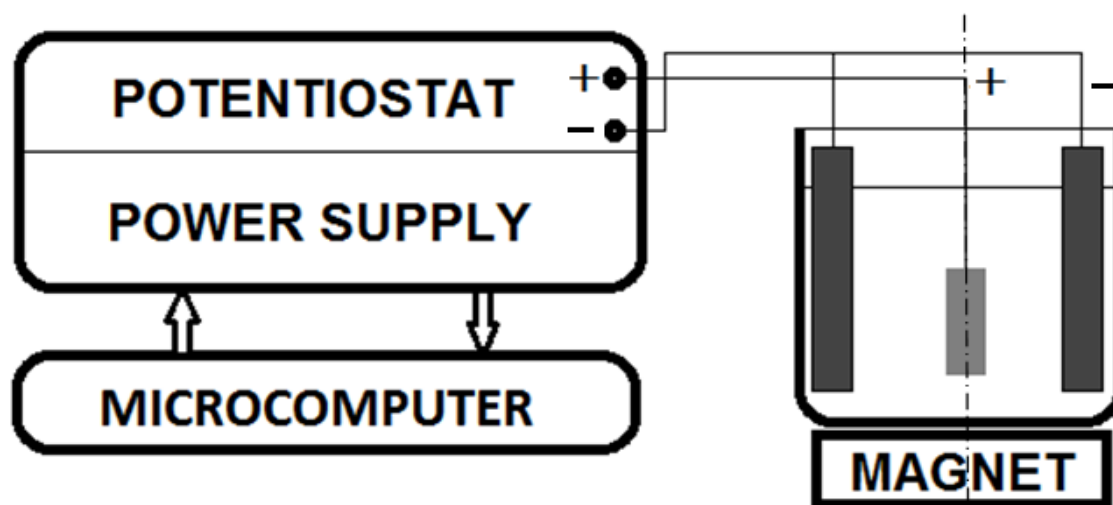


Fig. 1. Set up used for the electrochemical polishing processes: magnet used in case of magneto-electropolishing only.

2. 3. XPS studies

The X-ray photoelectron spectroscopy (XPS) measurements on AISI 316L SS samples surfaces were performed by means of SCIENCE SES 2002 instrument using a monochromatic (Gammadata-Scienta) Al K(alpha) ($h\nu = 1486.6$ 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 0.2 eV and 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 $6 \cdot 10^{-8}$ Pa. The XPS spectra were recorded in normal emission. For the XPS analyses the CasaXPS 2.3.14 software (Shirley background type) with the help of XPS tables [55-61] was used. All the binding energy values presented in this paper were charge corrected to C 1s at 284.8 eV. The XPS spectra analysis was carried out using Shirley background. For iron and chromium metal (Fe^0 , Cr^0) the non-symmetrical peaks LA(1.2,4.8,3) and LA(1.3,4,5) [59-61], respectively, were used. Iron and chromium compounds using GL(30) shape peaks were fitted with GL(p) being Gaussian/Lorentzian product formula where the mixing is determined by $m = p/100$, GL(100) is a pure Lorentzian while GL(0) is pure Gaussian [62].

3. RESULTS

In **Figures 2 and 3**, the high resolution XPS spectra of chromium (Cr 2p), iron (Fe 2p) and oxygen (O 1s) of passive layer obtained after mechanical polishing of AISI 316L SS are displayed. The presented spectra show that the formed passive layer in air atmosphere consists mainly of oxides and hydroxides of chromium and iron with the top nanolayer of organic contaminations that suggests the energies of the peaks O 1s equal to 530.2 eV (FWHM = 1.3), 531.6 eV (FWHM = 2), and 533 eV (FWHM = 2.1).

The detailed research and curve fitting, what is presented in **Figure 3**, explain that most likely the main iron and chromium compounds are Fe_2O_3 (BE = 710.9 eV, FWHM = 3.9) and Cr_2O_3 (BE = 576.7 eV, FWHM = 2.8). Additionally, the small peak of chromium Cr^{6+} detected in the binding energy equals 579 eV. The detected iron from about 10 nm is composed of iron metal Fe^0 (46.5 at%) and iron compounds Fe^{2+} and Fe^{3+} (53.5 at%). In case of chromium, the XPS spectra represent Cr^0 , Cr^{3+} and Cr^{6+} amounting for 16.5 at%, 80.8 at% and 2.7 at %, respectively.

