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XPS measurements of AISI 430 SS surface after electropolishing operations in a transpassive region of polarisation characteristics

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1. Introduction

The process of electropolishing is the controlled anodic dissolution of metals which improves their surface properties. Electropolishing is often referred to as electrochemical polishing, "reverse plating" or "super passivation" process. Commercial applications for electropolishing have been in use since the early 1950's [1]. Conventional mechanical finishing systems can smear, bend, stress or even fracture the crystalline metal surface to achieve smoothness or brightness. Electropolishing offers the advantage of removing metal from the surface producing a unidirectional pattern that is both stress and occlusion free, microscopically smooth and often highly reflective. Additionally, improved corrosion resistance and passivity is achieved on stainless steel [2].

Stainless steels are defined as iron based alloys containing at least 10.5 % chromium and a maximum of 1.2 % carbon. The ferritic stainless steel type AISI 430 (X6Cr17, 1.4016, H17) is very often used in automotive and architectural trim, vaults, heat exchangers, scientific apparatus and vending machine components. Its forming characteristics are similar to those of very popular industrial austenitic AISI 304 stainless steel without the same degree of ductility. Therefore, the ferritic stainless steel is an attractive alternative to the most often adopted austenitic stainless steel [3].

The authors of this paper intend to reveal the influence of different polishing methods on formation of the passive/oxide layer on the stainless steel surface. In the literature, it is very hard to find any remark about the surface of electrochemical polishing of the AISI 430 SS. From the own experience the authors can conclude that roughness [4] properties after this electropolishing are not very satisfactory, as in case of austenitic stainless steels [5-6], but the Cr/Fe ratio in passive layer formed after the electrochemical treatment is quite good and can be used for industrial applications.

2. Experimental set-up

2.1. Material used for experiments

Ferritic stainless steel type AISI 430 (16.3 % chromium, 0.2 % nickel, 0.45 % manganese, 0.04 % carbon, 0.4 % silicon and balance of iron) was used for the investigation. All samples of dimensions 30 × 5 × 1.22 mm were cleaned by C₂H₅OH. After cleaning the samples were treated by three different procedures: standard electrochemical polishing (EP), standard electrochemical polishing with mixing (MIX) and electrochemical polishing in a magnetic field, named magneto-electropolishing (MEP) [7]. The electrochemical set-up is shown in Fig. 1.

Abstract

The paper presents results of measuring the chemical composition of the passive film formed on the ferritic steel AISI 430 SS after mechanical and electrochemical treatments. XPS (X-ray Photoelectron Spectroscopy) measurements were taken to obtain the chemical composition of the passive film on AISI 430 SS. The study results show that the ratio of the chromium compounds to iron compounds (Cr/Fe) in the passive film varies depend on the kind of surface treatment, starting from 0.4 after abrasive polishing (MP), up to 2.59 after standard electropolishing (EP) operation. The results of Cr/Fe ratio after electropolishing with electrolyte stirring (MIX) and these after magneto-electropolishing (MEP) are between the two values. It was found that after electrochemical treatments the main compounds in the passive film consisted of Fe₂O₃, FeOOH, Cr₂O₃, Cr(OH)₃.

Keywords: XPS measurements, Ferritic stainless steel, Magneto-electropolishing.

Badania XPS powierzchni stali ferrytycznej AISI 430 po operacjach elektropolerowania w transpasywnym obszarze charakterystyk polaryzacyjnych

Streszczenie

W artykule przedstawiono wyniki pomiarów składu chemicznego warstwy pasywnej wytworzonej na stali ferrytycznej AISI 430 po polerowaniu ściernym oraz polerowaniu elektrolitycznym. Skład chemiczny warstwy wierzchniej stali AISI 430 zbadano przy użyciu fotoelektronowej spektroskopii promieniami Roentgena (XPS). Wyniki badań pokazują, że stosunek zawartości związków chromu do związków żelaza (Cr/Fe) w warstwie pasywnej zmienia się w zależności od rodzaju obróbki powierzchniowej, począwszy od 0.4 po polerowaniu ściernym (MP), do 2,59 po standardowym polerowaniu elektrolitycznym (EP). Wyniki Cr/Fe po elektropolerowaniu z mieszaniem (MIX) i po magnetoelektropolerowaniu (MEP) mieszczą się pomiędzy tymi wartościami. Na podstawie badań XPS stwierdzono, że warstwa wierzchnia stali składa się ze związków Fe₂O₃, FeOOH, Cr₂O₃, Cr(OH)₃.

