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Applications of soft X-ray absorption spectroscopy to the study of passive and oxide layers on stainless steels: influence of ion implantation

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Abstract

Soft X-ray absorption spectroscopy (XAS) has been used to study the influence of Si ion implantation on the passive layer of AISI 304 stainless steel, as well as on its high-temperature oxidation behaviour. Ion implantation is a usual technique to improve the corrosion and oxidation resistance of steels. To study the effects of ion implantation on the room temperature corrosion behavior of AISI 304 stainless steel, XAS was performed on the passive layer formed spontaneously in contact with air. To analyse the effects of ion implantation at high temperatures, the oxide layer formed after an isothermal oxidation at 900°C for 32 h was also studied. The results show a positive influence of Si ion implantation on the corrosion behaviour of AISI 304 stainless steel. XAS in the soft X-ray excitation mode has proved to be a very suitable technique to perform corrosion science studies.

Keywords: X-ray absorption spectroscopy; Oxidation; Corrosion; Stainless steel; Ion implantation methods

1. Introduction

X-ray absorption spectroscopy is a well-established spectroscopic technique to obtain information concerning the electronic structure of solids [1–3]. In the last years, however, XAS has also been devoted to some more technological topics, such as corrosion [4–7]. Although various parameters are involved in the corrosion process, it is mainly a surface problem [8]. Consequently, surface modification methods, as ion implantation, are being currently investigated to prevent corrosion. Corrosion-resistant materials develop a protective surface film called passive layer, which involves not only the outermost surface atoms, but also some deeper layers, being its thickness in the case of stainless steels of the order of 30–60 Å.

Soft X-ray absorption spectroscopy in the total electron yield mode (TEY) has a probing depth of the order of 70–100 Å for the transition metal 2p edges [9,10]. Therefore, this spectroscopic technique appears more suitable to study corrosion phenomena than other more surface sensitive spectroscopic

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methods. This work illustrates the use of XAS to study the chemical differences originated in the passive and high-temperature oxidized layers of AISI 304 stainless steel by Si ion implantation. The corresponding improvements in corrosion behaviour and oxidation resistance of AISI 304 stainless steel are evaluated.

2. Experimental

The chemical composition (wt.%) of AISI 304 stainless steel was 18.2 Cr, 9.4 Ni, 1.5 Mn, 0.4 Si, 0.2 Mo, 0.2 Cu, 0.1 Co, 0.047 C, 0.027 P, 0.005 N, 0.003 S, 0.003 Ti, 0.002 Al and balance Fe. The samples were mechanically polished with SiC emery paper up to #600, and then ultrasonically degreased in acetone. The Si ion implantation process was carried out at an energy of 150 keV with ion fluence of 1×10^{15} Si/cm^2. The implantation profile, calculated by means of TRIM96 [11] computational code, shows a projected range of about 982 Å depth. Oxidation treatment was performed in a muffle furnace at 900°C and at atmospheric pressure of air up to 32 h.

The XAS measurements were carried out at the PM-1 soft X-ray monochromator at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY). XAS spectra were obtained at the Si, Cr, Mn, Fe, Ni, and Cu 2p and at the oxygen 1s absorption thresholds by recording the total yield of secondary electrons from the sample surfaces, i.e., in TEY mode. The base pressure in the UHV-chamber during the measurements was better than 2×10^{-10} mbar.

3. Results and discussion

Fig. 1 exhibits the atomic composition percentages of the different elements for the as-received and for the Si ion-implanted samples both without and with thermal treatment (untreated and treated, respectively). The values were calculated from the XAS spectra taking into account the cross-section values of the different elements and show the contribution of the different elements to the surface region of the material. For the untreated samples, the main contribution corresponds to Fe. Since the passive layer of stainless steels is enriched in Cr, the high Fe content observed indicates that the signal comes mainly from the bulk, where Fe is the main component. As mentioned above, the XAS technique in TEY mode has a probing depth of 70–100 Å, which is larger than the passive layer thickness of this material. As can be seen in Fig. 1, the Si ion-implanted sample has a lower Fe content than the as-received sample. In addition, the contributions of the other elements are higher for the implanted material with the exception of Ni, which has the same value for implanted and non-implanted samples. It can be concluded that the ion implantation process favour the Cr, Mn and Si diffusion from bulk towards the surface to form the protective passive film.

