



Chemical-state information obtained by AES and XPS from thin oxide layers on duplex stainless steel surfaces

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ABSTRACT

Thin oxide films were produced by the exposure of polished, sputter-cleaned metallic surfaces kept in UHV to several thousands of Langmuirs at 10^{-5} mbar oxygen yielding oxide layers of several nanometers. Metallic substrates used were iron, chromium and duplex stainless steel (DSS 2205). AES and XPS profiling analyses were performed. An attempt was made to use certain features observed in the AES spectra, i.e. to correlate Fe and Cr MNN peak shapes with the chemical state of the corresponding element. A similar approach has been tried before and may, when combined with high-lateral-resolution AES, provide small-area chemical-state information. Localized chemical-state information derived from the MNN peak shapes by a Linear Least Squares Fit (LLSF) procedure appeared to match reasonably well with that provided by XPS, which is averaged over approximately 2 mm^2 . This is a plausible result for a thin homogeneous layer on a polished substrate.

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1. Introduction

This study is primarily motivated by our previous investigations of the formation of thin oxide films on DSS 2205 duplex stainless steel [1–5], as well as on AISI 300 types of stainless steel [6,7]. Alloy 2205, with 22% chromium, 5–6% nickel, and 3% molybdenum, is a nitrogen-alloyed duplex stainless steel with excellent corrosion resistance and mechanical properties [8]. It provides pitting and crevice corrosion resistance that is superior to the AISI 316L or 317L austenitic stainless steels in almost all corrosive media. It has also high corrosion and erosion fatigue properties as well as a lower thermal expansion and a higher thermal conductivity than austenitic. In addition, the yield strength is about twice that of austenitic stainless steels. This allows weight savings in the design, thus making the alloy more cost competitive with respect to 316L or 317L. DSS 2205 is particularly suitable for the temperature range from $-50 \text{ }^\circ\text{C}$ to $300 \text{ }^\circ\text{C}$. Temperatures outside this range may also be considered, but some restrictions must be applied, particularly for welded structures [9]. Some typical applications for duplex stainless steel are as follows: pressure vessels, tanks, piping and heat exchangers in the chemical processing industry; piping, tubing, and heat exchangers for the handling of gas and oil; rotors, fans, shafts, and press rolls requiring a combination of strength and corrosion resistance; cargo tanks for ships and trucks; food processing

equipment [10]. Duplex stainless steel can be expected to gradually displace the stainless steels of the AISI 300 series. The pickling of duplex stainless steel has proven to be much more difficult than that of the standard austenitic grade (AISI 300 series), and there is no complete agreement in the literature about the scale (high-temperature oxidation) dissolution mechanism in neutral pickling solutions [11–14]. One motivation for these studies was to investigate the initial phases of oxide growth on DSS 2205, also known as duplex stainless steel W. no. 1.4462. The thin oxide layers were produced by the exposure of polished and sputter-cleaned metallic samples to an oxygen atmosphere inside the rapid-entry chamber of the vacuum system. Profiling as well as non-destructive surface analysis techniques (angular-dependent XPS [4]) were used to analyze the oxide films thus formed, which simultaneously prevent any further corrosion of the bulk sample, while being an initial stage of the oxidation process for the topmost layer of the duplex stainless steel. In this study the emphasis was put on the possibility of obtaining localized chemical-state information from the AES measurements. This could be useful in investigating the earliest stages of the oxide film growths when lateral homogeneity of the films may be very low. AES allows for the extraction of information with lateral resolution below 100 nm, while information from XPS is averaged over macroscopic area (of the order of 1 mm^2). An approach examined by A.G. Sault for analyzing MNN lineshapes from the AES spectra of oxidized iron [15] was employed and simultaneous implementation of this approach onto oxidized iron and oxidized chromium attempted.

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2. Experimental

Polished iron, chromium and Alloy 2205 samples of approximately $8 \text{ mm} \times 8 \text{ mm} \times 1 \text{ mm}$ were prepared. These samples were then fixed onto holders for the AES/XPS investigations by means of UHV-compatible double-sided adhesive tape. The sputter-cleaning of the samples was performed under UHV conditions inside the main vacuum chamber of the AES/XPS apparatus, into which the samples were introduced via a rapid-entry airlock. The thin oxide layers were produced on the samples' surfaces by the exposure of the sputter-cleaned samples to approximately 10^{-5} mbar of oxygen inside the rapid-entry chamber, which was previously pumped down to 10^{-8} mbar. Thus, an approximately 99.9% oxygen atmosphere was ensured in the rapid-entry chamber. The exposure time was 10 min, corresponding to an exposure of several thousands of Langmuirs ($1 \text{ L} = 1.33 \times 10^{-6} \text{ mbar} \times \text{s}$). Not all iron and chromium samples were submitted to the oxygen exposure since some were to be used for measurements of metallic peak shape and others for the measurements of the oxide peak shape.

Sample was assumed to be at room temperature. Whether in airlock (oxygen exposure) or in the analysis chamber (sputtering, measurements), sample was in good thermal contact with the large body (approximately 300 kg stainless steel) of a vacuum system. Quick estimate assuming that total impinging ions energy is spent on sample heating and disregarding thermal contact shows that for the iron sample of this size at given sputtering parameters $dT/dt \approx 0.1 \text{ K/s}$. While total sputtering times go beyond 1000 s, they are divided into numerous subintervals with lengthy data acquisitions inbetween. In several surface segregation studies on electrical steels (e.g., Ref. [16]) sample temperature was measured by thermocouple attached to the upper surface of the similarly sized sample. It was established that any heating of the sample due to the long time ion sputtering with sputtering parameters as in this study was below 1 K.