Słowa kluczowe: pomiary XPS, ferrytyczna stal AISI 430, magneto-elektropolerowanie MEP.



Fig. 1. Setup used for electrochemical polishing, A – potentiostat, B – heating system, C – electrochemical cell, D – computer with software, E – digital multimeter
Rys. 1. Stanowisko do polerowania elektrolitycznego: A – potencjostat, B – system ogrzewania, C – elektrolizer, D – komputer z oprogramowaniem, E – multimetr cyfrowy

All the electrochemical treatments (EP, MIX, MEP) were conducted at $(65 \pm 5)^\circ\text{C}$ in phosphoric-sulfuric mixed acids ($\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4$) with volume ratio of 4:6, at current densities of approximately $(65 \pm 5) \text{ A/dm}^2$ in 3 minutes. Stainless steel cathode plates were immersed into the bath and installed to the negative side of the power source/potentiostat (Fig. 2). The steel sample was fixed to a rack. That rack was connected to the positive side of the power source/potentiostat. In case of electrochemical polishing in the magnetic field (MEP) the experiments were conducted at the field intensity of $B = 350 \text{ mT}$.

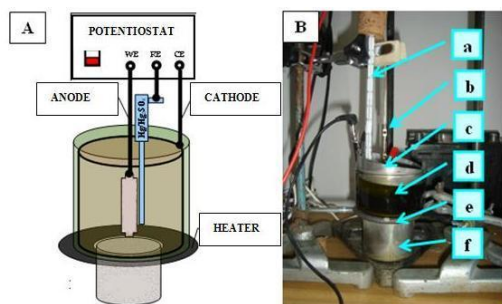


Fig. 2. Setup used for magnetoelectropolishing MEP: A – scheme of connections, B – photo (a – thermometer, b – anode, c – cathode, d – electrochemical cell, e – heater, f – neodymium magnet)
Rys. 2. Stanowisko do magnetoektopolerowania MEP: A – schemat połączeń, B – zdjęcie stanowiska (a – termometr, b – anoda, c – katoda, d – elektrolizer, e – grzałka, f – magnes neodymowy)

2.2. Set up for XPS measurements

In XPS analysis the sample is placed in an ultrahigh vacuum environment and exposed to a low-energy X-ray source. The X-ray excitation causes the emission of photoelectrons from the atomic shells of the elements present on the surface. The energy of these electrons is characteristic of the element from which they are emitted. The area under peaks in the spectrum is a measure of the relative amount of each element present, and the shape and position of the peaks reflect the chemical state for each element [8-11].

The XPS experiments were performed in an ultra-high-vacuum system with a base pressure of about 10^{-8} Pa . XPS measurements were made using an SES2002 electron energy analyzer in conjunction with a monochromatized Al $K\alpha$ ($h\nu = 1486.6 \text{ eV}$) X-ray source (GammaData-Scientia). A total resolution of about 0.7 eV was obtained for the presented spectra. Binding energies (BE) for XPS survey spectra were in the range (0-1100) eV, for XPS spectra for: iron Fe2p in the range (700-730) eV; chromium Cr2p in range (560-600) eV; oxygen O1s in the range (525-545) eV; phosphorus P2p in the range (125-140) eV; sulfur S2p in the range (160-175) eV. The spectra were recorded in normal emission (Fig. 3). The binding energy of the spectrometer is 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. The authors used CasaXPS Software for evaluation of XPS spectra.