In **Figure 4**, the high resolution XPS spectra of chromium (Cr 2p), iron (Fe 2p) and oxygen (O 1s) of passive layer obtained after standard electrochemical polishing (EP) of AISI 316L SS are presented. The bonding energy of O 1s equalling to 531.7 eV suggests that most likely the passive layer consists of chromium-iron phosphates within oxides and hydroxides as well as organic contaminations.

The fitting of Cr 2p_{3/2} and Fe 2p_{3/2} spectra, that is visible in **Figure 5**, shows that most likely the main iron and chromium compounds are FeOOH (BE = 711.2 eV, FWHM = 4.3) and CrOOH (BE = 577 eV, FWHM = 2.7), respectively. Additionally, the small peak of chromium Cr^{6+} in the binding energy equalling to 579 eV was detected. The detected iron from about 10 nm, containing of iron metal Fe^0 (39.5 at%) and iron compounds Fe^{2+} and Fe^{3+} (60.5 at%), is also visible. In case of chromium, the metallic Cr^0 , and ionic Cr^{3+} and Cr^{6+} represent the amounts of 6.6 at%, 83.8 at% and 9.6 at%, respectively.

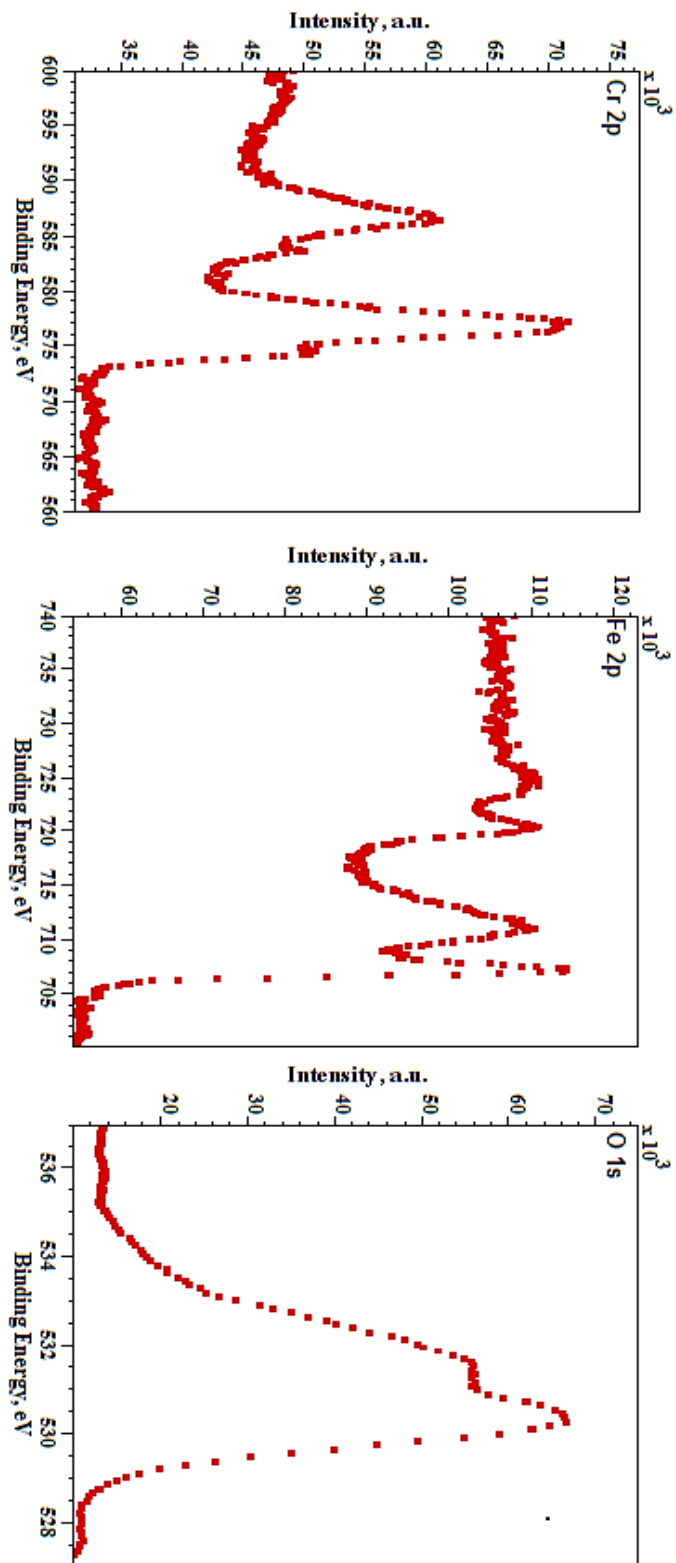


Fig. 2. XPS spectra of chromium Cr 2p, iron Fe 2p and oxygen O 1s of passive layer obtained after mechanical/abrasive polishing of AISI 316L SS

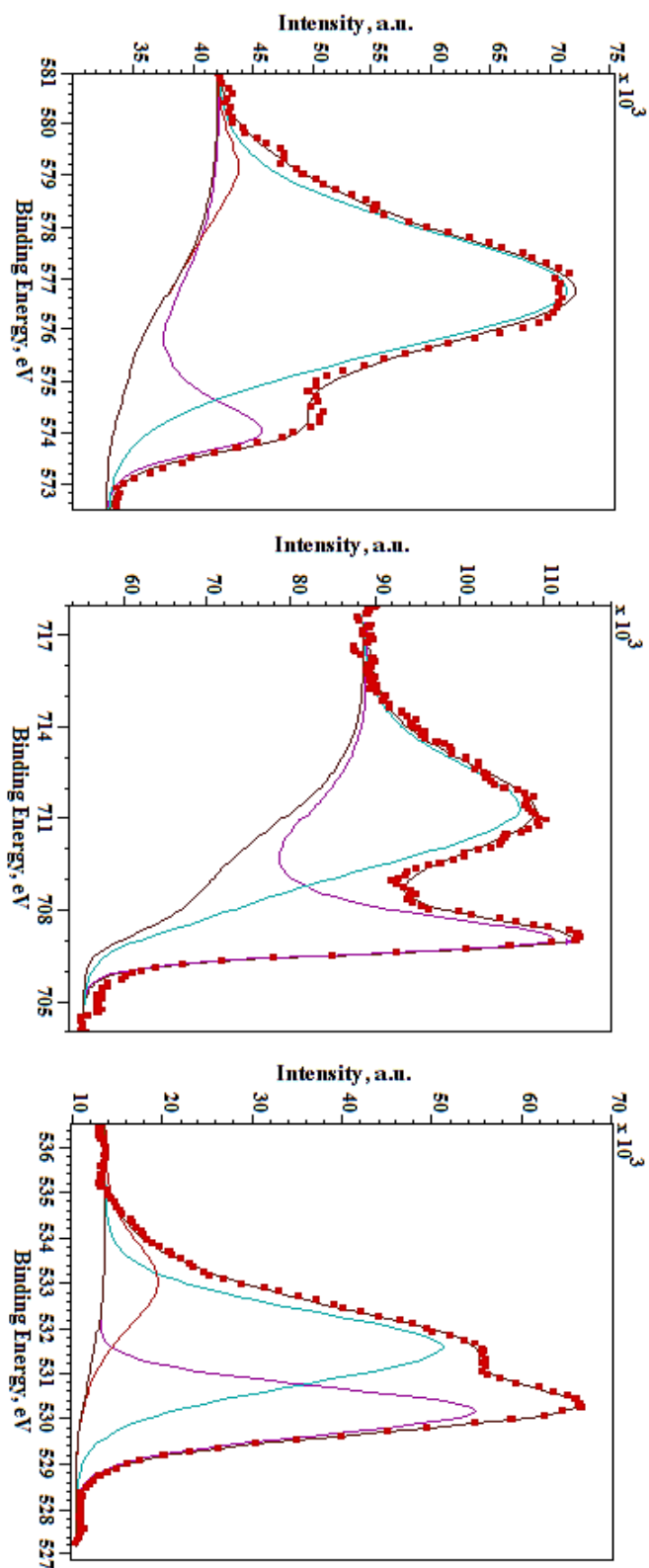


Fig. 3. Fitting of XPS spectra of chromium Cr 2p and iron Fe 2p of passive layer obtained o after mechanical/abrasive polishing of AISI 316L SS