The AES and XPS depth profiles of the oxide layers were measured with a VG Microlab 310F SEM/AES/XPS. For all the XPS measurements $\text{Mg } K_{\alpha}$ radiation at 1253.6 eV with anode voltage \times emission current = 12.5 kV \times 16 mA = 200 W power was used. For the depth profiling Ar^{+} energy of 3 keV at 1 μA ion current was used over the $4 \times 4 \text{ mm}^2$ area. Similar ion-beam parameters were used for sputter-cleaning the sample prior to oxidation, except that the raster area was closer to $10 \times 10 \text{ mm}^2$ in this case. A rough estimate for the sputtering rate at these profiling parameters is of the order of 1 nm/min, which is consistent with some calibration measurements performed on metallic and oxide-type samples as well as with some reference data for sputtering rates for Fe and Cr and their oxides [17]. Sample rotation during profiling was not used, since it is not compatible with the high lateral resolution obtainable by the AES.

The spectra were acquired using Avantage 3.41v data-acquisition & data-processing software supplied by the SEM/AES/XPS equipment manufacturer. The thickness of the passive layer was estimated by argon-ion sputtering for different time intervals. Casa XPS software [18] was also used for detailed data processing.

3. Results and discussion

Low-kinetic-energy MNN peaks have been shown to change shape with the chemical state [15]. It is to be noted, that differential rather than integral spectra are used here (as well as in Ref. [15]) since Cr MNN and Fe MNN in integral spectrum are superimposed onto high and highly-sloped background. In Fig. 1a series of AES spectra with Cr MNN, Fe MNN, Cr LMM, Fe LMM and O KLL peaks after successive sputterings of a thin oxide layer on DSS 2205 stainless steel are shown. In Fig. 1b only Cr MNN ($\sim 37 \text{ eV}$) and Fe

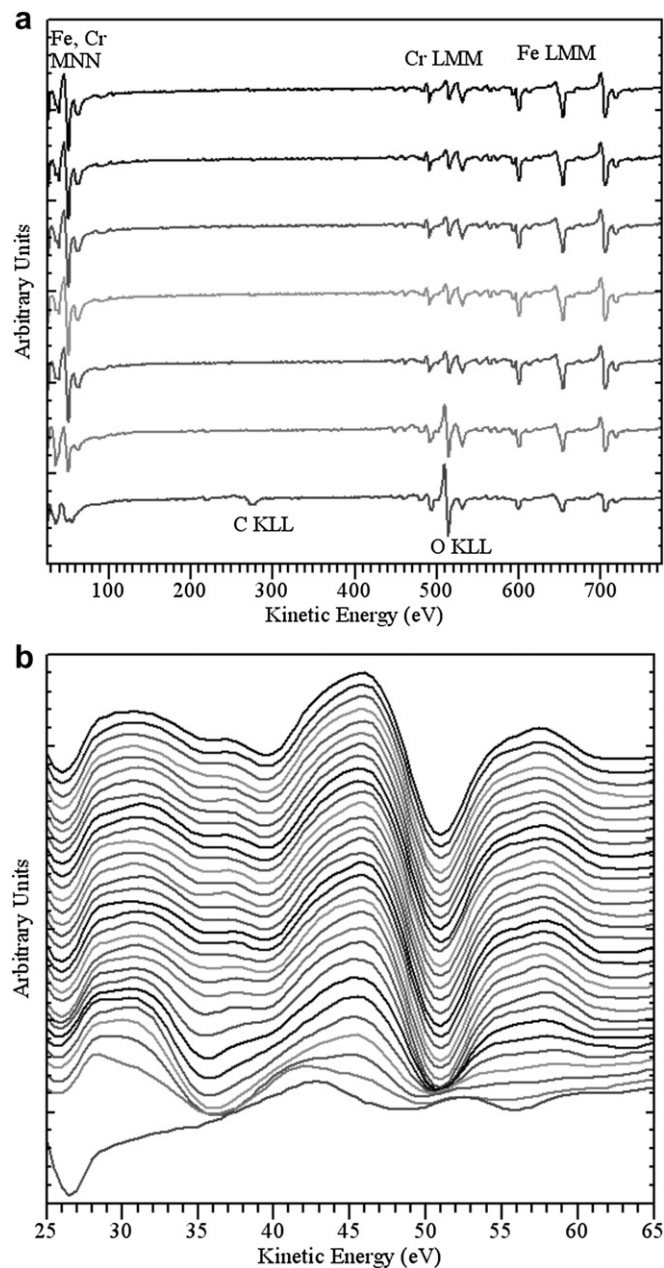


Fig. 1. AES spectra from surface of the oxide layer into the bulk in 100 s sputtering time intervals (a) Cr MNN ($\sim 37 \text{ eV}$) and Fe MNN ($\sim 51 \text{ eV}$) peaks from the same set of spectra in 20 s sputtering time intervals (b) Increasing sputtering time is shown upwards. Changes in the shapes of the Cr MNN and Fe MNN peaks can be observed.

MNN ($\sim 51 \text{ eV}$) peaks from the same series are shown. The topmost spectrum was acquired after the final sputtering. Changes in the shapes of the peaks on the way from the surface of the oxide layer, through and beyond it can be observed. In Ref. [15] similar series of Fe MNN spectra with changes due to increasing oxygen exposure is successfully simulated by linear combination of standard spectra from pure iron and iron oxide. Our sample was somewhat more complex due to considerable chromium content, thus necessitating 4 standard spectra. The Cr MNN and Fe MNN peaks on the oxidized and sputter-cleaned chromium and iron samples were measured to provide the standard peak shapes corresponding to the metallic and oxidized Cr and Fe, oxides being predominantly Cr_2O_3 and Fe_2O_3 as expected from sample preparation and confirmed by XPS. The linear combination of standard peak shapes shown in Fig. 2 was

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