



Cation profiling of passive films on stainless steel formed in sulphuric and acetic acid by deconvolution of angle-resolved X-ray photoelectron spectra

Jonas Högström*, Wendy Fredriksson, Kristina Edstrom, Fredrik Björefors, Leif Nyholm**, Claes-Olof A. Olsson

Department of Chemistry—Ångström, The Ångström Laboratory, Uppsala University, Box 538, 751 21 Uppsala, Sweden

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ABSTRACT

An approach for determining depth gradients of metal-ion concentrations in passive films on stainless steel using angle-resolved X-ray photoelectron spectroscopy (ARXPS) is described. The iterative method, which is based on analyses of the oxidised metal peaks, provides increased precision and hence allows faster ARXPS measurements to be carried out. The method was used to determine the concentration depth profiles for molybdenum, iron and chromium in passive films on 316L/EN 1.4432 stainless steel samples oxidised in 0.5 M H₂SO₄ and acetic acid diluted with 0.02 M Na₂B₄O₇ · 10H₂O and 1 M H₂O, respectively. The molybdenum concentration in the film is pin-pointed to the oxide/metal interface and the films also contained an iron-ion-enriched surface layer and a chromium-ion-dominated middle layer. Although films of similar composition and thickness (*i.e.*, about 2 nm) were formed in the two electrolytes, the corrosion currents were found to be three orders of magnitude larger in the acetic acid solution. The differences in the layer composition, found for the two electrolytes as well as different oxidation conditions, can be explained based on the oxidation potentials of the metals and the dissolution rates of the different metal ions.

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1. Introduction

It is well-known [1,2] that the high corrosion resistance of stainless steels is due to the formation of a 1–3 nm thick passive layer, mainly composed of chromium oxide, but also containing iron and molybdenum oxides. The thickness and composition of passive layer have been studied with different *ex situ* surface-analytical techniques for almost half a century [3–8]. Today, transmission electron microscopes are sufficiently powerful to allow studies of the films and concentration gradients below the oxide [9] but not elemental gradients within the passive film. In the past decades, *in situ* techniques have made it possible to follow film growth and changes in composition, as well as structures on a sub-nanometre scale with unprecedented temporal resolution [10–13]. *In situ* techniques can give access to information regarding the film dynamics, making it possible to refine existing models for film growth and

dissolution [12,13], and have also provided empiric information for film descriptions based on concepts such as the density functional theory [14]. Still, the limited thickness of the passive films and their dynamic composition make them elusive to the experimentalist. The ideal experimental technique for studies of passive films should have a surface sensitivity on the sub-nanometre level and provide depth information within a range of 3–4 nm. This excludes most sputtering techniques, as they tend to disturb the concentration gradients within the film. As has been demonstrated previously [15–18], angle-resolved X-ray photoelectron spectroscopy (ARXPS) is a good candidate for this type of experiments since it is non-destructive and the desired surface sensitivity can be obtained by applying a set of analysis angles with different effective analysis depths. This approach has consequently been successfully applied to thin-film analyses ever since the 1970s [19]. Numerical algorithms for deconvoluting the intensities into cation profiles are also available in the literature [20,21] and recent developments include the introduction of matrix-based analytical methods [22]. Compared to simpler systems such as SiO₂ or TiO₂, for which analytical solutions for the concentration profiles can be obtained [19,20], the passive film on a stainless steel constitutes a significantly more complex system with two, three or even more cations interacting to give the film its unique properties. In the latter case, the analysis requires a set of carefully selected boundary conditions. Access to

* Corresponding author. Tel.: +46 18 471 3737.

** Corresponding author. Tel.: +46 18 471 3742.

E-mail addresses: jhogstrom@gmail.com (J. Högström), wendy.fredriksson@kemi.uu.se (W. Fredriksson), kristina.edstrom@kemi.uu.se (K. Edstrom), fredrik.bjorefors@kemi.uu.se (F. Björefors), leif.nyholm@kemi.uu.se (L. Nyholm), drclabbe@kth.se (C.-O.A. Olsson).

the cation concentration profiles within passive films is required to reach an improved understanding of how the passive film is formed and how it interacts with the environment. Such profiles can also be used as a base for theoretical modelling and could therefore also be employed to tailor the properties of passive films with respect to different applications. There is therefore a need for the development of new and straightforward approaches for the calculation of metal ion concentration gradients in passive films.

One element of particular interest with respect to passive films on stainless steel is molybdenum. In empirical formulae, molybdenum is given a stronger influence on pitting resistance than chromium, but given its relatively low abundance in the bulk metal, as well as its rather complex chemistry [23–26], it has been difficult to obtain concentration profiles for molybdenum in passive films. The latter is due to the fact that destructive techniques may give rise to misinterpretations since molybdenum ions are sputtered slower than the iron and chromium ions [27–30]. In a recent study, Mesquita et al. [26] demonstrated that the presence of molybdenum in different types of stainless steels affects the properties of the passive films significantly and that the composition of the passive film depends on if the passive films were formed at open circuit in air or in solutions with different pH values. In this context it is also worth noting that pure molybdenum does not form a proper passive film in aqueous solutions at anodic potentials [27]. It has, however, been shown that it is possible to use thermal oxidation [23,24], or anodic polarisation in glacial acetic acid containing 0.02 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and 1 M H_2O [31] to obtain molybdenum oxide films. Olsson et al. [25] studied alloys with very high, *i.e.*, about 20 wt.%, bulk contents of molybdenum, manufactured using physical vapour deposition (PVD), and found molybdenum to be present in the +IV and +VI oxidation states within the film, much in line with the work of Brox and Olefjord [27]. The reasons why a molybdenum oxide film has been found to be formed in glacial acetic acid solutions but not in aqueous solutions is, at present, not fully understood. This question therefore requires additional attention since its answer may help to provide a better understanding of how molybdenum oxides are included in passive films on stainless steels.

