

A Comparative Study of the Native Oxide on 316L Stainless Steel by XPS and ToF-SIMS

S. Tardio^{1*}, M-L. Abel¹, R. Carr², J. E. Castle¹, J. F. Watts¹

¹ Department of Mechanical Engineering Sciences, University of Surrey, Guildford, Surrey, GU2 7XH, U.K.

² Huntsman PU, Everslaan 45, B-3078 Everberg, Belgium

*Corresponding author: s.tardio@surrey.ac.uk

Introduction

The native oxide film on stainless steels is very thin (ca. 2 nm) and known to be readily modified by immersion in aqueous media. XPS and ToF-SIMS are employed to investigate the nature of the film in the air-formed and water emmersed states. In particular the nature of the film in terms of oxide, hydroxide and water content and any preferential dissolution that occurs on water immersion is examined. As conventional ion bombardment is known to promote the solid-state redox reaction between iron oxide and chromium metal, an ARXPS study is employed.

Experimental

Stainless steel 316L Samples of 10 x 10 mm² were etched free of oxide in the XPS spectrometer and analysed after both air exposure and air exposure followed by high purity water immersion. XPS analyses were achieved by using a Thermo Scientific Theta Probe spectrometer. The samples were argon ion etched to remove the oxide using a Thermo EX05 ion gun.

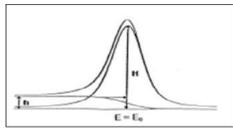
A TOF.SIMS⁵ (ION-TOF GmbH, Münster, Germany) system was employed for ToF-SIMS analyses. Static SIMS condition (ion dose < 1 x 10¹³ ions cm⁻²) using a 9.5 keV Bi₃⁺ primary ion beam, rastered over an area of 100 x 100 μm. Both positive and negative SIMS spectra were acquired over a mass range of 1-850 u. Sputter profiling was carried out using Cs⁺ ion sources in the non-interlaced mode.

The XPS data were fitted using a background function plus a peak function. The peak is a Voigt function (G/L) defined by binding energy. The background consists of a Shirley function which has been multiplied with a polynomial, P, so as to produce a background tail.

$$P = k + B_1 (E - E_0)^*$$

B₁: The slope parameter of the tail.

k: Kappa parameter; a shape parameter which defines the intensity of the intrinsic losses.



$k = h/A^*$
h: maximum value of the linear background projected to the peak centre
A: Voigt (G/L) peak area.

Figure 1: Peak's shape parameter*

*J.E. Castle et al., J. Electr. Spectr. 106 (2000) 65-80

XPS Analysis

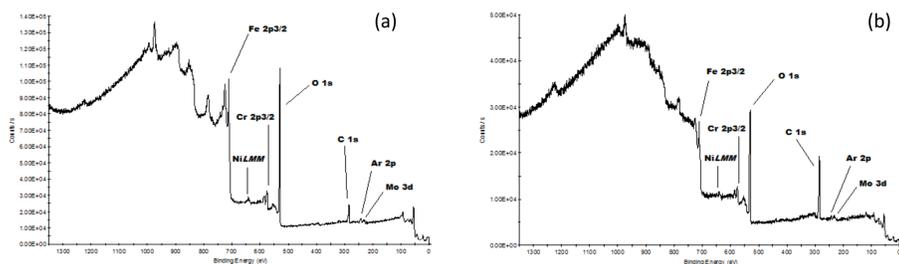


Figure 2: XPS survey spectra of (a) air exposed (b) water exposed stainless steel 316L