For the heat-treated samples, Fig. 1 shows a clear enhancement of the Cr and Mn signals. This result indicates that, upon high temperature oxidation, an enrichment in Cr and Mn is observed in the oxide scale, suggesting the formation of Cr–Mn oxides. This agrees with the results of a previous work using conventional X-ray diffraction, where MnCrO spinel-type oxides were observed [12]. On the other hand, It is interesting to note the high signal observed for Cu in the case of the treated as-received sample. This effect suggests a clear diffusion of Cu from bulk to surface to contribute to the oxidized layer, which is not present in the case of the ion-implanted sample.

Fig. 2 represents the Cr 2p soft X-ray absorption spectra of the as-received and Si ion-implanted AISI 304 stainless steel samples in both conditions, untreated and heat-treated. The heat-treated samples show a spectral shape typical of Cr_2O_3, as it can be deduced by comparing with previous works [13]. This result indicates that in both heat-treated samples Cr is in the form of Cr^{3+}. However, this is not the case for the untreated samples. The spectrum of the as-received untreated sample is typical of chromium native oxide [13], with a high contribution of metallic Cr and suboxide species. In this case, the shoulder at ≈575 eV is less defined than in the Cr_2O_3 case. The spectrum of the as-received Si ion-implanted sample is an intermediate case, with the shoulder more defined than in the as-received untreated sample and less than in the treated stainless steels. The less defined this shoulder, the larger the metallic

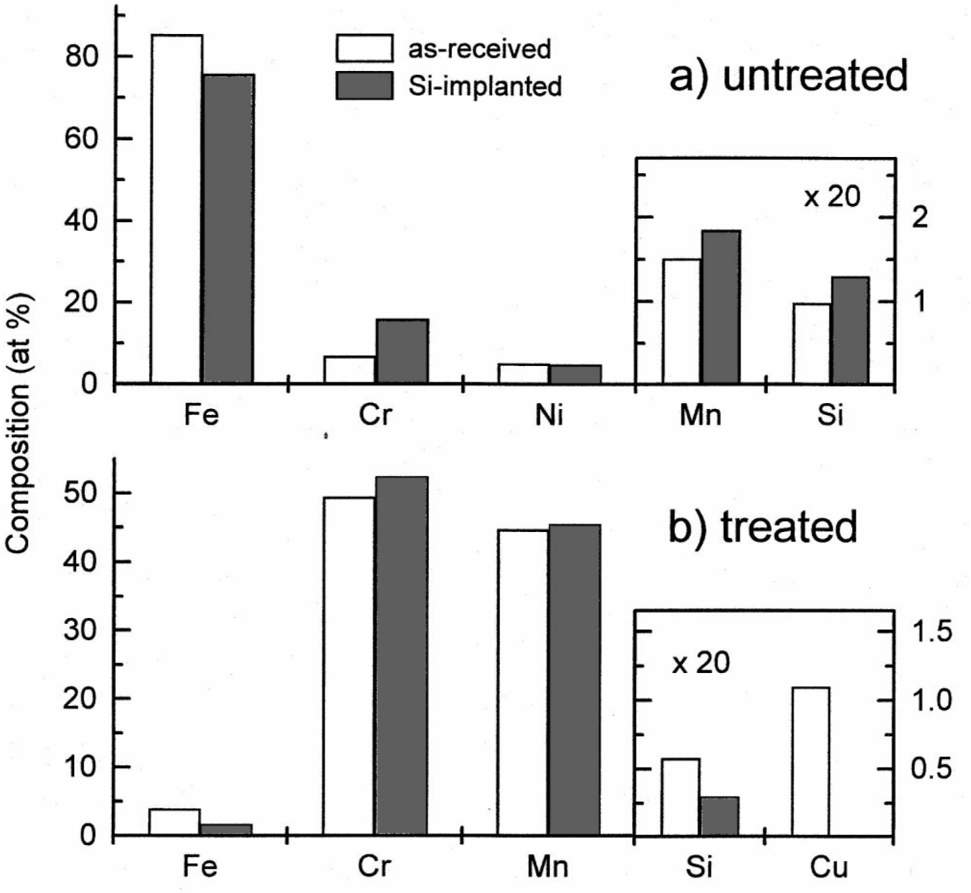

Fig. 1. Composition percentage of AISI 304 stainless steel, as-received and after Si ion implantation; (a) before (untreated) and (b) after a heat treatment at 900°C for 32 h (treated).