In this paper, we demonstrate that the concentration profiles for molybdenum, as well as iron and chromium, in passive films on a commercial stainless steel, 316L/EN 1.4432, can be obtained with a straightforward ARXPS approach. The approach used is based on a series of approximations involving: (1) a determination of the film thickness using the conventional oxide/metal peak ratios at an analysis angle close to perpendicular to the surface; (2) the subsequent use of only the oxide intensities and (3) the assumption that the density of the film is constant throughout the film. Although the latter is not strictly valid since the film consists of a hydroxide as well as an oxide layer, it is shown that the approach provides results enabling qualitative comparisons of the compositions and cation concentration gradients for different oxidation conditions. The concentration profiles for iron, chromium and molybdenum in passive films on 316L/EN 1.4432 stainless steel samples oxidised in 0.5 M H_2SO_4 and acetic acid diluted with 0.02 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and 1 M H_2O , respectively, are compared and it is shown that the structure of the passive layers can be explained merely based on the oxidation potential of the metals and the dissolution rates of the obtained metal ions in the two electrolytes. We are not aware of any previous studies in which ARXPS has been used to calculate and compare fully deconvoluted concentration profiles for molybdenum, iron and chromium in passive films on stainless steel obtained in different electrolytes using different oxidation conditions. The approach discussed in this paper is not only applicable to the passive films on stainless steels. It can be used on any oxide film with a thickness up to about 3 nm using conventional ARXPS. For thicker films, the attenuation will be too large and the entire film will not be probed.

The probing depth can, however, be extended to about 10–15 nm with hard X-ray photoelectron spectroscopy (XPS) [32]. Thin oxide films that also could be analysed with this technique include films on a wide range of passivating alloys such as Co–Cr–Mo (stellite) and Ni- and Ti-base alloys. It is particularly interesting to apply this method to alloys, as these may present cation gradients in the film.

2. Materials and methods

The experiments were carried out using commercially available stainless steel, *i.e.*, AISI 316L/EN 1.4432 (17Cr–11Ni–2.6Mo), samples, which were polished to mirror finish on one side using 1 μm diamond paste, followed by cleaning with Deconex 12 PA-x in an ultrasonic bath. The samples, which had a size of 10 mm \times 18 mm, were then left in contact with air for several hours to allow the formation of a native passive film. Before the experiments, the steel samples were transferred to deionised water, or an electrolyte composed of either 0.5 M H_2SO_4 , or acetic acid diluted with 0.02 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and 1 M H_2O . In the electrolytes, the samples were either polarised electrochemically, or maintained at the open circuit potential (OCP) to enable the OCP to be measured after 900 s.

The electrochemical three-electrode set-up used in the polarisation experiments comprised an Ag/AgCl (sat. KCl) reference electrode, a Pt counter electrode and the steel samples serving as the working electrodes. The reference electrode was placed in a bridge containing the electrolyte to minimise the effect of the leakage of chloride into the solution on the experiments. The reference electrode was positioned close to the backside of the steel sample, while the counter electrode was placed about 15 mm in front of the steel sample. The steel sample was hung in a platinum wire (0.3 mm diameter) that also acted as the electrical contact to the working electrode. Since the samples were completely submerged, the backsides and edges of the steel samples also contributed to the currents. Although this complicated the determinations of the current densities, the approach still allowed comparisons of different samples and different polarisation conditions, which was the main objective of this study. Prior to the polarisation experiments, which were performed at 22 °C with a Solartron 1285 potentiostat, the steel samples were pre-polarised at $-1.5\text{ V vs. Ag/AgCl}$ (sat.) in 0.5 M H_2SO_4 for 60 s. Next, the samples were either left in this solution or transferred to a solution composed of glacial acetic acid containing 0.02 M $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and 1 M H_2O . During the polarisation experiments, the potential of the steel samples was either scanned at a rate of 10 mV/s, or stepped, to the final polarisation potential, *i.e.*, +0.7 or +1.5 V vs. Ag/AgCl (sat.), at which the sample was maintained for 15 min. The transfers of the electrodes between the electrolytes took less than 5 s and were performed by merely lowering the electrolyte containing beaker and replacing it with the new one. At the end of each experiment, the working electrode was removed from the electrolyte with the polarisation potential switched on. The steel samples were stored in deionised water during transfer to the XPS instrument.

The XPS experiments were carried out using a Physical Electronics Quantum 2000 X-ray photoelectron spectrometer employing Al K_{α} (1486.6 eV) radiation, a pass energy of 46.95 eV and an energy step of 0.4 eV. The energy scale was calibrated by placing the adventitious carbon C1s peak at 285 eV. In the ARXPS experiments, the angular set was defined to be linear in sine, giving the following angles: 85°, 64°, 53°, 44°, 37°, 30°, 24°, 17°, and 12° with respect to the sample surface. Curve fits were made using CasaXPS, while the relative sensitivity factors and asymmetry functions were taken from the PHI ESCA handbook [33]. Raw intensities were extracted from CasaXPS, while all calibration corrections were performed by the ARXPS software. To determine the curve fit parameters for the metal peaks, spectra were recorded after sputter-cleaning to

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