ToF-SIMS Analysis

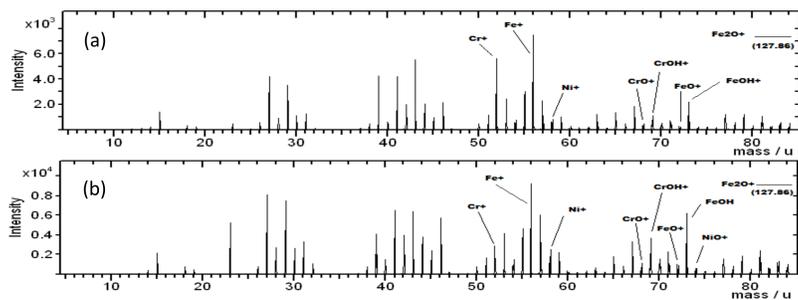


Figure 6: SIMS positive ion spectra of (a) air exposed (b) water exposed stainless steel 316L

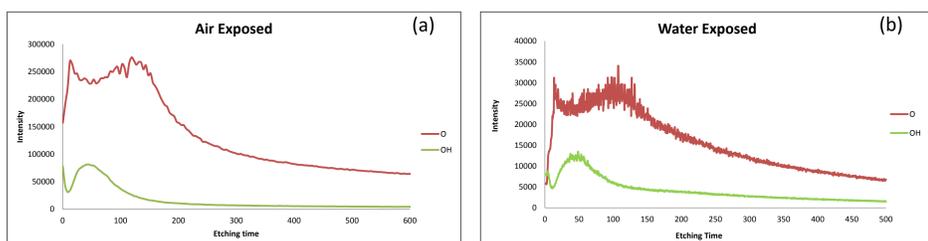


Figure 7: SIMS negative ion profile of (a) air exposed (b) water exposed stainless steel 316L

Conclusions

- 1) For a good peak fit of transition metal peaks, the p (or d) doublet peaks should be fitted together; the energy loss tail of each individual component should be taken into account as well as the satellite structure.
- 2) For both the air and water exposed 316L stainless steel samples there seem to be a contamination and a water adsorbed layer followed by an hydroxide layer before the oxide. The water and hydroxide layer are thicker in the water exposed sample. It is suggested that the Mo is situated between the oxide and the substrate. In the water exposed sample preferential dissolution of Fe₂O₃ is observed.
- 3) The combination of XPS and SIMS is a powerful tool in the field of corrosion science.

Discussion and Results

The survey spectrum of the air exposed sample shows, as illustrated in Figure 2a, the presence at the surface of a low level of carbon contamination and implanted argon. There are peaks characteristic of the native oxide film and sub-surface metal: O1s, Cr2p, Fe2p, weak NiLMM feature and the Mo3d doublet. As it can be seen in Figure 1b the same peaks are visible for the water exposed sample. Nevertheless some important differences between the two samples can be noticed. In the water exposed sample the carbon contamination is higher (25.6% against 13.7%) and the Fe intensity is lower (18.9% against 23.8%). The background of a peak is related to the extrinsic energy losses associated with the transport of photoelectrons through the solid; the deeper is the element in the solid the more its electrons will be inelastically scattered showing an higher binding energy and so giving a rising background on the left side of the peak. Inspection of the energy loss backgrounds of Fe and Cr (from Figure 1) seems to suggest that in the first sample the iron oxide is present above the chromium oxide layer. In the second sample the Fe shows a negative background meaning that the signal comes from underneath the surface. This could be explained by a preferential dissolution of Fe in water.

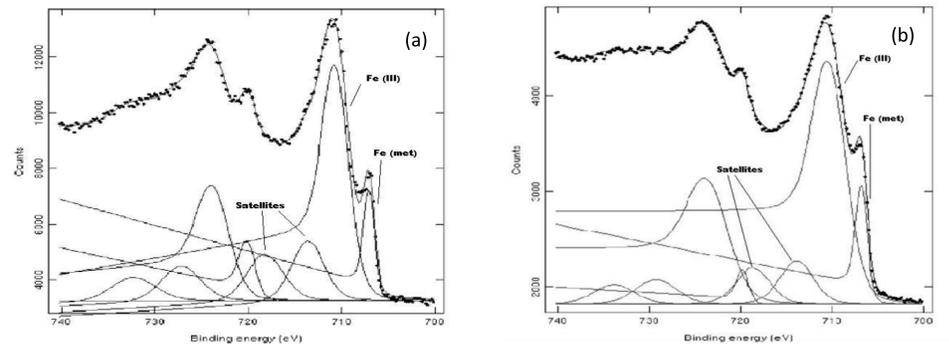


Figure 3: XPS Fe2p high resolution spectra: (a) air exposed (b) water exposed stainless steel 316L