Cr contribution. This indicates that the passive layer of the untreated as-received sample is thinner than that of the implanted sample and, consequently, less protective.

Fig. 3 exhibits the Fe 2p XAS spectra of all investigated samples. The different spectral shapes observed between implanted and non-implanted specimens are an indication of the chemical changes induced by the ion implantation process. These spectral features can be compared to several reference spectra measured in previous works. The as-received untreated sample seems to be a mixture of Fe^{2+} and Fe^{3+} oxides, whereas the Si ion-implanted untreated sample exhibits a similar spectral shape to Fe metal, suggesting almost no presence of Fe oxides or hydroxides in this passive layer [13]. The Fe 2p spectral shape obtained for the heat treated AISI 304 samples corresponds to Fe_2O_3, as can be deduced by comparing it with the Fe_2O_3 spectra of previous work. The intensity of the Fe-signal in this case is much smaller than in the case of the non heat-treated samples, as was already shown in Fig. 1.

Fig. 4 shows the O 1s X-ray absorption spectra of all samples. The O 1s XAS signal is the result of the electronic transitions into unoccupied states with O 2p character hybridized with metal states. The O 1s spectra of the untreated AISI 304 stainless steel are quite similar, except for the shoulder at ≈528.5 eV in the as-received sample, which is not observed in the ion-implanted sample. By comparing with reference spectra from other works, these spectra seem quite similar to native Cr oxide [4]. The shoulder observed

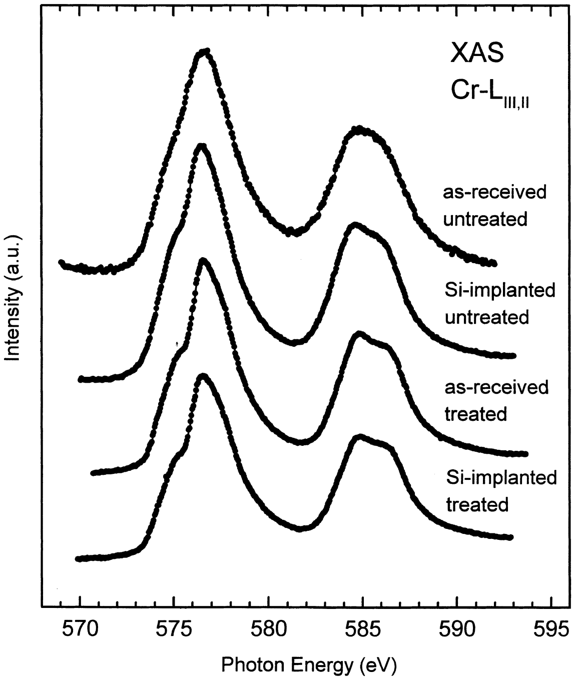

Fig. 2. Cr 2p soft X-ray absorption spectra of as-received and Si ion-implanted AISI 304 stainless steel samples, both thermally untreated and treated. The solid lines through the data points serve as a guide to the eyes.

in the as-received sample can be related to a higher presence of Fe oxides in this sample. Since the onset of the Fe 3d band in native Fe oxide lies at lower photon energies than in the case of Cr native oxide, it also lowers the energy of the oxygen 2p states hybridized with Fe 3d states. A similar, though smaller effect has been already discussed for electrochemically formed passive layers on AISI 304 stainless steel [4]. This result agrees with those deduced from Fig. 2, where a higher amount of Fe oxides was observed for the as-received untreated AISI 304 as compared to the ion-implanted sample. The treated samples show O 1s spectral shapes compatible with a mixture of Cr_2O_3 and MnO [14,15]. For the Si ion-implanted sample the higher intensity of the shoulder at $\approx$533 eV could be related to a higher amount of Mn oxide. Nevertheless, these spectra indicate that in the oxide films formed at elevated temperature, Cr is in the form of Cr^{3+} and Mn of Mn^{2+}. Therefore, the oxide layer is formed by Cr and Mn oxides, and the presence of spinels CrMnO can not be excluded.