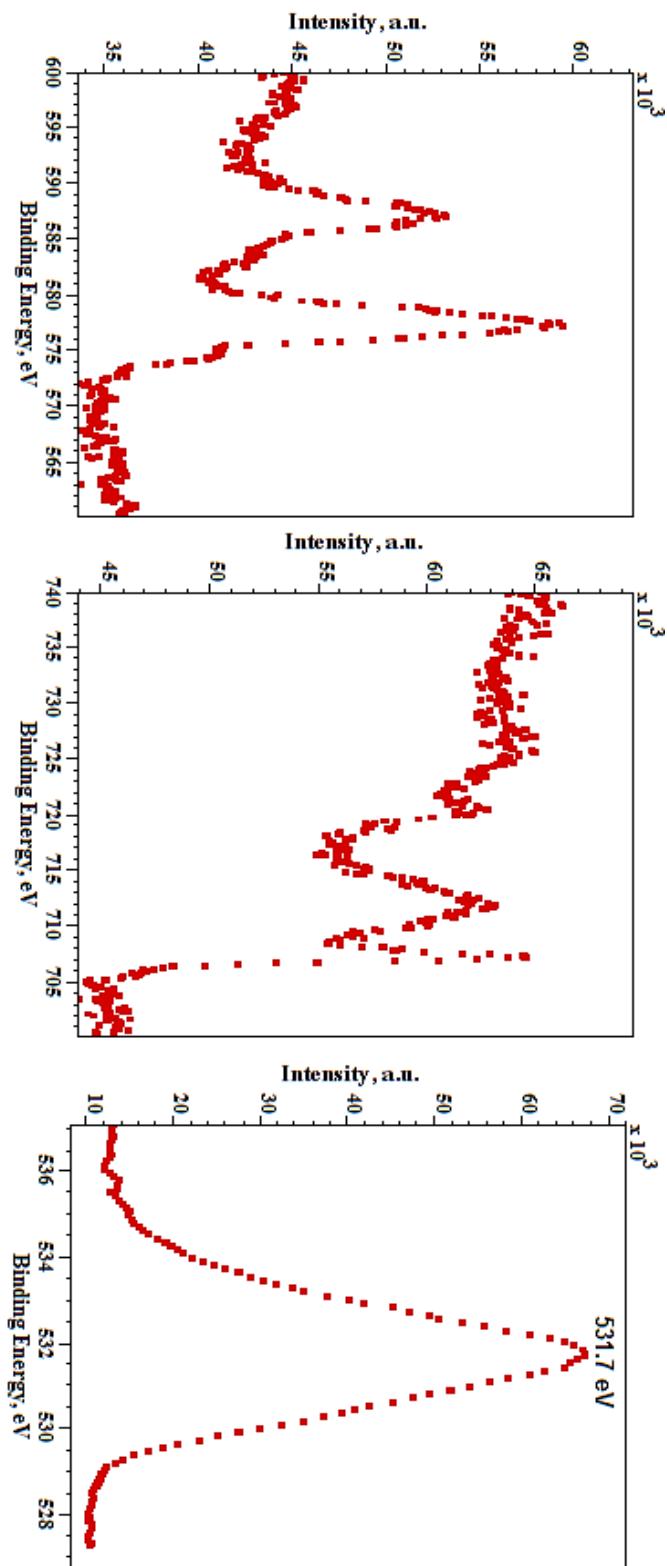


Fig. 4. XPS spectra of chromium Cr 2p, iron Fe 2p and oxygen O 1s of passive layer obtained on AISI 316L SS after standard electropolishing at current density of 50 A/dm²

