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A study of the 42CrMo4 steel surface by quantitative XPS electron spectroscopy

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Abstract

Quantitative X-ray photoelectron spectroscopy was used to characterize the native oxide film formed on 42CrMo4 steel surface by air exposure in normal conditions. In order to determine the thickness and composition of the oxide layer we have used a stacking layer model together with experimental XPS sputtering depth profiling. At a nanoscale study, to obtain quantitative results one must take into account fundamental parameters like the attenuation depth of photoelectrons. We have found that both lepidocrocit (γ-FeOOH) and magnetite (Fe_3O_4) were present and the total thickness of the oxide layer was 16 monolayers.

Keywords: Steel; Iron oxide; X-ray photoelectron spectroscopy; Argon ion sputtering; Depth profiling

1. Introduction

The surface of metals reacts with the ambient atmosphere contaminating the surface (adsorbed species O_2, H_2O, CO, CO_2 etc.). This native surface thin film, of nanoscale thickness, consists of different oxides, oxyhydroxides, covered by a carbon and oxygen contamination layer [1–5].

The study of oxides on metals surfaces provides information on many important industrial processes, including corrosion, catalysis and lubrication [6]. Also for subsequent thermo-chemical treatments, as nitriding, we need a clean and active surface. Usually, for UHV analysis the argon ion sputtering is used for the surface cleaning and for depth profiling, which shows the distribution of elements from the surface into the bulk of the sample.

Many studies reported the formation of a layered structure in air exposure of pure polycrystalline iron substrate. For example, Suzuki et al. [1] assert the formation of a Fe_2O_3 layer covered by FeOOH with an overall thickness of 3 nm. After exposure in air for 1 h (humidity of 70%), Bhargava et al. [2] report the formation of an 1.2 nm Fe_3O_4 and $Fe(OH)_2$ layer. Grosvenor et al. [3] found that after exposure in dry air for 2 h, the sample is covered by Fe_3O_4, followed by a mixed layer (Fe_3O_4, γ-Fe_2O_3) with Fe_2O_3 on top, with a thickness of 4.9 nm. Brundle et al. [4] depict that only the Fe_3O_4 oxide is formed in atmospheric exposure. According to the iron–oxygen equilibrium diagram [5] the thermodynamically stable structure of an oxide layer below 570 °C is composed of magnetite (Fe_3O_4) and α-Fe saturated with oxygen.

So, one may notice that there is not an unanimous view regarding the composition of the native film formed on iron surface. There are computational methods for determining the oxide thickness. QUASES™ software developed by Tougaard and co-workers [3] is using, as variables, the energy loss cross-section and the IMFP of electron contributing to the signal. A multiplicity of other algorithms was proposed for the determination of natural oxide layer formed on the surface of metals [7,8].

Our purpose is to determine the thickness and the composition of the native film formed on 42CrMo4 steel substrate, using a stacking atomic layer model describing the surface region. The theoretical approach predicts the intensity coming from different atoms (oxygen and iron, in the case of iron oxides) as a function of number of oxide monolayers. Comparing the theoretical nanoscale study and experimental intensities, and using the attenuation depth of photoelectrons

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Table 1
Chemical composition of the 42CrMo4 steel sample

	Element								
	C	Si	Mn	P	S	Cr	Mo	Cu	Ni
Content (wt.%)	0.42	0.3	0.68	0.019	0.014	0.99	0.18	0.33	0.15

we can determine the number of oxide monolayers. The experimental curve is obtained after measuring the oxygen and iron XPS peaks intensity (represented by the area of the peak, after Shirley background subtraction), at different stages of argon ion sputtering.

2. Experimental

2.1. Sample preparation

The material used in this study was a 42CrMo4 type steel with the chemical composition given in the Table 1. The sample of ~10 mm × 10 mm size and 1 mm thickness was cut from a rod which had undergone an improvement heat treatment – quenching (850 °C/water/30 min) followed by tempering (600 °C/water/45 min) – the resulted structure being sorbite. It is well known that this structure is needed for the subsequent thermochemical treatment of nitriding [5].

A native film was formed after polishing the sample surface with silicon carbide paper up to 1200 grift, and exposing it in atmosphere at ambient conditions during 30 days. The argon ion sputtering is used to eliminate this oxide layer and activate the surface for nitriding. This article presents only the experiments made for oxide cleaning, prior to nitriding.

