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XPS STUDY OF AISI 316L SS SURFACES AFTER MECHANICAL AND ELECTROCHEMICAL POLISHING AND CHELATING/ELECTRO-CHELATING TREATMENTS

ABSTRACT

In the paper, there are presented the analyses of iron Fe2p_{3/2} and chromium Cr2p_{3/2} and oxide O1s XPS spectra of surfaces obtained after abrasive and electrochemical polishing with additional treatment as chemical chelating in the solution containing of 10% Citric Acid and 2% Ethylenediaminetetraacetic Acid. There was also performed electro-chelating after mechanical polishing in the electrolyte for chemical chelating. The maximum values of chromium compounds to iron compounds ratio were obtained after electropolishing with and without stirring with chemical chelating in Citric Acid and EDTA and they were in range from 3.5 to 3.6. The minimum value was obtained for the steel surface after abrasive polishing and electro-chelating and was equal 1.3. After electrochemical polishing and chemical passivation in the surface layer there were detected FeO and Cr(OH)₃ as dominated compounds. After abrasive polishing and electro-chelating there were mostly Fe₂O₃ and Cr₂O₃.

Keywords: XPS spectra fitting; Surface layer; AISI 316L SS; Electropolishing; Chelating; Passivation; Electro-chelating; Cr/Fe ratio; Fe 2p; Cr 2p; O 1s

INTRODUCTION

Surface finishing methods of stainless steel surfaces can be realized by using abrasive polishing (MP) and electrochemical polishing without stirring (EP) as well as with stirring (MIX). After these treatments there are obtained surfaces with different passive layers (different chromium to iron ratios). Our previous studies have shown [1-6], that after electrochemical polishing operations carried out both with stirring MIX and without stirring EP, the steel surface layer is enriched in chromium compounds much more than that one obtained after abrasive treatment MP. Further modification of the stainless steel surface is usually obtained by passivation in nitric acid and/or chelating in citric acid with addition of ethylenediaminetetraacetic acid (EDTA) [7-12].

These procedures of passivation in citric acid, chelating, and electro-chelating in citric acid with addition of EDTA were used in order to prepare more homogeneous passive layer with a domination of chromium compounds relative to iron compounds. During mechanical and/or electrochemical polishing and chelating in citric acid with addition of EDTA the sur-

face layer changes considerably. After electrochemical polishing that Cr/Fe ratio increases significantly.

In the paper authors present the influence of chelating and electro-chelating in citric acid and EDTA after abrasive and electrochemical polishing on the passivation of surface layer. It is considered as the amount of chromium compounds relative to iron compounds. Such obtained surfaces of AISI 316L stainless steel were investigated using X-ray photoelectron spectroscopy (XPS).

METHOD AND EXPERIMENTAL SET UP

Stainless steel AISI 316L (S31603, 1.4404) is a material used very often in industry. It has a good corrosion resistance, because of high chromium compounds to iron compounds ratio ($\text{Cr/Fe} = 0.25$). The bulk composition of the steel, in wt% as measured, is shown in Table 1.

Table 1. Chemical composition of AISI 316L SS, wt. %

Element	Content as measured	Element	Content as measured
Chromium	16.92	Phosphorus	0.32
Nickel	10.38	Sulfur	0.01
Manganese	1.30	Copper	0.28
Molybdenum	2.01	Vanadium	0.09
Nitrogen	0.04	Cobalt	0.19
Carbon	0.02	Aluminum	0.01
Silicon	0.39	Iron	68.04

The samples for XPS measurements were treated by abrasive and electrochemical polishing with chelating or electro-chelating treatment in the solution containing of 10% citric acid and 2% ethylenediaminetetraacetic acid. The electrochemical polishing and electro-chelating was carried out in the electrolyte of temperature of 65 °C, with the temperature control of ± 10 °C. Proprietary mixed sulfuric/phosphoric acids electrolyte $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4 = 1.5$ and 10% H_2O of the whole acids' volume to electrochemical polishing process was used. The electrolytic cell was made of glass, containing up to 500 cm³ of electrolyte.

The XPS experiments were carried out in an ultra-high-vacuum system with a base pressure of about 10^{-8} Pa. The XPS measurements, with the angle of 90°, were performed using a SES2002 electron energy analyzer with a monochromatized Al K α ($h\nu = 1486.6$ eV) X-ray source (Gammadata-Scienta). A total resolution of about 0.6 eV was obtained for the presented spectra. In view of optimizing the signal-to-noise ratio, one XPS measurement cycle covered 100 sweeps. For the XPS analyses the CasaXPS 2.3.14 software was used [13-15]. The XPS spectra were analysed by using Shirley background [16-18].

RESULTS

In Figures 1-3 there are shown the results of XPS spectra of chromium (Fig. 1) iron (Fig. 2) and oxygen (Fig. 3) for surfaces after abrasive and electrochemical treatments with chelating in citric acid with addition of EDTA. The highest amount of chromium is observed after electrochemical polishing with stirring MIX and chemical chelating, and the smallest one after electro-chelating. After electro-chelating the passive layer, which is formed after that electrochemical treatment is worse than that obtained after abrasive polishing MP (Fig. 1). In case of analysis the iron spectra the amounts of iron after abrasive polishing MP and electrochemical polishing operations EP & MIX and chelating are similar and higher than these ones after electro-chelating (Fig. 2).

