Soft x-ray absorption spectroscopy study of electrochemically formed passive layers on AISI 304 stainless steels

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Stainless steels (SS) are materials of great interest in technological applications. One of their characteristic properties is their high corrosion resistance provided by the presence of a passive layer formed on their surface. This surface passive layer improves the corrosion resistance of the material, being a protective barrier against the aggressive environment [1]. Consequently, the study of the chemical composition of the passive films formed on SS is a topic of great interest. The passive film can be also electrochemically formed depending on the time and potential of passivation and on the existence of chloride ions in the electrolyte. The aim of the present study is to investigate the chemical composition of the passive layers electrochemically formed on the AISI 304 SS surface by using soft x-ray absorption spectroscopy.

The chemical composition of AISI 304 SS is (wt %) 19.7 Cr, 9.4 Ni, 1.7 Mn, 0.28 Si, 0.036 C, 0.003 S, 0.022 P and remainder Fe. Anodic polarization curves were carried out at room temperature using as electrolyte 500 ml of a 5 % NaCl aqueous solution (pH $\approx$ 8) prepared from reagent grade NaCl and distilled water. Two sweep rates were used: 0.16 and 5.0 mV s^{-1}. Additionally, for each polarized SS sample two different regions were studied: the passive region and the pitting region. In the first one, the anodic curve ends in a potential with low current density where the material is still in a passive state. In the pitting region, however, the curve continues until the breakdown potential is reached. At this potential, the current density drastically increases, which is attributed to the activation of a local corrosion process. Therefore, four different AISI 304 SS samples were studied, which were labelled: sample A (0.16 mV s^{-1} sweep rate and in the passive region), sample B (0.16 mV s^{-1} sweep rate and in the pitting region), sample C (5.0 mV s^{-1} sweep rate and in the passive region), and sample D (5.0 mV s^{-1} sweep rate and in the pitting region). After the polarization tests, the samples were extracted from the electrochemical cell, rinsed in distilled water, and placed in the ultrahigh vacuum (UHV) chamber for the XAS measurements. For comparative purposes and as reference materials, the following samples were also studied: (a) unpolarized AISI 304 SS samples; (b) Fe, Cr, and Ni pure metal polycrystalline samples that were scraped *in situ* in the UHV chamber with a diamond file; and (c) FeO, NiO, oxidized Fe, and oxidized Cr samples. Both Fe and Cr oxidized samples were produced by air exposure of the metal samples, generating spontaneously a native oxide layer on each sample surface. FeO and NiO were also scraped *in situ* in the UHV chamber with a diamond file to remove surface contaminants.

XAS measurements were carried out at the SX700/II soft x-ray monochromator operated by the Freie Universität Berlin at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY). XAS spectra were obatined by recording the total yield of secondary electrons from the sample surfaces. The base pressure in the UHV-chamber during measurements was better than $2 \cdot 10^{-10}$ mbar.

