SYNCHROTRON RADIATION STUDY ON THE HIGH TEMPERATURE BEHAVIOUR OF ION IMPLANTED AISI 304 STAINLESS STEEL

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High temperature corrosion is a phenomenon of great scientific and technological importance due to its detrimental effect on materials used for elevated temperature applications. Stainless steels have found a widespread use because of their good properties/price ratio. The high oxidation-resistance of stainless steels makes them good materials also for elevated temperature applications. However, nowadays much work is being devoted to modify the stainless steel surface by different methods with the aim of improving their oxidation resistance. Among the surface modification techniques, ion implantation presents several advantages: no high temperatures are needed, the bulk material remains unaffected after the implantation process, and the surface to be modified can be tailored by controlling the accelerating potential and the implanted dose. In previous works [1,2], X-ray absorption spectroscopy (XAS) in total electron yield (TEY) mode has been proved to be very suitable to study the chemical state of the species located at the stainless steel outer layer.

The aim of the present work is the study of the possible chemical changes induced at the material surface of AISI 304 stainless steel by ion implantation and its effects on the high temperature behaviour. To perform this study, we apply XAS at the transition metal *2p* and at the oxygen *1s* edges in TEY mode to determine the composition of the oxide layer of AISI 304 stainless steel. This material was studied without and with Si, Mo, and Ce ion implantation after oxidation at 1173 K for 32 hours.

The chemical composition of the AISI 304 stainless steel 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. Some of the samples were exposed to an ion implantation process of Mo, Ce and Si. To study the oxidation behaviour of these materials both the as-received sample and the samples after Mo, Ce, and Si ion implantation were studied after an oxidation treatment at 1173 K for 32 hours. As reference materials oxidized Fe, and oxidized Cr samples were also investigated. XAS measurements were carried out at the PM-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.

As an example, Figure 1 represents the Mn *2p* soft x-ray absorption spectra of all AISI 304 stainless steel samples. These spectral shapes as well as the Cr *2p* XAS spectra, which are not showed, indicate that after the oxidation treatment the outer layer is formed mainly by spinel-type oxides. These results are in agreement with previous conventional X-ray diffraction data obtained in these samples, where $Mn_{1.5}Cr_{1.5}O_4$ spinel-type oxides were identified together with some amount of $Cr_{1.3}Fe_{0.7}O_3$ oxides.

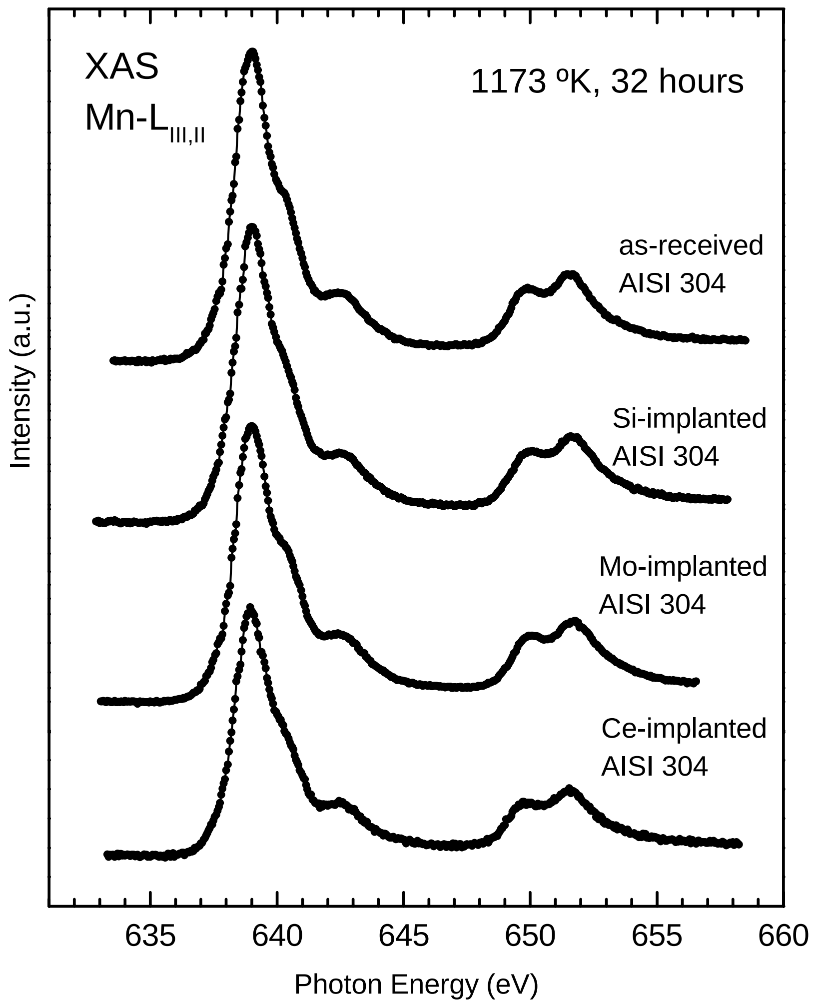

Figure 1: Mn *2p* soft x-ray absorption spectra for all AISI 304 stainless steel samples.