Fig. 1. XPS results of chromium spectra (Cr 2p) of AISI 316L SS after MP, EP, MIX and Electro-Chelating

Fig. 2. XPS results of iron spectra (Fe 2p) of AISI 316L SS after MP, EP, MIX and Electro-Chelating

The highest amount of oxygen (Fig. 3) is observed after electrochemical treatments EP & MIX and chelating and the smallest one for electro-chelating. The shapes of O 1s spectra for abrasive polishing MP and electro-chelating are similar with an indication that the oxygen amount after electro-chelating is lower than that after mechanical treatment MP. One can notice that in the steel surface after these treatments there are two dominating compounds, which most probably may be interpreted as oxides and hydroxides. In case of electrochemical polishings EP & MIX and chemical chelating there are single peaks visible meaning that there is one dominating type of oxides, most probably hydroxides.

Fig. 3. XPS results of oxygen spectra (O 1s) of AISI 316L SS after MP, EP, MIX and Electro-Chelating

In Figures 4-11 there are presented fitted data of XPS spectra (Cr 2p and Fe 2p) after abrasive MP and electrochemical EP & MIX polishing operations and chemical chelating as well as after electro-chelating. It can be noted, that after abrasive polishing MP in the steel surface layer, except from metallic chromium ($BE = 574.1$ eV) and iron ($BE = 707.2$ eV), there are also chromium and iron compounds visible. In the case of iron the dominating compound most probably is FeO ($BE = 709.2$ eV) and for chromium compound: CrOOH ($BE = 577$ eV). Inside the passive surface layer after a standard electropolishing without stirring EP and with stirring MIX and chemical chelating most probably there are FeO ($BE = 709.4$ eV) and Cr(OH)₃ ($BE = 577.4$ eV). After electrochemical polishing there are Fe₂O₃ ($BE = 710.7$ eV) and Cr₂O₃ ($BE = 576.8$ eV). Regarding the analysis of XPS spectra it is characteristic that in case of chromium in the surface layer measured there is always constant ratio metal-to-compounds, i.e. M : X = 1 : 9. In case of iron spectra analysis there is noticed that for the surfaces after abrasive polishing MP and electropolishing operations EP & MIX the M : X ratio is equal 4:6, but for electro-chelating the ratio is changing to 2:8.

Fig. 4. XPS spectrum analysis of Cr 2p of AISI 316L SS after MP and chelating

Fig. 5. XPS spectrum analysis of Fe 2p of AISI 316L SS after MP and chelating

Fig. 6. XPS spectrum analysis of Cr 2p of AISI 316L SS after EP and chelating

Fig. 7. XPS spectrum analysis of Fe 2p of AISI 316L SS after EP and chelating

Fig. 8. XPS spectrum analysis of Cr 2p of AISI 316L SS after MIX and chelating

Fig. 9. XPS spectrum analysis of Fe 2p of AISI 316L SS after MIX and chelating

Fig. 10. XPS spectrum analysis of Cr 2p of AISI 316L SS after MP and Electro-Chelating

Fig. 11. XPS spectrum analysis of Fe 2p of AISI 316L SS after MP and Electro-Chelating

Fig. 12. Calculated Cr-X/Fe-X ratio of AISI 316L SS after MP, EP, MIX and Electro-Chelating

On the basis of results obtained under the investigation one should note that the maximum values of chromium compounds to iron compounds (Cr-X/Fe-X) ratio after a standard electropolishing with and without stirring (MIX and EP) with chelating in citric and EDTA acids are in the range from 3.5 to 3.6 (Fig. 12). The minimum value (1.3) was obtained for surface after abrasive polishing MP and electro-chelating in citric and EDTA acids.

CONCLUSIONS

Based on the experiments carried out and XPS study results with the calculations performed, the following conclusions may be formulated:

1. Chelating and electro-chelating have significant influence on the chromium compounds to iron compounds (Cr-X/Fe-X) ratio
2. After mechanical polishing MP and after chelating in citric acid and EDTA the chromium compounds to iron compounds (Cr-X/Fe-X) ratio is equal 2.8
3. After electrochemical polishing (EP and MIX) and after chelating in citric acid and EDTA the chromium compounds to iron compounds (Cr-X/Fe-X) ratio is in the range from 4.5 to 3.6 (maximum values)
4. After mechanical polishing MP and after electro-chelating in citric acid and EDTA the chromium compounds to iron compounds (Cr-X/Fe-X) ratio is equal 1.3 (minimum value)
5. The electro-chelating after mechanical polishing MP should not be used because of the worst passive layer obtained after these treatments
6. The chelating in citric acid with EDTA after electrochemical polishing should be used because of the best passive layer obtained after these treatments.

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