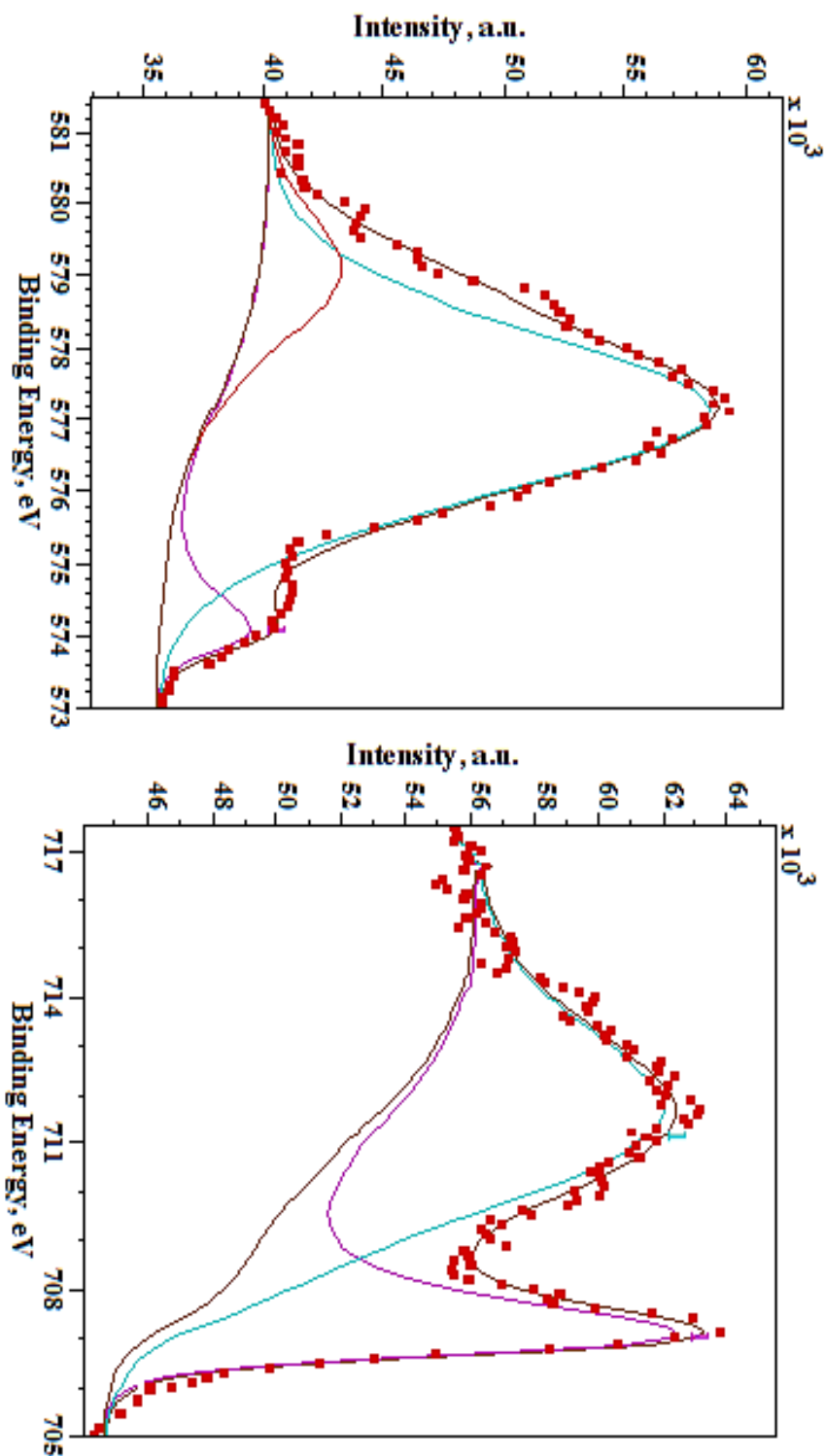


Fig. 5. Fitting of XPS spectra of chromium Cr 2p and iron Fe 2p of passive layer obtained on AISI 316L SS after standard electropolishing at current density of 50 A/dm²

