

A STUDY OF STEEL SURFACE CONTAMINATION BY XPS ELECTRON SPECTROSCOPY

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Abstract:

By means of XPS electron spectroscopy we have investigated the surface contamination of 42 CrMo 4 steel samples. The determination of the thickness of the carbon contamination layer formed in atmosphere exposure is based on a three-layer stacking model (contamination, oxide layer and substrate). We have found that 7 monolayers of carbon were formed onto the surface.

Key words:

steel, surface contamination, XPS electron spectroscopy

1. INTRODUCTION

It is often recognized that fine reactions products are formed on the metals surface by exposure to air with normal moisture for a prolonged time. These products are formed due to the presence of chemisorbed gases as O₂, H₂O, CO, CO₂ etc. from ambient atmosphere. The surface of contaminated metals was thus shown to consist of three distinct layers: hydrocarbon pollution, oxyhydroxide and uniformly oxidized metal [1, 2, 3].

In this study the reactions products formed on the surface of 42 CrMo 4 steel samples may be summarized as shown in figure 1.

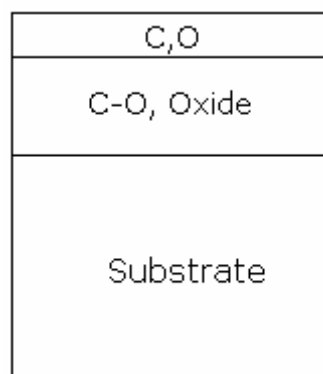


Figure1. Schematic illustration of the layered structure formed in air exposure of steel samples

X-ray spectroscopic studies were employed to investigate the composition and thickness of the carbon contamination layer formed on the 42 CrMo 4 steel samples. This technique permits a chemical analysis at a nanoscale level of the

surface of samples. Absorption of a photon results with an ionisation of atomic core-level and the ejection of an electron via the photoelectric effect. Governing this process is the well-known equation expressed by:

$$E_k = h\nu - E_b \quad (1)$$

In this formula E_k is the kinetic energy of the emitted photoelectron, $h\nu$ is the energy of the primary X-rays ($h\nu_{Mg}=1253,6$ eV and $h\nu_{Al}=1486,6$ eV), E_b is the electron binding energy. Since values of the binding energy are element-specific, atomic identification is possible through measurement of photoelectrons.

2. EXPERIMENTAL

2.1. Sample preparation

The samples were realised of 42 CrMo 4 type steel with the chemical composition given in the table 1.

Table 1. Chemical composition of 42 MoCr 4 steel samples

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

Samples of ~ 10 mm \times 8 mm size and 1 mm thickness were cut from a rod in the normalized state (860°C/air/45 minutes). All the samples were submitted to a heat treatment of quenching (850°C/water/30 minutes) followed by tempering (600°C/water/45minutes). The resulted structure is sorbite.

For the chemical cleaning (degreasing) of the samples we have used 2 methanol successive baths (each of 5 minutes duration old) in an ultrasonic bath. Immediately after this chemical cleaning, the samples were introduced into the ultra-high vacuum chamber.

2.2. Analysis by X-ray photoelectron spectroscopy

Surface analysis by XPS was performed using an EA 125 OMICRON spectrometer employing an MgK_{α} (1253.6 eV) X-ray source operated at 15 kV and 240 W. The take-off angle measured with respect to the surface of the sample was 90°. Typical operating pressures were $\sim 1 \cdot 10^{-9}$ mbar. The sputtering was carried out in a separate chamber using an argon sputtering gun operated at 500 V, 5 $\mu A/cm^2$ and $1 \cdot 10^{-4}$ mbar.

Survey (wide-scan) spectra were obtained with a pass energy of 50 eV, while 20 eV pass energy was used for high resolution measurements. The O_{1s} region peak was used for the surface chemical identification. For the curve fitting to the raw data we have used the XPS Peak Fit software.

3. RESULTS

Figure 2 show a high sensitivity and wide energy spectra (0-1200 eV) taken from a 42 CrMo 4 steel sample with the native surface thin film, using a pass energy of 50 eV, after chemical cleaning (a) and after argon sputtering during 2 minutes (b).