3. Results of the study

In Fig. 3 there are shown XPS survey spectra of samples after mechanical polishing (MP), electrochemical polishing (EP), electrochemical polishing with stirring (MIX) and magnetoelectropolishing (MEP). On the mechanically treated surface there are visible peaks of iron (Fe2p), oxygen (O1s) and carbon (C1s). On all the electrochemically treated samples (EP, MIX, MEP) there are the peaks of phosphorus and/or sulfur compounds visible in addition to oxygen, iron and carbon.

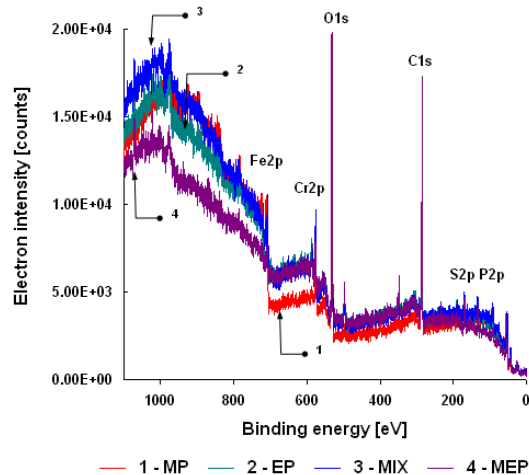


Fig. 3. XPS survey spectra of AISI 430 SS after abrasive/mechanical polishing (MP), standard electrochemical polishing (EP), standard electrochemical polishing with stirring (MIX), magnetoelectropolishing (MEP)
Rys. 3. Widma XPS stali ferrytycznej AISI 430 po mechanicznym polerowaniu ściernym (MP), standardowym elektropolerowaniu bez mieszania (EP), elektropolerowaniu z mieszaniem (MIX), magnetoektopolerowaniu (MEP)

In Figs. 4-8 there are visible XPS spectra for: iron Fe 2p (Fig. 4), chromium Cr2p (Fig. 5), phosphorus P 2p (Fig. 6), sulfur S 2p (Fig. 7), oxygen O1s (Fig. 8). From the curves (Figs. 4-8) it can be seen that after mechanical/abrasive polishing on the surface there are a lot of oxide- and hydroxide compounds, and there are no phosphorus or sulfur compounds. After all electrochemical treatments there are visible peaks of phosphorus- and sulfur-compounds especially in combination with iron and chromium.

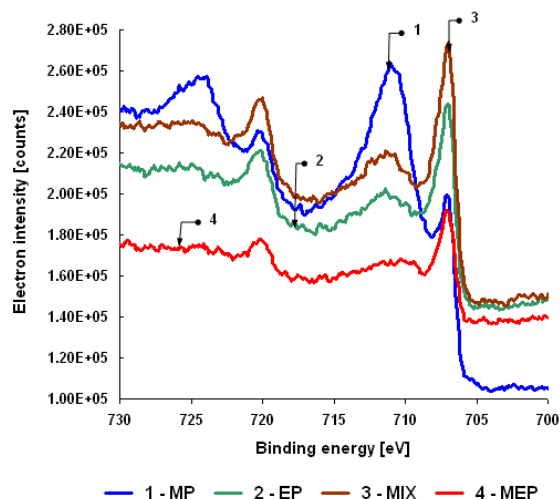


Fig. 4. XPS spectra of Fe 2p of AISI 430 SS after abrasive/mechanical polishing (MP), standard electrochemical polishing (EP), standard electrochemical polishing with stirring (MIX), magnetoelectropolishing (MEP)
Rys. 4. Widma XPS dla żelaza Fe 2p w stali AISI 430 po mechanicznym polerowaniu ściernym (MP), standardowym elektropolerowaniu bez mieszania (EP), elektropolerowaniu z mieszaniem (MIX), magnetoektopolerowaniu (MEP)

In Fig. 4, there are shown XPS spectra of Fe2p of AISI 430 SS after abrasive/mechanical polishing (MP), standard electrochemical polishing (EP), standard electrochemical polishing with stirring (MIX), and magnetoelectropolishing (MEP). On both surfaces mechanically (MP) and electrochemically (EP, MIX, MEP) polished a peak of metal iron ($BE = 707$ eV) is clearly visible.