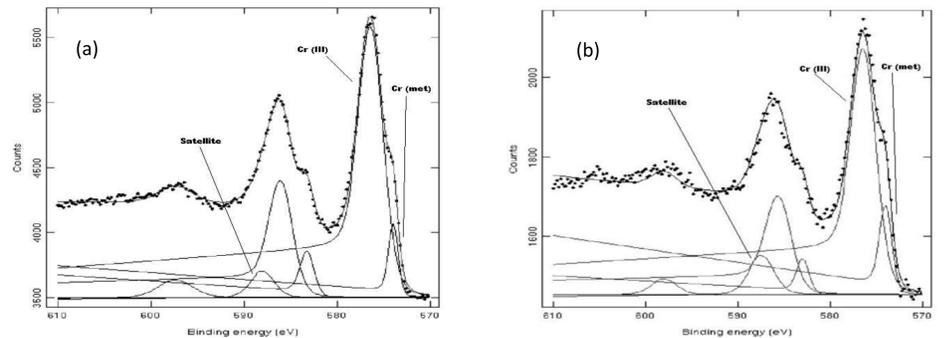


Figure 4: XPS Cr2p high resolution spectra: (a) air exposed (b) water exposed stainless steel 316L

This is confirmed by the high resolution spectra of Fe and Cr for both the samples. In Figure 3 a huge difference in both background tail and intensity of the peaks can be noticed, whilst in Figure 4 there is no sensible difference in the tail and the difference in intensity is less than in the Fe case. Table 1 (obtained using the angle resolved data) shows that a big part of the iron oxide is dissolved in water whilst the chromium oxide remains almost the same.

Oxide	Air formed thickness (nm)	Water formed thickness (nm)
Fe ₂ O ₃	2.9	1.4
Cr ₂ O ₃	4.0	3.7

Table 1: Fe and Cr oxides thickness obtained using the Beer-Lambert equation considering the approximation Overlayer/substrate: Fe(III) on pure Fe and Cr(III) on pure Cr.

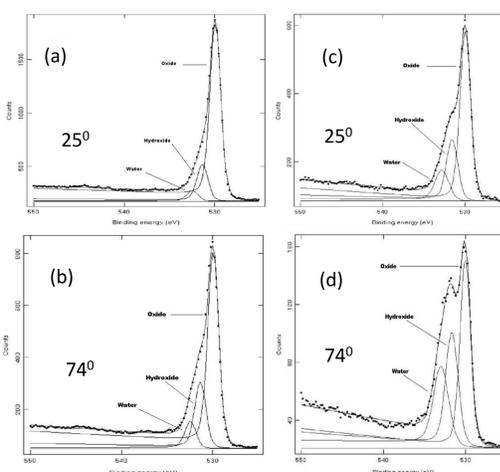


Figure 5: XPS O1s high resolution spectra (a) air exposed 25° (b) air exposed 74° (c) water exposed 25° (d) water exposed 74° stainless steel 316L. (angles from the normal to the surface)

The high resolution O1s spectra of Figure 5 show that there are water and hydroxide layers present at the surface of both the samples. It also shows how these layers are much thicker in the water exposed sample.

The SIMS positive spectra (Figure 6) show the presence of Fe, Cr and Ni on the surface but no Mo which is visible in the XPS in different oxidation states. This seems to suggest the Mo is present at the interface between the oxide and the substrate. The negative SIMS profile illustrated in Figure 7 confirm the presence of a hydroxide layer above the oxide one.