

XPS analysis of AISI 316L (EN 1.4404) austenitic stainless steel surfaces after passivation in nitric acid HNO₃

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Abstract

The XPS results of AISI 316L passive surface layer after mechanical MP and electrochemical (EP, MIX) polishing with additional passivation in 20 vol% nitric acid HNO₃ at 50 °C for 30 min are presented. The studies revealed the highest iron Fe 2p and chromium Cr 2p signals from surface layer after electrochemical polishing without stirring EP and passivation in HNO₃ whereas the lowest signals were recorded after mechanical polishing MP and similar passivation. After the passivation of abrasively treated MP samples done the atomic concentration of chromium compounds was over 93 at% and after passivation of electropolished EP and MIX samples the atomic percentage of chromium compounds was about 88 at% of the whole chromium concentration. The iron compounds after MP equaled about 65 at%, and after EP and MIX about 58 at% of the whole amount of detected iron. In all samples and all studied passive layers mainly oxides and hydroxides as well as sulfates and phosphates of iron and/or chromium were detected. Presented results can be used as reference data for the analysis of other passive layers usually obtained after chemical and electrochemical treatments as well as electro-machining operation.

Key words: XPS spectroscopy, Shirley Background, 316L SS; EN 1.4404, HNO₃, Cr/Fe ratio.

1. Introduction

The austenitic chromium-nickel-molybdenum low carbon stainless steel AISI 316L (EN 1.4044) has been increasingly used in many industries, for e.g. food processing equipment, brewery equipment, chemical and petrochemical equipment, laboratory benches & equipment, coastal architectural paneling, coastal balustrading, boat fittings, chemical transportation containers, heat exchangers, mining screens, nuts and bolts, springs, medical implants, etc. [1]. The steels have good machinability, as well as good corrosion resistance, because of their chemical composition. In previous papers the Authors described the chemical compositions of passive surface layers formed on austenitic AISI 316L stainless steel after a standard electropolishing EP, and magnetoelectropolishing MEP [2-14]. In that paper, XPS results of AISI 316L after abrasive finishing MP as well as after electropolishing without (EP) and with stirring (MIX), including additional passivation in 20 vol% nitric acid HNO₃, are presented.

2. Material

The AISI 316L (EN 1.4404) stainless steel samples were used for the study. In Table 1, the chemical composition of studied material is presented. The samples were cut off a cold-rolled metal sheet of the stainless steel after plate rolling so that the austenitic structure was retained. They were prepared in the form of rectangular specimens of dimensions 30 × 5 mm cut of the metal sheet 1 mm thick. One part of the samples was treated by abrasive polishing MP and after that operation passivated in 20 vol% HNO₃ at the temperature 50 ± 2 °C for 30 min, and the second one electrochemically polished without stirring EP as well as with stirring MIX and passivated in the

same conditions as the first one. After the passivation treatment all the samples were cleaned in distilled water and dried in the air.

Table 1. Composition of AISI 316L SS, wt%

Tablica 1. Skład chemiczny stali AISI 316L, %wag

C	0.02	Co	0.19	Mn	1.3	Sn	0.014
Cr	16.92	V	0.09	Si	0.39	S	0.011
Mo	2.01	W	0.04	P	0.032	N₂	0.0405
Ni	10.38	B	0.0019	Al	0.007	Fe	balance

3. Set up and parameters

The electrolytic polishing operations were performed at the current density of 60±1 A/dm². The main elements of electro-polishing set-up were: a processing cell, a dc power supply Telzas PDN 24-48-(60)/30(25), the electrodes and connecting wiring. Generally, the electrolyte temperature during electropolishing was 65±5 °C. For the studies, a mixture of sulfuric/orthophosphoric acids electrolyte in the following proportions H₃PO₄:H₂SO₄ = 3:2 was used. For each run, the electrolytic cell made of glass was used, containing up to 500 cm³ of electrolyte solution.

4. XPS studies

The XPS measurements on electrochemically polished and passivated AISI 316L stainless steel samples were performed using 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 3×1 mm and a pass energy of 500 eV with energy step 0.2 eV and the 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 $6 \cdot 10^{-10}$ Pa. The XPS spectra were recorded in normal emission. In view of optimizing the signal-to-noise ratio to about 3.2, one XPS measurement cycle covered 10 sweeps. For the XPS analyses the CasaXPS 2.3.14 software with Shirley type background setup was used.

5. Results

In Figure 1, there are visible XPS spectra of iron Fe 2p and chromium Cr 2p after abrasive and electrochemical polishing and additional after passivation in 20 vol% HNO₃.

