

XPS study of AISI 304 stainless steel surface layer after abrasive and electrochemical polishing

Krzysztof Rokosz, Tadeusz Hryniewicz

Abstract

The paper discusses the chromium compounds to iron compounds ratio of austenitic AISI 304 stainless steel after mechanical and electrochemical treatments. The tested stainless steel is widely used in many industries. The X-ray Photoelectron Spectroscopy (XPS) studies show, that after electrochemical polishing EP there is much more chromium compounds in the passive layer than those after abrasive polishing MP and there is observed a significant increase in the Cr/Fe ratio after EP up to 2.4 versus MP (0.64).

Key words: XPS study, stainless steel, surface layer, abrasive polishing, electrochemical polishing.

1. Introduction

Nowadays the austenitic stainless steel AISI 304 (X5Cr-Ni18-10, 1.4301, 0H18N9) is very often used in many branches of the world industry (agriculture, automotive, food production, paper and textile industry, etc.). It has a good corrosion resistance, excellent formability as well as high strength and low weight. Because of its application in industry it is advantageous to increase corrosion protection by final treatment. To attain this aim, there are two methods used in industry: abrasive polishing (MP) and electropolishing (EP). After the electropolishing, in addition to the desired surface roughness and shine, the surface gains better corrosion resistance [1, 2], higher chromium compounds to iron compounds ratio as well as the lack of carcinogenic elements in the surface layer [2-4]. Changes in mechanical properties of surface layer (nanohardness, and reduced Young's modulus) [5] are also observed. The paper presents the differences in surface layer after mechanical and electrochemical polishing in view of chromium compounds to iron compounds ratio investigated by XPS method.

2. Method

The set up used for electrochemical polishing is presented in **Figure 1**, and it has been designed based on the authors' own concept. The set up consisted with a potentiostat ATLAS 98, cylindrical austenitic stainless steel cathode of the area of more than 100 times larger than that of the tested sample-anode, which was placed inside the cathode (the anode-cathode distance was about 45 mm), Hg/Hg₂SO₄ MSE reference electrode, heater and thermometer. The electrochemical treatments were conducted at 60°C in phosphoric-sulfuric mixed acids with the volume ratio of 4:6, at current density 50 A/dm² in 3 minutes' time.

The AISI 304 austenitic stainless steel samples served for the study, with the material measured composition vs. literature composition [6] presented in **Table 1**. They were prepared in the form of rectangular specimens of dimensions 25 × 45 mm cut of the metal sheet 2 mm thick.

The XPS measurements on electrochemically polished AISI 316L SS samples were performed using SCIENCE SES 2002 instrument. The XPS spectra were recorded in

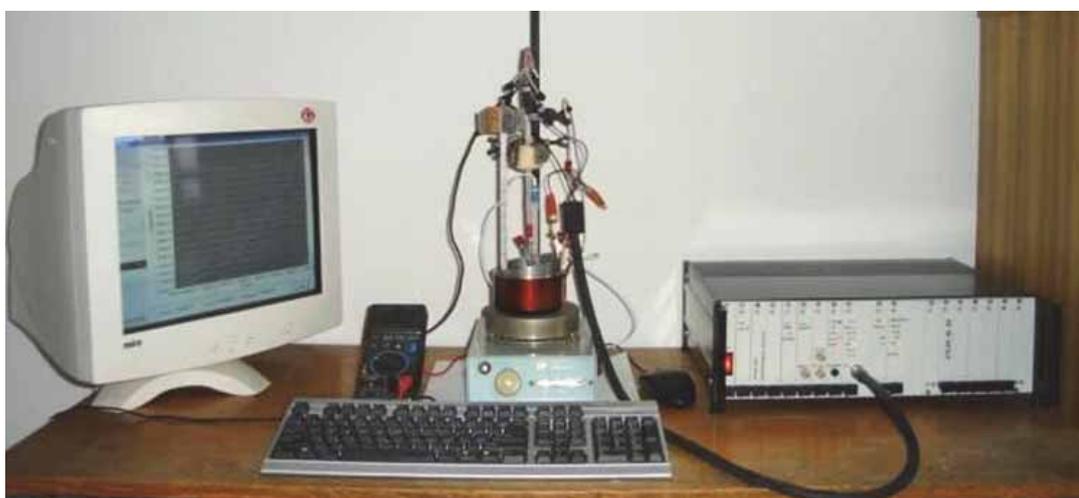


Fig. 1. Set up for electrochemical polishing (EP)