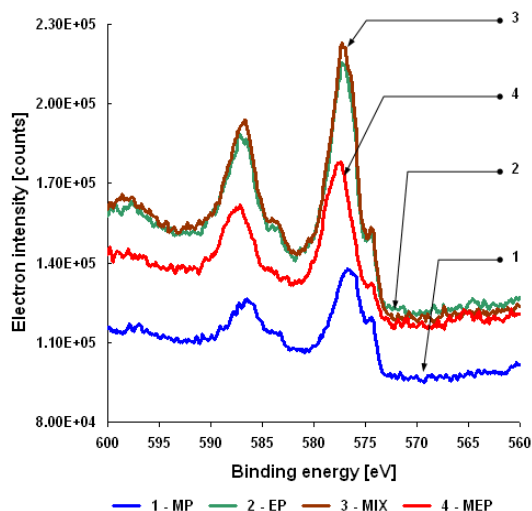


Fig. 5. XPS spectra of Cr 2p of AISI 430 SS after abrasive/mechanical polishing (MP), standard electrochemical polishing (EP), standard electrochemical polishing with stirring (MIX), magnetoelectropolishing (MEP)

Rys. 5. Widma XPS dla chromu Cr 2p w stali AISI 430 po mechanicznym polerowaniu ściernym (MP), standardowym elektropolerowaniu bez mieszania (EP), elektropolerowaniu z mieszaniem (MIX), magnetoelktropolerowaniu (MEP)

For the mechanically polished specimen the most intensive peak at binding energy 710.9 eV corresponds to Fe_2O_3 and for the standard electrochemical polishing (EP) the binding energy 711.3 eV corresponds to $FeOOH$. For the standard electrochemical polishing with stirring (MIX) the binding energies 710.8 eV, 711.5 eV and 712.1 eV correspond to the following compounds: Fe_2O_3 , $FeOOH$ and $Fe_x(SO_4)_y$, respectively; and for magnetoelectropolishing (MEP) the binding energies 709.4 eV, 710.2 eV, 711.4 eV corresponding to FeO , Fe_3O_4 , $FeOOH$ can be noticed.

In Fig. 5, there are shown XPS spectra of Cr2p of AISI 430 SS after abrasive/mechanical polishing (MP), standard electrochemical polishing (EP), standard electrochemical polishing with stirring (MIX), and magnetoelectropolishing (MEP). On both surfaces, mechanically (MP) and electrochemically polished (EP, MIX, MEP) a peak of chromium oxide Cr_2O_3 ($BE = 576.9$ eV), and a peak of metal chromium ($BE = 574.4$ eV) are shown. However, it should be noted that in the case of abrasive treatment there is more metallic chromium.

One can easily calculate that Cr/Fe ratio of the steel surface after abrasive polishing (MP) equals approximately 0.4, whereas after the standard electrochemical polishing (EP) it equals approximately 2.25. After the magnetoelectropolishing (MEP) operation the Cr/Fe is very low and equals 0.7, and after the standard electrochemical polishing with stirring (MIX), the ratio equals 0.96, meaning this value of Cr/Fe is between those measured after EP and MEP.

It is probably connected with the ferritic stainless steel feature which as a ferromagnetic undergoes magnetizing; that feature impedes transition of iron as the ferromagnetic element to the solution.

In Fig. 6, there are shown XPS spectra of P2p of AISI 430 SS after abrasive/mechanical polishing (MP), standard electrochemical polishing (EP), standard electrochemical polishing with stirring (MIX), and magnetoelectropolishing (MEP). In the case of mechanically polished samples, on the surface there are not visible any peaks representing the phosphorus compounds. In the case of the steel surface after electrochemical polishing there are clearly visible peaks of phosphorus compounds at the binding energy $BE = 133.6$ eV corresponding to PO_4^{3-} . This testifies that the phosphate ions from the solution are bound with the polished surface elements like iron and/or chromium.