The O *1s* XAS spectra of all samples as well as oxidized Fe and oxidized Cr as reference samples are represented in Figure 2. These spectral shapes exhibit some differences which can be attributed to slight chemical differences between different element ion implantation processes.

An important parameter in determining the elevated temperature behaviour of stainless steels is the Cr/Fe ratio in the oxide layer, since a higher value of this parameter is associated with a higher oxidation resistance. Figure 3 represents the Cr/Fe ratio calculated from the XAS spectra for the heat treated samples. The Mo implanted sample has the lower Cr/Fe ratio followed by the Ce implanted sample, while the higher ratio was showed by the Si implanted stainless steel. These ratios are in agreement with the oxidation kinetics curves previously obtained [3]. Mo implantation on stainless steels leads to a linear oxidation behaviour at high temperatures. The higher Cr/Fe ratio found on the Si-implanted steel could explain its higher mass gain at the first stages of oxidation giving rise to the formation of a protective oxide scale composed of $Cr_{1.3}Fe_{0.7}O_3$ and $Mn_{1.5}Cr_{1.5}O_4$.Once this oxide scale is established, the kinetics behaviour change dramatically from linear to parabolic. A similar behaviour to Si implanted sample, i.e. parabolic oxidation, is found for the Ce implanted stainless steel. These results emphasise the different oxidation behaviour of the different element implanted materials.

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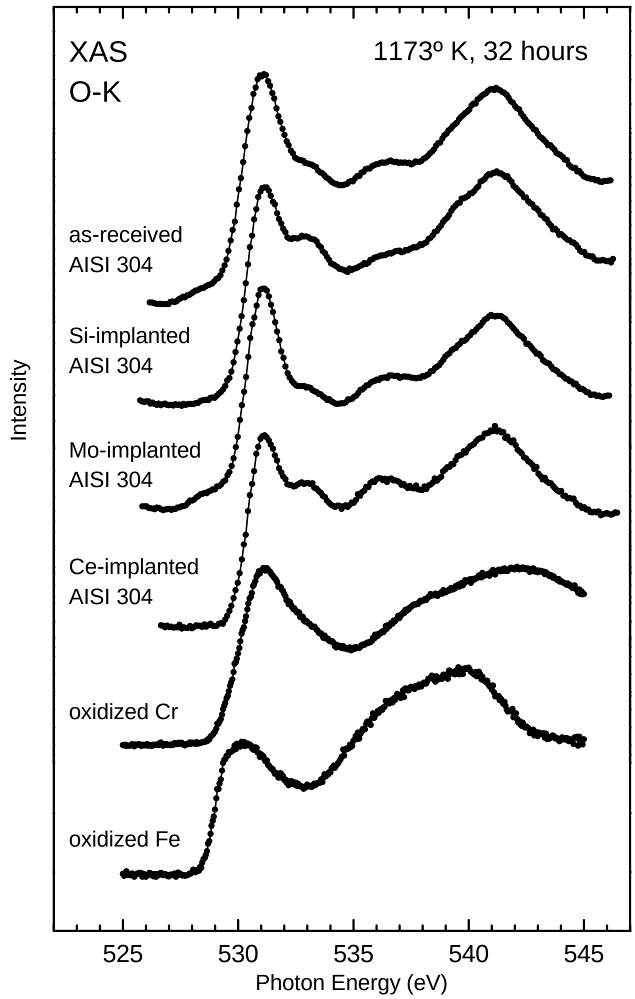

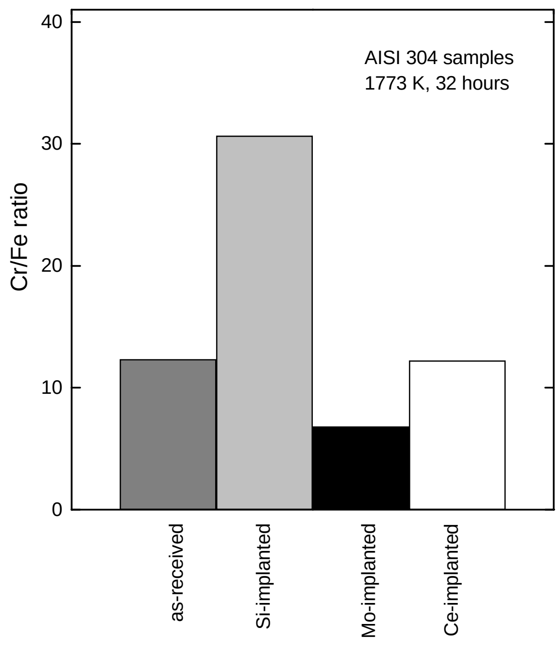

<u>Figure 2</u>: O *1s* soft x-ray absorption spectra for all AISI 304 stainless steel samples, oxidized Cr and oxidized

<u>Figure 3</u>: Cr/Fe ratio calculated from the XAS data.

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[3] A. Gutiérrez, M. F. López, F. J. Pérez Trujillo, M. P. Hierro, F. Pedraza, *Surf. Interface Anal.* (in print).