XAS study of the influence of Si, Ce and Mo ionic implantation on the oxidation behaviour of AISI 304 stainless steel

A. Gutiérrez
Universidad Miguel Hernández, Avda. Ferrocarril s/n, Elche 02302, Spain

M. F. López
Departamento de Corrosión y Protección, Centro Nacional de Investigaciones Metalúrgicas, Avda. Gregorio del Amo 8, Madrid 28040, Spain

F. J. Pérez Trujillo and M. P. Hierro
Departamento de Ciencia de Materiales, Universidad Complutense de Madrid, Spain

Stainless steels are materials that, due to their high Cr-content, develop a protective oxide layer on the surface. The properties of this passive film, like adherence or stability, determine the corrosion resistance of these materials [1]. Much work has been devoted to modify these passive layers by adding small amounts of some reactive elements, which could improve their corrosion behaviour. One of the techniques used to modify the surface composition of materials is ionic implantation. The changes introduced at the material surface by this technique and the effects on the corrosion behaviour can be evaluated by investigating the chemical composition of the surface. The aim of the present study is to investigate the chemical composition of the passive layer generated spontaneously on the AISI 304 stainless steel (SS) with and without Si, Mo and Ce ionic implantation by using soft x-ray absorption spectroscopy. X-ray absorption spectroscopy (XAS) is a particularly suitable technique to study the chemical state of the different species in the outer layer. The absorption cross section is measured by detecting electrons, which escape from the surface after the decay of the core hole. In the total electron yield mode (TEY) in which all escaping electrons are countered, the probing depth is of order of 70-100 Å for transition metal *2p* edges [2]. Applying this technique at the transition metal *2p* edges in TEY mode, it is possible to determine the main contributions to the composition of the passive layers formed spontaneously on the surface of these materials.

The chemical composition of the AISI 304 SS sample was (wt %) 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 remainder Fe. The AISI stainless steel sample was studied as-received and after Mo, Ce, and Si ionic implantation processes. As reference materials Fe, Cr, and Ni pure metal polycrystalline samples and FeO, oxidized Fe, and oxidized Cr samples were also investigated. The pure metal samples were scraped *in situ* in the UHV chamber with a diamond file. 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 was also scraped *in situ* in the UHV chamber with a diamond file to remove surface contaminants.

XAS measurements were carried out at the SX700/I soft x-ray monochromator at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY). XAS spectra were obtained 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.

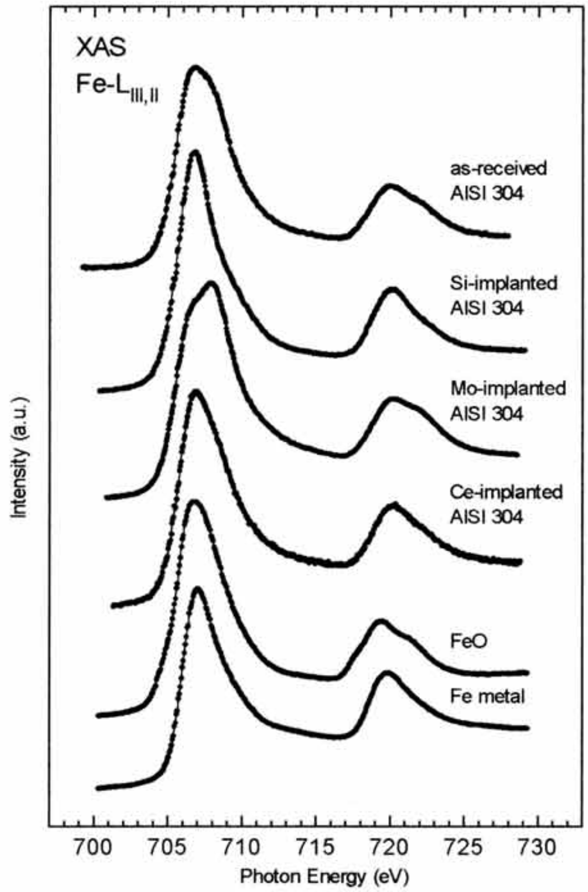

Figure 1: Fe *2p* soft x-ray absorption spectra for all AISI 304 SS samples, Fe metal and FeO.