The highest iron Fe 2p signal was recorded from the passive surface layer after electrochemical polishing EP and passivation. A little smaller signal was observed after electropolishing with stirring MIX and passivation, and the minimum was detected after mechanical polishing MP and passivation. In case of chromium Cr 2p spectra, which are presented also in Figure 1, the maximum signal was observed after EP plus passivation and the minimum one after MP and passivation.

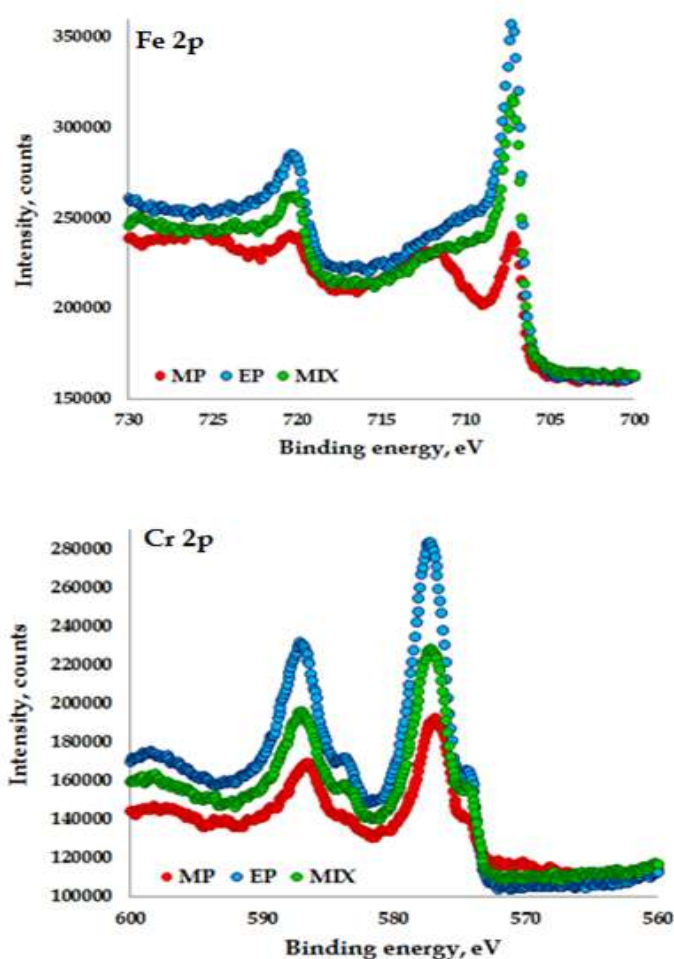


Fig. 1. XPS results of iron (Fe 2p) and chromium (Cr 2p)

Rys. 1. Wyniki XPS dla żelaza (Fe 2p) oraz chromu (Cr 2p)

In Figures 2 and 3, there are presented fittings by two peaks (metal peak and compound peak) for the three surface layers formed after mechanical and electrochemical polishing plus additionally passivated surfaces. In case of abrasive finishing MP the chromium compound peak covers over 93 at% of total detected chromium. After passivation of electropolished EP and MIX samples the atomic percentage of chromium compounds is

close to 88 at% of total detected chromium. The iron compounds after MP is about 65 at%, and after EP and MIX about 58 at% of total detected iron. After passivation in nitric acid of the abrasively treated MP as well as electrochemically polished (EP & MIX) samples in all surface layers mainly oxides and hydroxides of iron and/or chromium (Figures 4 and 5) were detected.