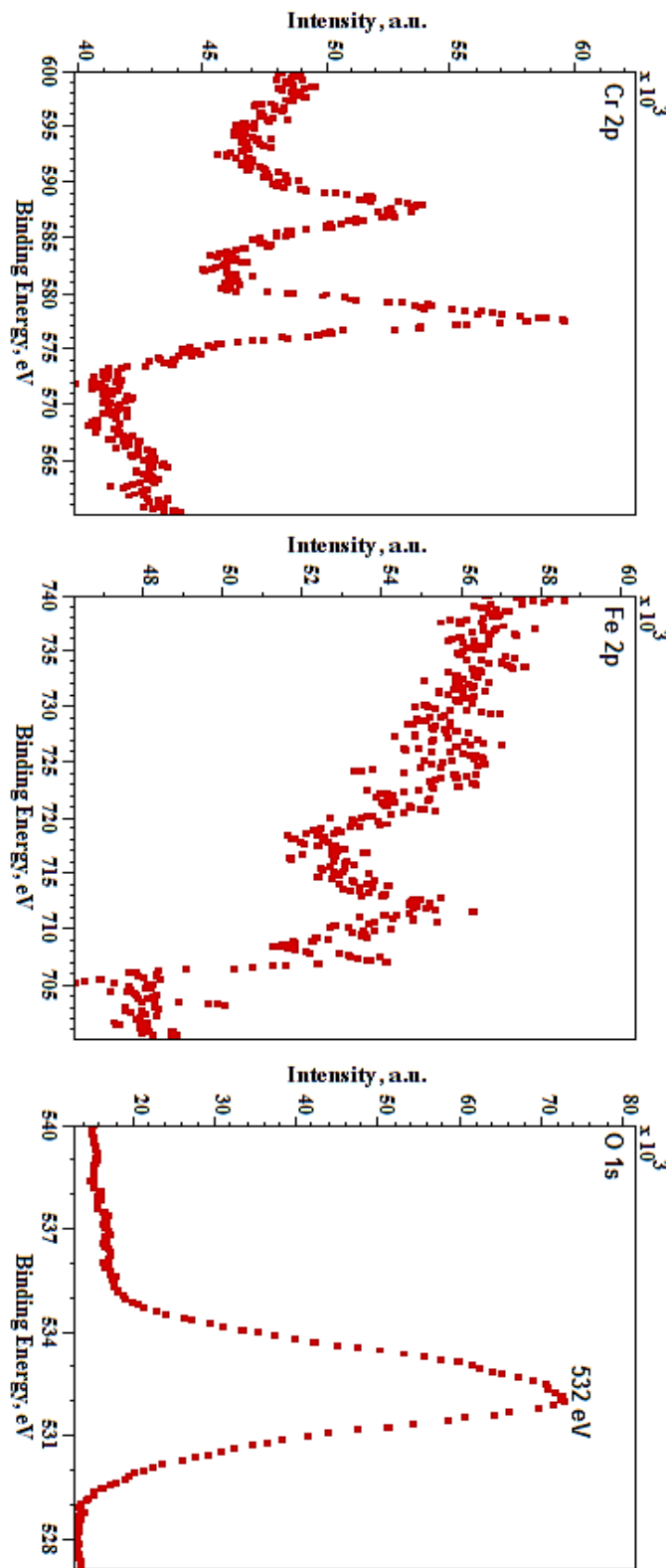


Fig. 6. XPS spectra of chromium Cr 2p, iron Fe 2p and oxygen O 1s of passive layer obtained on AISI 316L SS after magnetoelectropolishing at current density of 300 A/dm²