Rys. 1. Stanowisko do polerowania elektrochemicznego (EP)

Table 1. Chemical composition of AISI 304 SS
Tablica 1. Skład chemiczny stali AISI 304 SS

ELEMENT	CONTENT, wt% [6]	CONTENT, wt%
chromium	18-20	18.21
nickel	8-10.5	8.05
manganese	max. 2	1.44
carbon	max. 0.08	0.05
phosphor	max. 0.045	0.03
sulfur	max. 0.03	0.003
nitrogen	max. 0.1	0.049
silicon	max. 1	0.46
vanadium	-	0.08
cobalt	-	0.21
aluminum	-	0.003
copper	-	0.42
tungsten	-	0.06
boron	-	0.002
molybdenum	-	0.34
iron	balance	70.593

normal emission. The binding energy of the spectrometer has been calibrated by the position of the Fermi level on a clean metallic sample. The power supplies are stable and of high accuracy. The Fermi level is determined by the work function of the electron energy analyzer and does not vary from sample to sample. The experiments were carried out in an ultra-high vacuum system with a base pressure of about 10^{-8} Pa. The XPS measurements were performed using a SES2002 electron energy analyzer with a monochromatized Al-K α (1486.6 eV) and X-ray source (Gamdata-Scienta). A total resolution of about 0.6 eV was obtained for the presented spectra. For the XPS analyses

the CasaXPS 2.3.14 software [7] was used. In **Figure 2** there is shown the example of fitting $Fe2p_{3/2}$, $Cr2p_{3/2}$ spectra by two peak analysis with Shirley type background and GL(30) Gaussian-Lorentzian line shape.

The mathematical formula of Gaussian-Lorentzian line is shown as the multiplication of the Gaussian and Lorentzian functions [8]:

$$GL(x : E, F, m) = \frac{e^{-4 \ln 2 (1-m) \cdot \frac{(x-E)^2}{F^2}}}{1 + 4m \cdot \frac{(x-E)^2}{F^2}} \quad (1)$$

where the FWHM is related to F and position to E in equations. In Casa XPS the line $GL(x : E, F, m) = GL(m)$, for $m=0$ represents pure Gaussian one and for $m=100$ just pure Lorentzian. For the $0 < m < 100$ is obtained a mix of the two lines by the formula (1).

3. Results

The **Figures 3** and **4** show the high resolution XPS spectra ($Cr 2p_{3/2}$ and $Fe 2p_{3/2}$) of AISI 304 SS. After electrochemical polishing EP more chromium compounds than after abrasive polishing in surface is observed. In case of the iron compounds the situation is opposite, i.e. after EP there is a lower amount of iron compounds than that after MP treatment. The values are shown in **Table 2**. On the basis of the data, the chromium compounds to iron compounds ratios can be calculated for surface layers after MP and EP treatments, and they are 0.64 and 2.4, respectively. Following that, it appears that after the electrochemical polishing EP the Cr/Fe ratio has increased approximately 3.75 times versus the one after abrasive treatment MP.