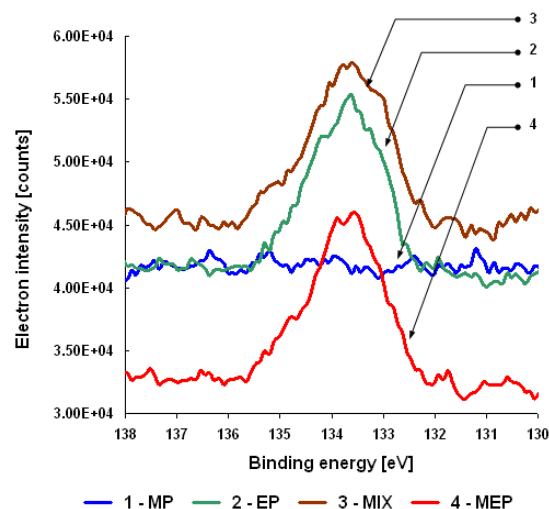


Fig. 6. XPS spectra of P 2p of AISI 430 SS after abrasive/mechanical polishing (MP), standard electrochemical polishing (EP), standard electrochemical polishing with stirring (MIX), magnetoelectropolishing (MEP)

Rys. 6. Widma XPS dla fosforu P 2p w stali AISI 430 po mechanicznym polerowaniu ściernym (MP), standardowym elektropolerowaniu bez mieszania (EP), elektropolerowaniu z mieszaniem (MIX), magnetoelktropolerowaniu (MEP)

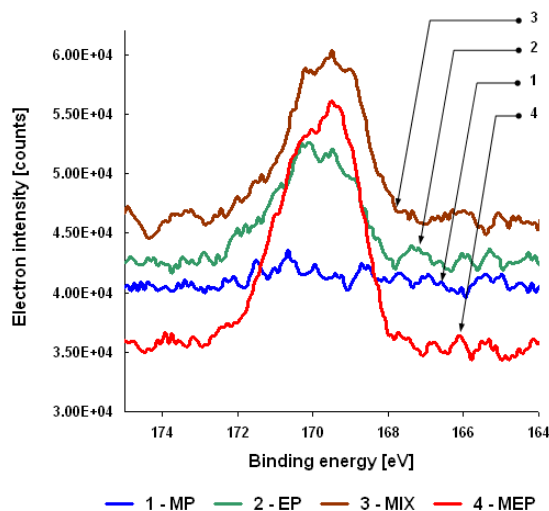


Fig. 7. XPS spectra of S 2p of AISI 430 SS after abrasive/mechanical polishing (MP), standard electrochemical polishing (EP), standard electrochemical polishing with stirring (MIX), magnetoelectropolishing (MEP)

Rys. 7. Widma XPS dla siarki S 2p w stali AISI 430 po mechanicznym polerowaniu ściernym (MP), standardowym elektropolerowaniu bez mieszania (EP), elektropolerowaniu z mieszaniem (MIX), magnetoelktropolerowaniu (MEP)

In Fig. 7 there are shown XPS spectra of S 2p of AISI 430 SS after abrasive/mechanical polishing (MP), standard electrochemical polishing (EP), standard electrochemical polishing with stirring (MIX), and magnetoelectropolishing (MEP). In the case of mechanically polished samples, on the surface there are not visible any peaks representing the sulfur

compounds. In the case of the surface after electrochemical polishing there are clearly visible peaks of sulfur compounds at the binding energy $BE = 169.3$ eV corresponding to SO_4^{2-} . This testifies that the sulfate ions from the solution are bound with the polished surface elements like iron and/or chromium.