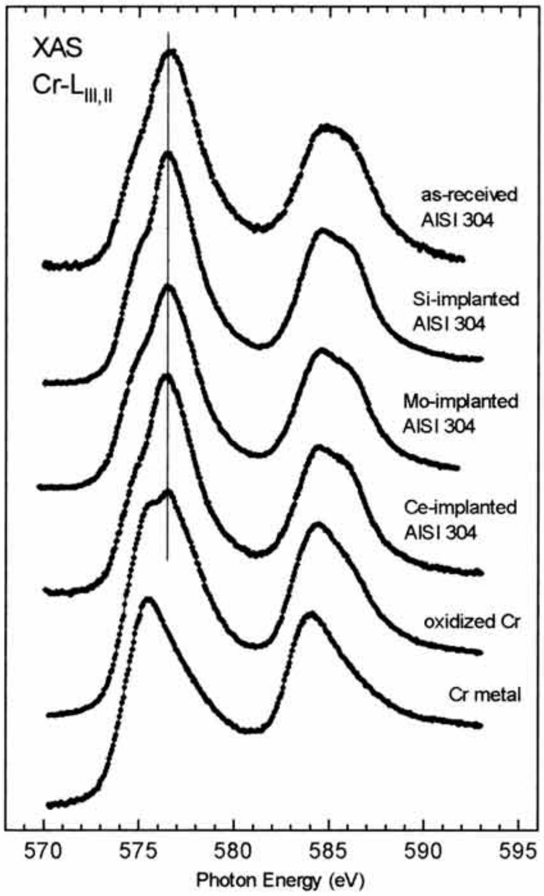

Figure 2: Cr *2p* soft x-ray absorption spectra for all AISI 304 SS samples, oxidized Cr and Cr metal.

Figure 1 represents the Fe *2p* soft x-ray absorption spectra of all AISI 304 stainless steel samples as-received and after Si, Mo, and Ce ionic implantation, as well as Fe metal and FeO for comparison. The different spectral shapes obtained for the AISI 304 samples indicate that the ionic implantation process causes chemical changes at the outer layers of the material. The Fe *2p* spectrum of the as-received AISI 304 sample is similar to that of FeO although the presence of a spectral structure at ≈708 eV is clearer in the AISI 304 sample. This effect could be assigned to a small amount of Fe_2O_3 as can be deduced by comparing with the Fe_2O_3 spectrum of previous works [3], which would increase the spectral structure at ≈708 eV. The Fe *2p* Si-implanted AISI 304 sample exhibits, however, the typical spectrum of Fe metal suggesting that the Fe signal is coming mainly from the substrate, and, therefore, in this sample Fe oxides are not present in the passive layer. On the other hand, the shape of the Fe *2p* Mo-implanted AISI 304 signal is rather different to the other AISI 304 samples. This shape is typical of Fe_3O_4 suggesting the formation of this oxide in the passive layer. Finally, the Fe *2p* Ce-implanted AISI 304 spectrum exhibits mainly the presence of Fe metal coming from the substrate as can be deduced from its similarity with the Fe metal signal. However, the spectral shape is slightly broader with a more pronounced spectral feature at ≈708 eV, which may be assigned to a small amount of Fe oxide.

Figure 3 shows the Cr *2p* soft x-ray absorption spectra of all AISI 304 stainless steel samples as well as oxidized Cr and Cr metal for comparison. The typical shape of Cr_2O_3 soft x-ray absorption spectrum exhibits in the $2p_{3/2}$ region a main peak at ≈ 576.5 eV, and a distinctive shoulder located at ≈ 575 eV [3]. The spectrum of Cr metal has a different shape to that of Cr_2O_3 with a main peak located at ≈ 575.5 eV. The oxidized Cr spectrum that corresponds to the native oxide film is a mixture of metallic chromium and Cr_2O_3. As the metallic contribution increases, also the intensity of the shoulder at ≈ 575.5 eV increases. The spectrum of Si-implanted AISI 304 sample exhibits the spectral feature corresponding to the shoulder at ≈ 575 eV better defined than for the other samples. This result suggests that the spectral width of the two peaks, shoulder and main structure, is smaller in the Si-implanted AISI 304 sample than for the other samples, which indicates the presence of the primary Cr_2O_3 oxide structure as can be concluded by comparing with the Cr_2O_3 spectrum of previous works [3]. In the Mo-implanted, Ce-implanted and as-received AISI 304 Cr *2p* signals although the spectral shapes are similar to Cr_2O_3 the shoulder is not so well defined. This result suggests the modification of the primary Cr_2O_3 oxide structure in these samples. The Cr *2p* Mo-implanted AISI 304 spectrum shows the broadest $2p_{3/2}$ structure with the highest shoulder intensity. This intensity is higher when the Cr emission corresponding to metallic Cr is higher. Therefore, it can be concluded that the passive layer of the Mo-implanted sample is narrower than for the other AISI 304 samples.

Both Fe and Cr *2p* spectra suggest a clear influence of the different element ionic implantation on the composition of the passive layer of the AISI 304 stainless steel sample. The main effect produced by Si-implantation is the formation of a Cr_2O_3 outer layer which could give to the material substrate more stability. On the contrary, Mo seems to favour the formation of a thin layer formed by a mixture of Fe_3O_4 and Cr_2O_3. The intermediate case is given by Ce-implantation, which allows the formation of a layer composed mainly by Cr_2O_3 with a modified structure.

This work was supported by the EU under the TMR programme, contract number ERBFMGE-CT95-0031. We acknowledge the BESSY staff for their help.

[1] J. M. Bastidas et *al.*, *Corros. Sci.* **40**, 431 (1998).
[2] M. Abbate et *al.*, *Surf. Interface Anal.,* **18**, 65 (1992).
[3] L. Soriano et *al.*, *Surf. Interface Anal.,* **20**, 21 (1993).