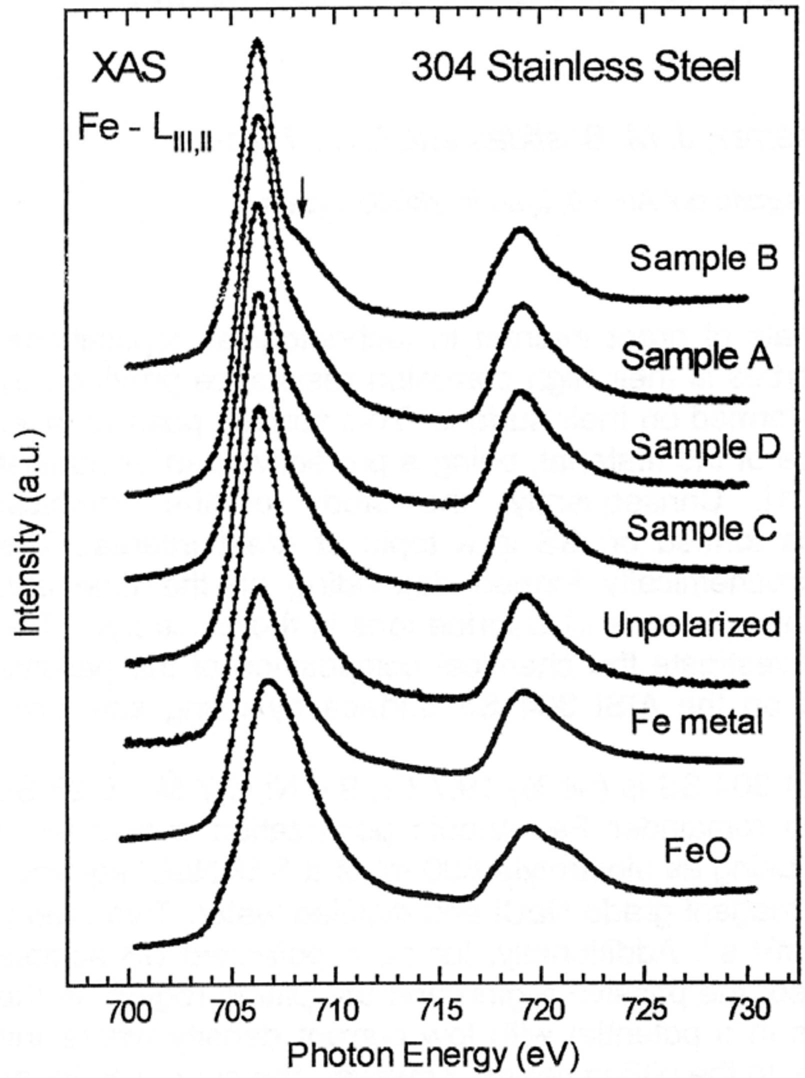

Figure 1: Fe *2p* soft x-ray absorption spectra for the four polarized AISI 304 SS, the unpolarized AISI 304 SS, Fe metal and FeO samples.

Figure 1 exhibits Fe *2p* soft x-ray absorption spectra of AISI 304 SS samples, polarized and unpolarized, Fe metal and FeO. The spectra present two broad multiplets separated by the spin-orbit splitting of the Fe *2p* core hole. All spectra are similar to Fe metal although some differences can be observed. In general, the spectra of AISI 304 SS samples show a $2p_{3/2}$ peak narrower than in the pure metal case. This effect can be related to the narrowing of the metal *3d* bands in the alloys as compared to the pure metal [2]. Another difference of all SS spectra with the Fe metal spectrum is the presence of a small shoulder marked by a vertical arrow in Figure 1 at a photon energy of ≈ 708.5 eV. The spectrum corresponding to FeO is different to all SS samples spectra, with a broader $2p_{3/2}$ structure and a $2p_{1/2}$ structure that exhibits a well defined shoulder at ≈ 721 eV. Consequently, the shape spectral differences found between SS samples and Fe metal can not be attributed to FeO. Besides, by comparison of the SS Fe-*2p* spectra with Fe_3O_4 and Fe_2O_3 spectra of previous works [3], it can be concluded that the differences between SS and Fe metal spectra do not represent neither any of these two iron oxides. It may be concluded that the differences between SS spectra and Fe metal spectrum could be associated to the presence of hydroxide compounds or hydrated molecules in the SS samples. For the AISI 304 SS sample B the differences with Fe metal are more evident. The shoulder at ≈ 708.5 eV is slightly more intense and the $2p_{3/2}$ peak is narrower than in the other SS samples. Also for this sample a shoulder at ≈ 723 eV in the $2p_{1/2}$ region is observed. Samples A and C were obtained at the passive region, where the passive layer has no damage. Samples B and D were obtained in the pitting region, where local corrosion is present. Sample D showed a lower number of pits than sample B; slower scan rates produce a more intense attack. This can explain the higher presence of hydroxide compounds in the sample B as compared to the other samples, since the scan rate used for sample B produced a more intense attack. Nevertheless, all Fe *2p* spectra of the SS samples exhibit high similarity with the Fe *2p* spectrum of Fe metal. Since the probing depth of XAS in TEY is larger than the thickness of the passive layer of SS, the influence of the metallic contribution in the Fe *2p* spectra was expected.

The XAS spectra at the Cr *2p*, Ni *2p* and O *1s* edges for all SS samples, polarized and unpolarized were also measured. For the Cr *2p* XAS spectra, similar spectral features to that of Cr_2O_3 were found. The XAS spectra at the Ni *2p* edges show similar spectral shapes to that of metallic Ni suggesting almost no Ni oxides nor hydroxides incorporation to the passive layer. The XAS O *1s* spectra support the main conclusions obtained with the transition metal edges spectra.

In summary, the composition of passive films electrochemically formed on AISI 304 SS in a chloride-containing solution has been studied with XAS. Soft x-ray absorption spectra were taken at the transition metals (Cr, Fe, Ni) *2p* edges and at the O *1s* edge making it possible to determine the main contributions to the passive films composition. The XAS spectra at the Fe *2p* edges exhibit no significant contribution of Fe oxides to the passive layer composition. However, differences in spectral shape with respect to metallic Fe suggest the presence of a small amount of Fe hydroxides, which is maximum for the AISI 304 SS polarized at the lowest scan rate and at the pitting region. The spectra at the Cr *2p* edges indicate that in all cases the passive film is mainly formed by Cr_2O_3. The spectra at the O *1s* edges confirm the results obtained at the transition metal edges. These results indicate that the scan rate has an influence on the passive layer electrochemically formed on the material.

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