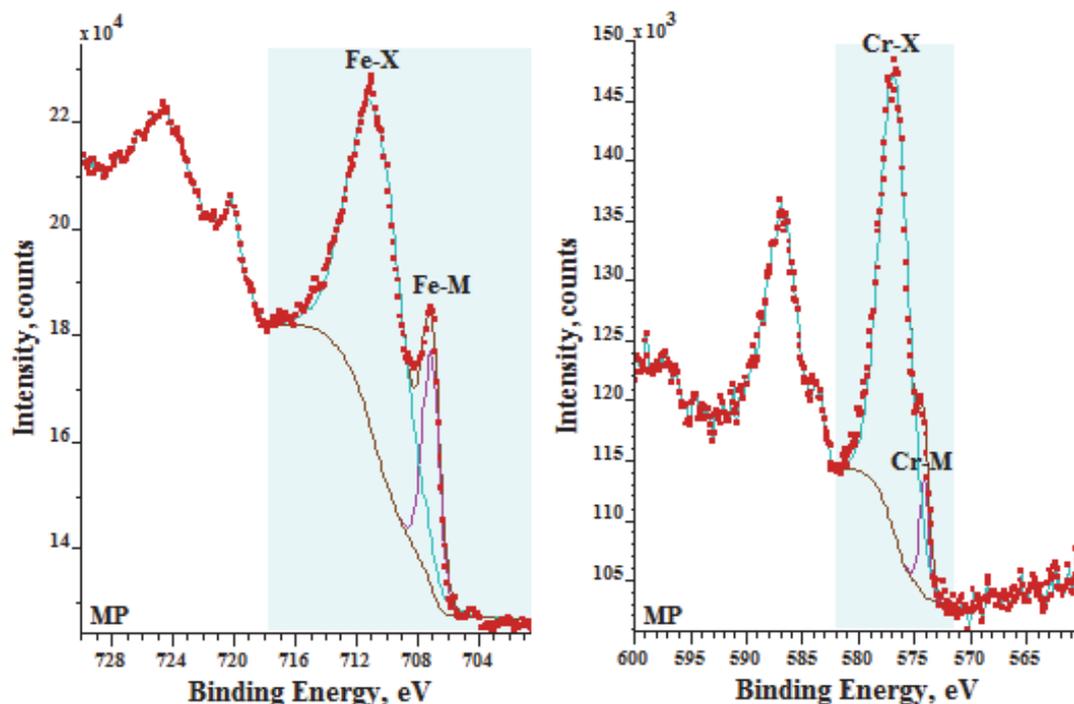


Fig. 2. Method of XPS spectra ($Fe2p_{3/2}$, $Cr2p_{3/2}$) fitting of surface after MP polishing
Rys. 2. Metoda analizy widm ($Fe2p_{3/2}$, $Cr2p_{3/2}$) powierzchni po polerowaniu MP

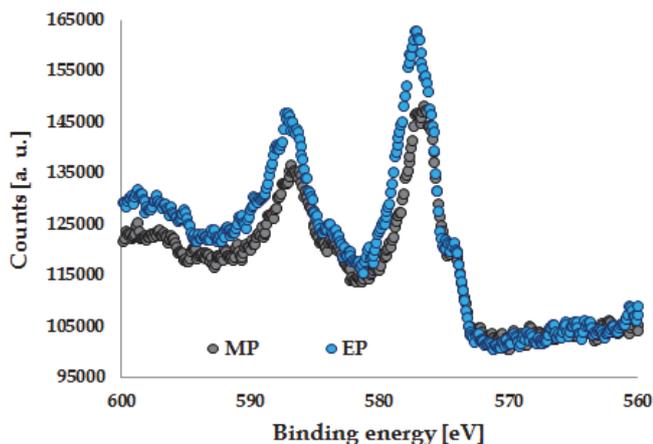


Fig. 3. High resolution XPS Cr_{2p} spectrum of AISI 304 SS

Rys. 3. Widmo wysokiej rozdzielczości XPS Cr_{2p} dla stali AISI 304 SS

Numerical results of fitting Cr 2p_{3/2} and Fe 2p_{3/2} are shown in **Table 2**. The two-peak analyses of iron and chromium spectra are the simplest form of interpretation of XPS data, but give the possibility of finding significant differences. After abrasive polishing MP in the surface layer iron and chromium oxides were dominated. In case of surface layer after the electrochemical polishing EP, iron and chromium oxide/hydroxide as well as phosphates and sulfates were observed.

Conclusion

Electrochemical polishing EP as a finishing treatment of steel surfaces is much better than abrasive polishing MP especially because of the corrosion resistance and an ease of processing complex shapes. The study shows, that after electrochemical polishing in the surface layer more chromium compounds versus these after abrasive treatment were observed. Chromium compounds to iron compounds ratio was 0.64 for MP and 2.4 for EP. That means the Cr/Fe ratio after EP has increased about 3.75 times.