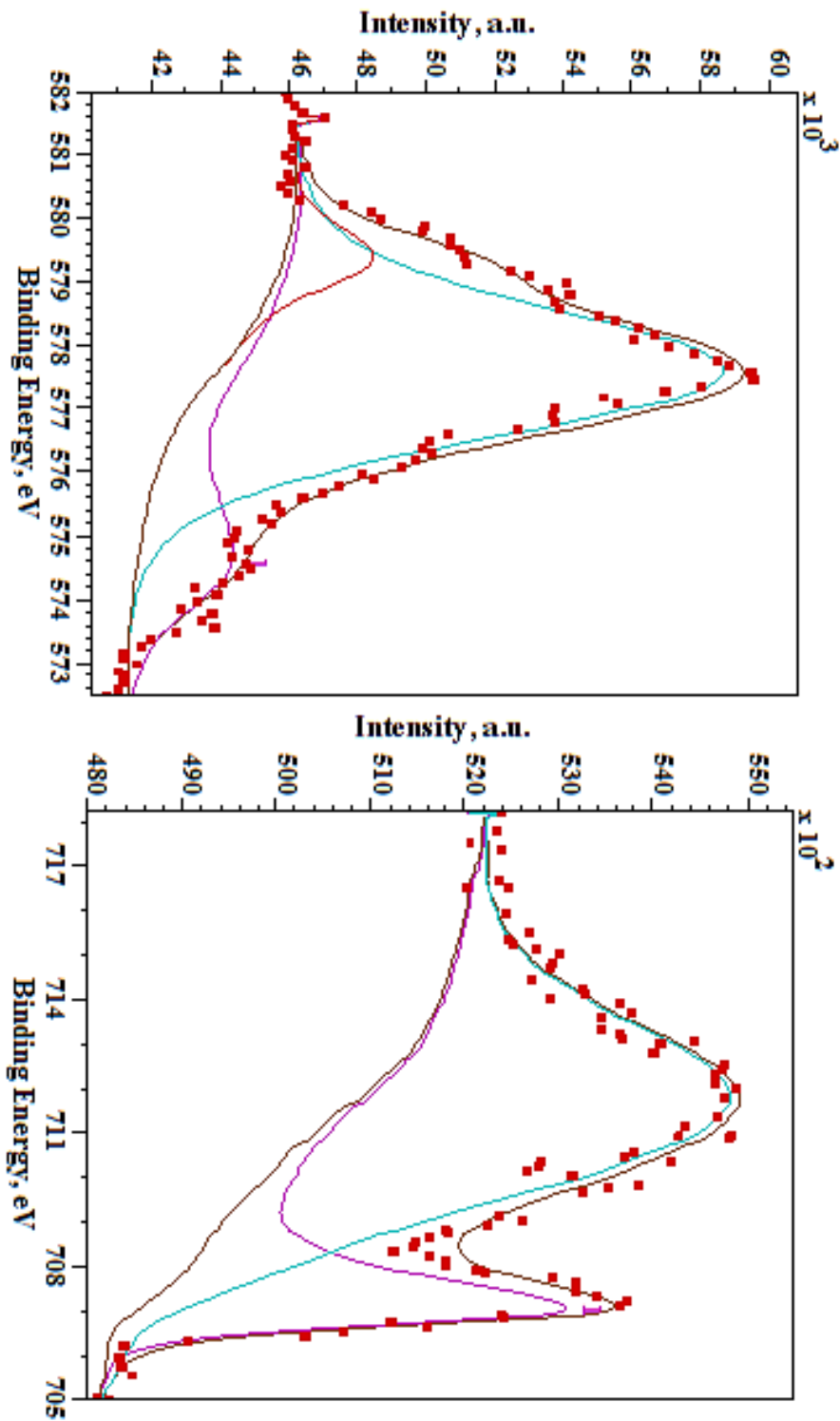


Fig. 7. Fitting of XPS spectra of chromium Cr 2p and iron Fe 2p of passive layer obtained on AISI 316L SS after magnetoelectropolishing at current density of 300 A/dm^2

In **Figure 6**, the high resolution XPS spectra of chromium (Cr 2p), iron (Fe 2p) and oxygen (O 1s) of passive layer obtained after standard electrochemical polishing (EP) of AISI 316L SS, are presented. The bonding energy of O 1s equaling 532 eV suggests that most likely the passive layer consists of chromium-iron phosphates within oxides and hydroxides as well as organic contaminations.

The fitting of Cr 2p_{3/2} and Fe 2p_{3/2} spectra, that is visible in **Figure 7**, shows that most likely the main iron and chromium compounds are FeOOH (BE = 711.3 eV, FWHM = 4.6) and Cr(OH)₃ (BE = 577.5 eV, FWHM = 2.4), respectively. Additionally, the small peak of chromium Cr⁶⁺ was detected in binding energy equaling to 579 eV. The detected iron from about 10 nm, containing of iron metal Fe⁰ (27.1 at%) and iron compounds Fe²⁺ and Fe³⁺ (72.9 at%), are visible. In case of chromium, the Cr⁰, Cr³⁺ and Cr⁶⁺ represent the amounts of 18 at%, 76 at% and 6 at%, respectively.

In **Figure 8**, a bar graph with chromium compounds to iron compounds (Cr/Fe) ratio is presented. The smallest Cr/Fe ratio, close to 1, after mechanical polishing was found, whereas the highest one, which was close to 3, after MEP was registered. It may be explained by the influence of magnetic field on austenitic stainless steel, which is paramagnetic material within the ferromagnetic iron compounds. The electrochemical treatment in the magnetic field allowed for an efficient formation of the passive layer enrichment in chromium compounds.