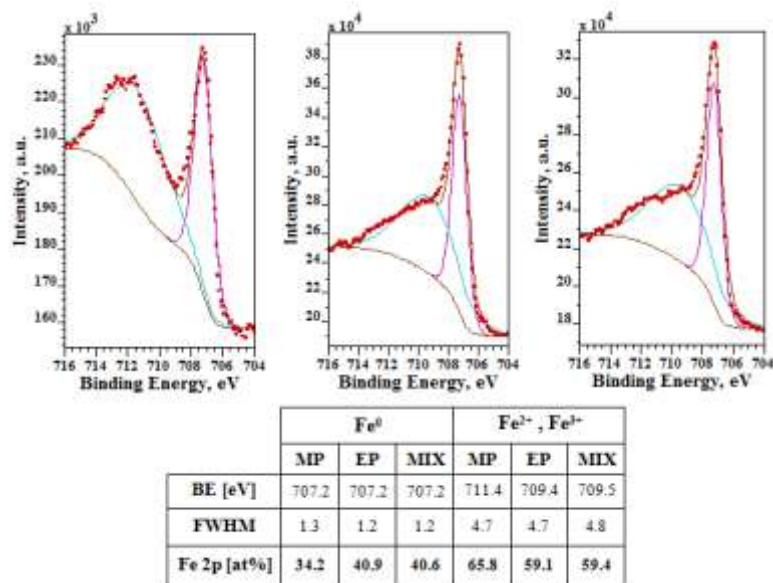


Fig. 2. Results of fitting Cr 2p_{3/2} data

Rys. 2. Wyniki fittingu danych XPS Cr 2p_{3/2}

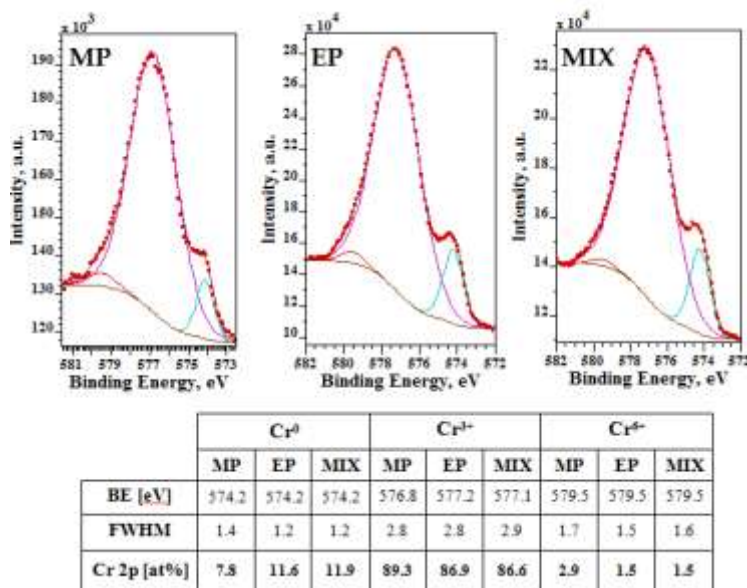


Fig. 3. Results of fitting Fe 2p_{3/2} data

Rys. 3. Wyniki fittingu danych XPS Fe 2p_{3/2}

6. Conclusions

- The biggest iron Fe2p and Cr 2p signals from surface layer were noted after electrochemical polishing without stirring EP and passivation in 20 vol% HNO₃.
- the smallest iron Fe2p and Cr 2p signals were noted after mechanical polishing MP and passivation in 20 vol% HNO₃.
- after passivation in 20 vol% HNO₃ of abrasively finished MP sample the atomic concentration of chromium compounds was over 93 at% of total detected chromium.

- after passivation in 20 vol% HNO₃ of electropolished (EP, MIX) samples the atomic percentage of chromium compounds was about 88 at% of total detected chromium.
- the iron compounds after mechanical polishing MP was about 65 at% of total detected iron.
- the iron compounds after EP and MIX equaled about 58 at% of total detected iron.
- passive layers in all samples consisted mainly of oxides and hydroxides of iron and/or chromium.

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Analiza XPS powierzchni austenitycznej stali stopowej AISI 316L (EN 1.4404) po pasywacji w kwasie azotowym HNO_3

Streszczenie

W artykule przedstawiono wyniki XPS warstw wierzchnich po pasywowaniu w 20 obj% HNO_3 w temperaturze 50 °C przez 30 minut powierzchni na stopowej stali austenitycznej AISI 316L zarówno po wcześniejszej obróbce mechanicznej MP, jak i standardowym polerowaniu elektrochemicznym bez mieszania EP jak i z mieszanym elektrolitu MIX. Odnotowano największą sygnał zarówno dla żelaza Fe 2p, jak i dla chromu Cr 2p w warstwie wierzchniej po standardowym elektropolerowaniu EP, natomiast najmniejszy sygnał został zarejestrowany dla pasywowanej powierzchni stali polerowanej mechanicznie. Po pasywacji, w pasywnej warstwie wierzchniej znajdowały się związki chromu i żelaza: odpowiednio po MP ponad 93 at% i 65at%, natomiast po EP i MIX około 88 at% i 58 at%. We wszystkich zbadanych warstwach pasywnych przeważały tlenki i wodorotlenki oraz fosforany i siarczany żelaza i/lub chromu. Zaprezentowane wyniki należy traktować jako punkty odniesienia do dalszych studiów nad warstwami pasywnymi otrzymanymi poprzez chemiczne, elektrochemiczne oraz elektromechaniczne obróbki.

Słowa kluczowe: spektroskopia, tło Shirley, 316L SS; EN 1.4404, HNO_3 , stosunek Cr/Fe .

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