Before the introduction into the ultra-high vacuum chamber, the sample was degreased (chemically cleaned) during 5 min in two ultrasonic methanol successive baths.

2.2. Sputter cleaning and XPS analysis

Surface analysis by XPS was performed using an EA 125 OMICRON spectrometer and an MgKα X-ray source (1253.6 eV) operated at a power of 240 W (15 kV and 16 mA). The take-off angle θ, measured with respect to the surface of the sample was 90°, while the angle between the X-ray source and the direction of the hemispherical analyzer was 50°. Typical operating pressures in the chamber were about 1×10^{-9} mbar.

The sputtering process was carried out in the preparation chamber, using an argon ion sputtering gun at normal incidence. We have made two types of cleaning using different parameters: one for the carbon and oxygen contamination layer and another for the oxide layer. The conditions for the first type of cleaning were: energy of 500 eV, intensity of 5 μA/cm^2. For the cleaning of the oxide layer we have used a medium energy bombardment (1 kV) with a ionic density of 3 μm/cm^2. For helping the cleaning process, it was necessary to hold the sample at 300 °C [9,11].

The sputter depth profile was obtained in two steps: after the carbon and oxygen contamination layer cleaning (sputtered for 2, 3, 4, 6, 8, 10 and 15 min) and after the oxide layer cleaning (sputtered for 0.5, 1, 1.5, 2, 3, 4, 6.5 and 7 h). In this article we present the results concerning the sputtering of the iron oxide. After each sputtering stage wide-scans spectra were obtained with a pass energy of 50 eV, while 20 eV pass energy was used for high resolution measurements of the O_{1s} and $Fe_{2p3/2}$ peaks. For the curve fitting to the raw data, we have used the XPS Peak Fit software.

3. Results and discussions

The XPS wide energy spectra (0–1200 eV) of the 42CrMo4 steel sample are shown in Fig. 1, after chemical cleaning (with the native surface film) and after argon sputtering during 2 min and 7 h.

It can be seen that carbon and oxygen are the principal contaminations present on the surface. In a previous work [10] we have determined the thickness of the contamination layer (carbon and oxygen coming from ambient environment) which was equal to 1.7 nm. The parameters used for this sputter cleaning were different from those used in the sputter cleaning of oxide layer, as mentioned in Section 2.2. After 2 min of argon ion sputtering only a small quantity of carbon (7%) remained on the surface. In the present study the sample was cleaned up to 7 h, having the oxide contamination layer totally eliminated.

On the clean surface, the iron electron peaks (XPS, Auger) are now well precise, having their intensities increased.

Fig. 2a and b is showing the dynamics of the sputtering process. The peaks variation (highlighted in the area of 706.7 eV, in the case of $Fe_{2p3/2}$, respectively 530.1 eV, in the case of O_{1s}), indicates the cleaning end of the oxide layers after 7 h.

Fig. 3 shows the variation of the O_{1s} and $Fe_{2p3/2}$ peaks intensity with the sputtering time. The main contribution from the O_{1s} peak is due to oxygen present in the form of oxide (O^{2-})

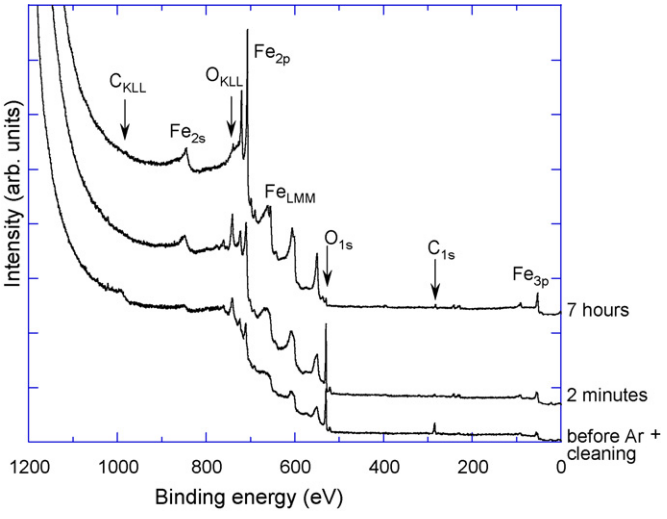

Fig. 1. XPS spectra of the 42CrMo4 steel sample after chemical cleaning and after argon sputtering during 2 min and 7 h.