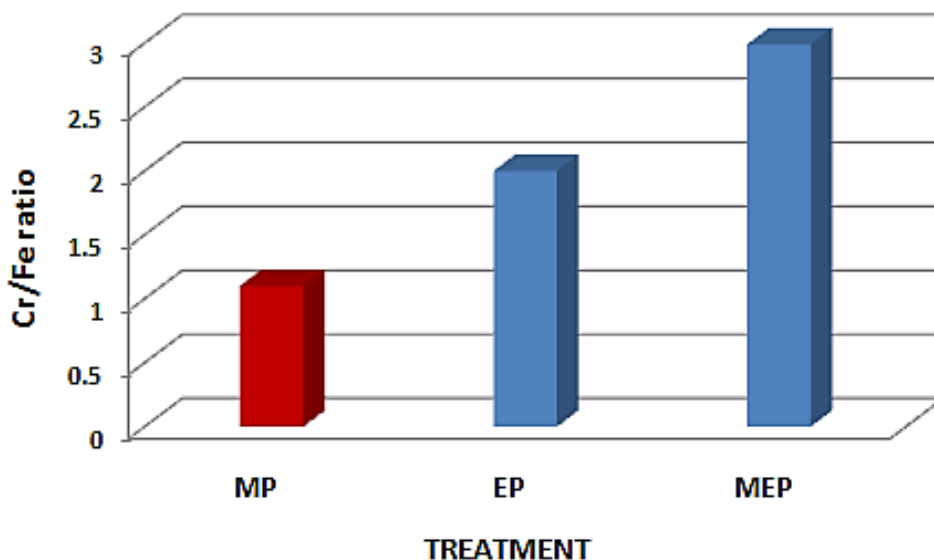


Fig. 8. The effect of type of treatment (MP, EP, MEP) on the chromium-to-iron ratio in the 316L SS nanolayer.

4. CONCLUSIONS

The following conclusions may be drawn after the research on XPS analysis of AISI 316L SS carried out:

- the lowest Cr/Fe ratio, close to 1, was noted after abrasive MP treatment
- the highest Cr/Fe ratio, close to 3, was obtained after MEP

- the passive layer after MP consists mainly of Cr_2O_3 and Fe_2O_3
- the passive layer after EP consists mainly of CrOOH and FeOOH
- the passive layer after MEP consists mainly of $\text{Cr}(\text{OH})_3$ and FeOOH
- in passive layer formed after MP the detected iron consisted of Fe^0 (46.5 at %) and iron compounds Fe^{2+} and Fe^{3+} (53.5 at %)
- in passive layer formed after EP the detected iron consisted of slightly lower amount of Fe^0 (39.5 at %) and a higher amount of iron compounds Fe^{2+} and Fe^{3+} (60.5 at %)
- in passive layer formed after MEP the detected iron consisted of the lowest Fe^0 (27.1 at %) and much higher iron amount of compounds Fe^{2+} and Fe^{3+} (72.9 at %)
- in passive layer formed after MP the detected chromium consisted of Cr^0 (16.5 at %) and chromium compounds Cr^{3+} (80.8 at %) and Cr^{6+} (2.7 at %)
- in passive layer formed after EP the detected chromium consisted of much lower amount of Cr^0 (6.6 at %) and similar amount of chromium compounds Cr^{3+} (83.8 at %) but higher Cr^{6+} (9.6 at %)
- in passive layer formed after MEP the detected chromium consisted of a little higher Cr^0 (18 at %) and a little lower chromium amount of compounds Cr^{3+} (76 at %) and Cr^{6+} (6 at %).

ACKNOWLEDGMENTS

The BerlinerLuft company, especially Bogusław Lackowski, PhD, is acknowledged for delivering samples for the studies.

Authors of the paper highly appreciate of the XPS apparatus made available by the NTNU Trondheim University, Norway. Special thanks are directed to Professor Steinar Raaen of the Institute of Physics, NTNU Trondheim, for his valuable instructions concerning XPS measurements.

Professor Dr Gregor Mori of the Institute of Schadensanalytik, Montanuniversität Leoben, Austria, is greatly acknowledged for getting chemical analysis of the AISI 316L austenitic stainless steel samples.

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(Received 15 January 2016; accepted 28 January 2016)