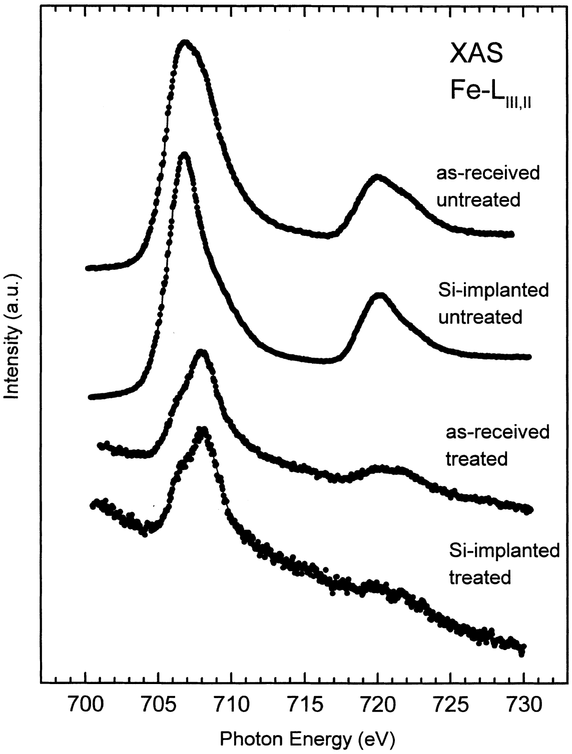

Fig. 3. Fe 2p soft X-ray absorption spectra of as-received and Si ion-implanted AISI 304 stainless steel samples, both thermally untreated and treated. The solid lines through the data points serve as a guide to the eyes.

4. Conclusions

X-ray absorption spectroscopy has been applied to study the influence of Si ion implantation on the passive and oxide layers of AISI 304 stainless steels. The main differences in the passive layer of as-received and Si ion-implanted samples are related to the different contribution of Fe and Cr oxides. The Fe-signal in the case of the as-received sample is higher than in the case of the ion-implanted sample. Contrary to this effect, the ion-implanted sample has a higher contribution of Cr oxides than the as-received sample. In general, a passive layer rich in Cr oxides provides more stability and protection

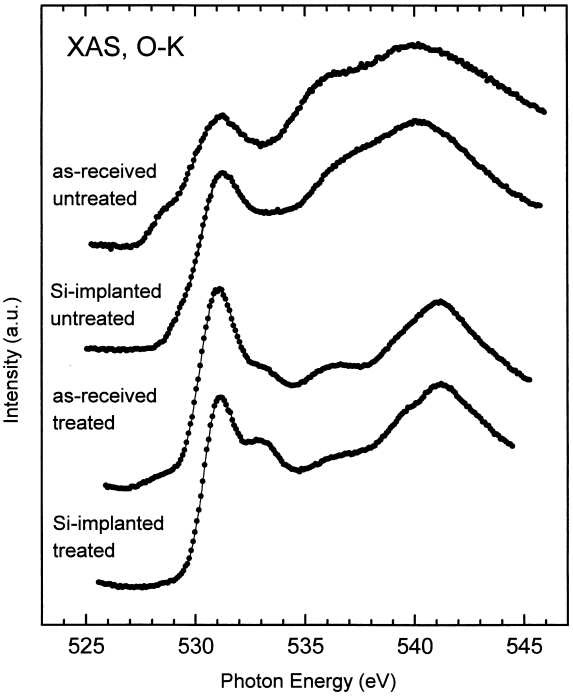

Fig. 4. O 1s soft X-ray absorption spectra of as-received and Si ion-implanted AISI 304 stainless steel samples, both thermally untreated and treated. The solid lines through the data points serve as a guide to the eyes.

against corrosion. Therefore, the Si ion implantation process has a positive influence on the corrosion behaviour of the material. For the heat-treated samples, almost no differences are observed between the oxide layers. A higher contribution of Mn oxides is observed for the Si ion-implanted sample. The thickness of the oxide layers is high enough to screen the initial effects of the ion implantation process. In summary, XAS has demonstrated to be a very suitable technique to provide information on the chemical differences produced by ion implantation on the passive and oxide layers of stainless steels. The effects originated by the ion implantation process are relatively small and, however, they could be detected by XAS.

Acknowledgements

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