The calculated P/S ratio of the steel surface after standard electrochemical polishing (EP) equals 1.28, whereas after the magnetoelectropolishing (MEP) its value reaches 2.59 and is the highest. After the standard electrochemical polishing with stirring (MIX), the P/S ratio is just between those measured after EP and MEP and equals 1.48.

In Fig. 8 there are shown XPS spectra of O1s of AISI 430 SS after abrasive/mechanical polishing (MP), standard electrochemical polishing (EP), standard electrochemical polishing with stirring (MIX), and magnetoelectropolishing (MEP). In the case of mechanically polished samples, on the surface there are visible 2 peaks at binding energies 530.2 eV and 531.7 eV corresponding to O^{2-} and OH^- . For the standard electrochemical polishing with and without stirring (EP and MIX) the binding energy 531.3 eV corresponds to OH^- . In the case of sample treatment by magnetoelectropolishing (MEP) the main peak is shifted to 532.2 eV that corresponds to SO_4^{2-} .

The electrochemical polishing (EP, MIX, MEP) is performed in the transpassive range which favours the formation of chemical compounds containing oxygen, such as phosphates and sulfates of iron and chromium. The magnetic field results in magnetizing the ferritic steel; that considerably hampers getting out the ferromagnetic elements from the steel structure and getting into reactions with ions coming from the solution.

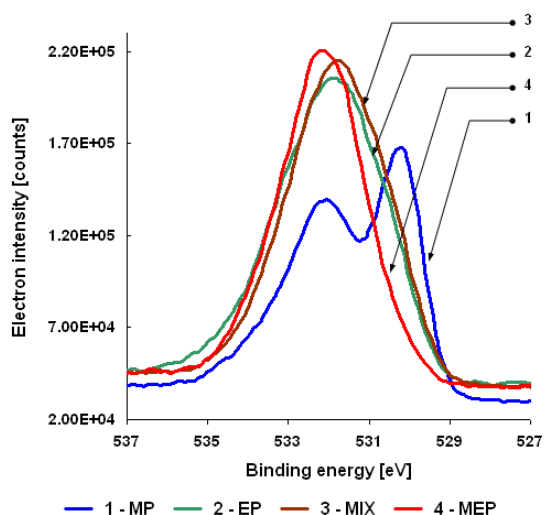


Fig. 8. XPS spectra of O 1s of AISI 430 SS after abrasive/mechanical polishing (MP), standard electrochemical polishing (EP), standard electrochemical polishing with stirring (MIX), magnetoelectropolishing (MEP)

Rys. 8. Widma XPS dla tlenu O 1s w stali AISI 430 po mechanicznym polerowaniu ściernym (MP), standardowym elektropolerowaniu bez mieszania (EP), elektropolerowaniu z mieszaniem (MIX), magnetoelektropolerowaniu (MEP)

4. Conclusion

The following conclusions can be drawn from the studies carried out on AISI 430 stainless steel:

- After abrasive treatment there are no phosphorus or sulfur compounds detected
- After all electrochemical polishing processes there are visible peaks of phosphorus PO_4^{3-} and/or sulfur SO_4^{2-} compounds

- On the sample surfaces after all electrochemical treatments there are clearly visible peaks of iron (III) compounds (Fe_2O_3 , $FeOOH$) and chromium (III) compounds (Cr_2O_3 , $Cr(OH)_3$)
- Cr/Fe ratio of the sample surface of the ferritic AISI 430 stainless steel after abrasive polishing (MP) equals approximately 0.4
- Cr/Fe ratio of the steel sample surface after the standard electrochemical polishing (EP) is the highest and equals approximately 2.25
- Cr/Fe ratio of the sample surface after the standard electrochemical polishing with stirring (MIX) equals only about 0.96
- Cr/Fe ratio of the sample surface after magnetoelectropolishing (MEP) is very low and equals 0.7.

This last conclusion testifies that in case of electrochemical polishing treatments of ferromagnetic AISI 430 stainless steel the magnetic field does not improve but rather hampers the enrichment of the steel surface film with chromium compounds.

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