Table 2. Results of fitting Cr 2p_{3/2} and Fe 2p_{3/2}

Tablica 2. Wyniki dopasowania dla Cr 2p_{3/2} i Fe 2p_{3/2}

		CHROMIUM		IRON	
		Cr-M	Cr-X	Fe-M	Fe-X
MP	BE [eV]	574.1	576.8	707.1032	710.6723
	FWHM	0.976174	3.0676	1.29223	4.07901
	Line Shape	GL(30)	GL(30)	GL(30)	GL(30)
	AREA [at%]	10347.9	126988.8	61389.3	277195.5
EP	BE [eV]	574.1820	577.1809	707.2525	710.3262
	FWHM	1.11636	3.14531	1.16083	4.84848
	Line Shape	GL(30)	GL(30)	GL(30)	GL(30)
	AREA [at%]	15701.7	174290.9	43322.4	101113.5
Fe 2p [at%]		8	92	30	70

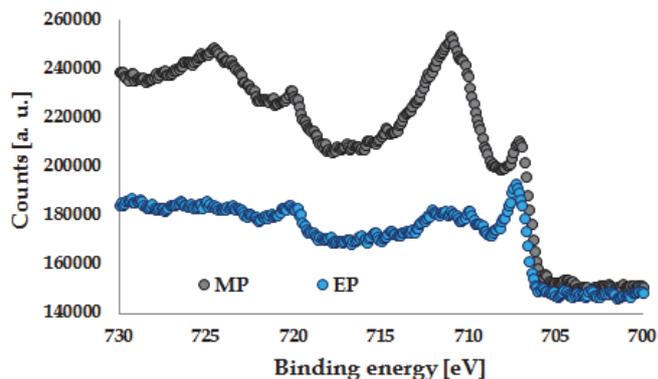


Fig. 4. High resolution XPS Fe_{2p} spectrum of AISI 304 SS

Rys. 4. Widmo wysokiej rozdzielczości XPS Fe_{2p} dla stali AISI 304 SS

Acknowledgment

Professor **Steinar Raaen**, Department of Physics, Norwegian University of Science and Technology, NTNU in Trondheim, Norway, is highly acknowledged for making available the XPS instrument for the studies.

Professor **Gregor Mori** of the Institute of Schadensanalytik, Montanuniversität Leoben, Austria, is greatly acknowledged for getting chemical analysis of the AISI 304 austenitic stainless steel samples.

References

- Rokosz K., Hryniewicz T., *Pitting corrosion resistance of AISI 316L SS in Ringer's solution after magnetochemical polishing*. Corrosion (J. Sci. Eng.) 2010, 66 (3).
- Rokosz K., *Polerowanie elektrochemiczne stali w polu magnetycznym*. Monografia nr 219, Wydawnictwo Politechniki Koszalińskiej, Koszalin 2012.
- Rokosz K., Hryniewicz T., Raaen S., *Characterization of Passive Film Formed on AISI 316L Stainless Steel after Magnetochemical Polishing in a Broad Range of Polarization Parameters*. Steel Research International 2012, 83(9).
- Hryniewicz T., Rokosz K., *Analysis of XPS results of AISI 316L SS electropolished and magnetochemical polished at varying conditions*. Surface & Coatings Technology 2010, 204(16-17).
- 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).
- Specification Sheet 304 Chromium-Nickel, Sandmeyer Steel Company
- CasaXPS Version 2.3.16 (Pre-rel 1.4)
- Walton J., Carrick A., *The Casa Cookbook-The CasaXPS User's Manual, Part 1: Recipes for XPS data proceedings*. Acolyte Science 2009.

Badania XPS stali AISI 304 SS po polerowaniu mechanicznym i elektrochemicznym

Streszczenie

W artykule omówiono wpływ rodzaju polerowania, mechanicznego ściernego oraz elektrochemicznego, austenitycznej stali stopowej AISI 304 na zawartość związków chromu oraz żelaza w warstwie wierzchniej, jak i na ich stosunek Cr/Fe. Badana stal nierdzewna jest szeroko stosowana w wielu gałęziach przemysłu. Badania XPS pokazują, że po elektrochemicznym polerowaniu EP obserwuje się więcej związków chromu niż związków żelaza w warstwie wierzchniej. Obserwuje się również istotny wzrost stosunku Cr/Fe z 0,64 dla MP do 2,4 dla EP.

Słowa kluczowe: stal AISI 304, badania XPS, polerowanie mechaniczne, polerowanie elektrochemiczne.

Autorzy:

prof. nadzw. dr hab. inż. **Krzysztof Rokosz** – Politechnika Koszalińska

prof. dr hab. inż. **Tadeusz Hryniewicz** – Politechnika Koszalińska