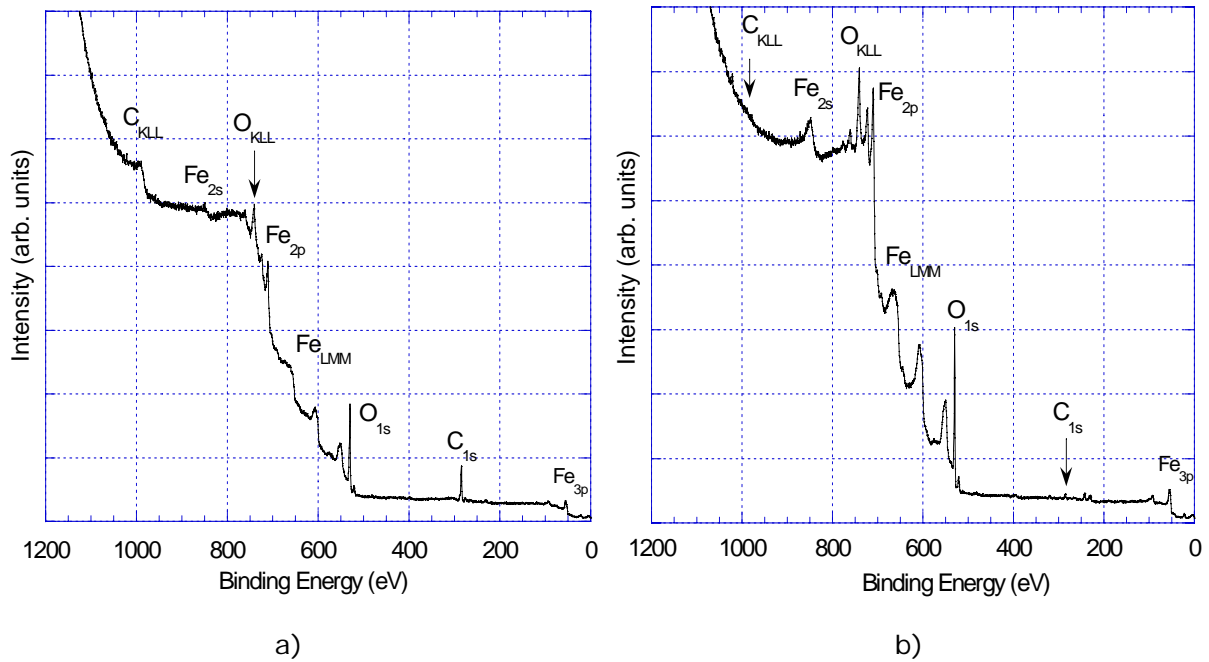


Figure 2. XPS spectra of 42 CrMo 4 steel sample after chemical cleaning (a) and after argon sputtering during 2 minutes (b)

It can be seen that carbon and oxygen are the principal contaminations, originate from the ambient environment, present on the surface. We can observe that after 2 minutes of argon sputtering the quantity of carbon extremely decreases.

On the other hand, peaks (XPS, Auger) coming from iron atoms as well oxygen atoms are now well precised, having their intensities increase.

The determination of the thickness of the carbon contamination layer formed in atmosphere exposure is made after measuring the intensities of the O_{1s} peak after 2, 3, 4, 6, 8, 10, 15 minutes of argon sputtering.

The figure 3 shows the variation of the intensity of the O_{1s} and C_{1s} peaks as a function of the sputtering time.

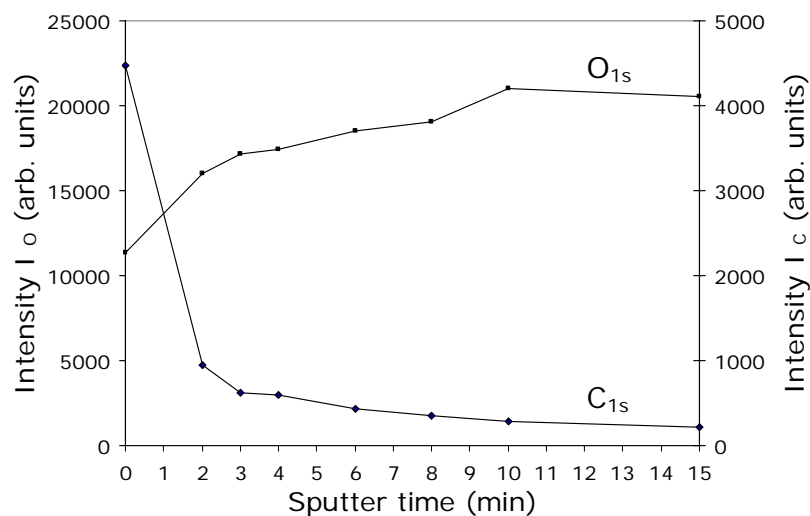


Figure 3. Variation of the intensity of the O_{1s} and C_{1s} peaks with sputtering time

One can observe that the O_{1s} peak intensity increases slowly while the C_{1s} peak intensity decreases strongly up to 2 minutes of argon sputtering. This indicates that the carbon contamination layer is thin enough to allow photoelectrons originating from the bulk metal to be detected. Also, we can conclude that the carbon contamination layer, which was covering the iron oxide layers, is practically eliminated.

Quantitative analysis of the oxygen core level

Figure 4 shows the high resolution spectra of O_{1s} region fitted to the native surface thin film raw data using XPS Peak Fit software with a Lorentzian function and a non-linear Shirley background subtraction.

The O_{1s} signal can be decomposed into four peaks (figure 4). The position of all components is in accordance with the values reported in the literature for O_{1s} peak [2, 4]. The main contribution is the oxygen present in the form of oxide (O^{2-}) at a binding energy of 530.1 eV. The other three peaks correspond to the OH^- at binding energy of 531,5 eV, C-O and O-C=O at binding energy of 532,5 eV, H_2O at binding energy of 533,7 eV .

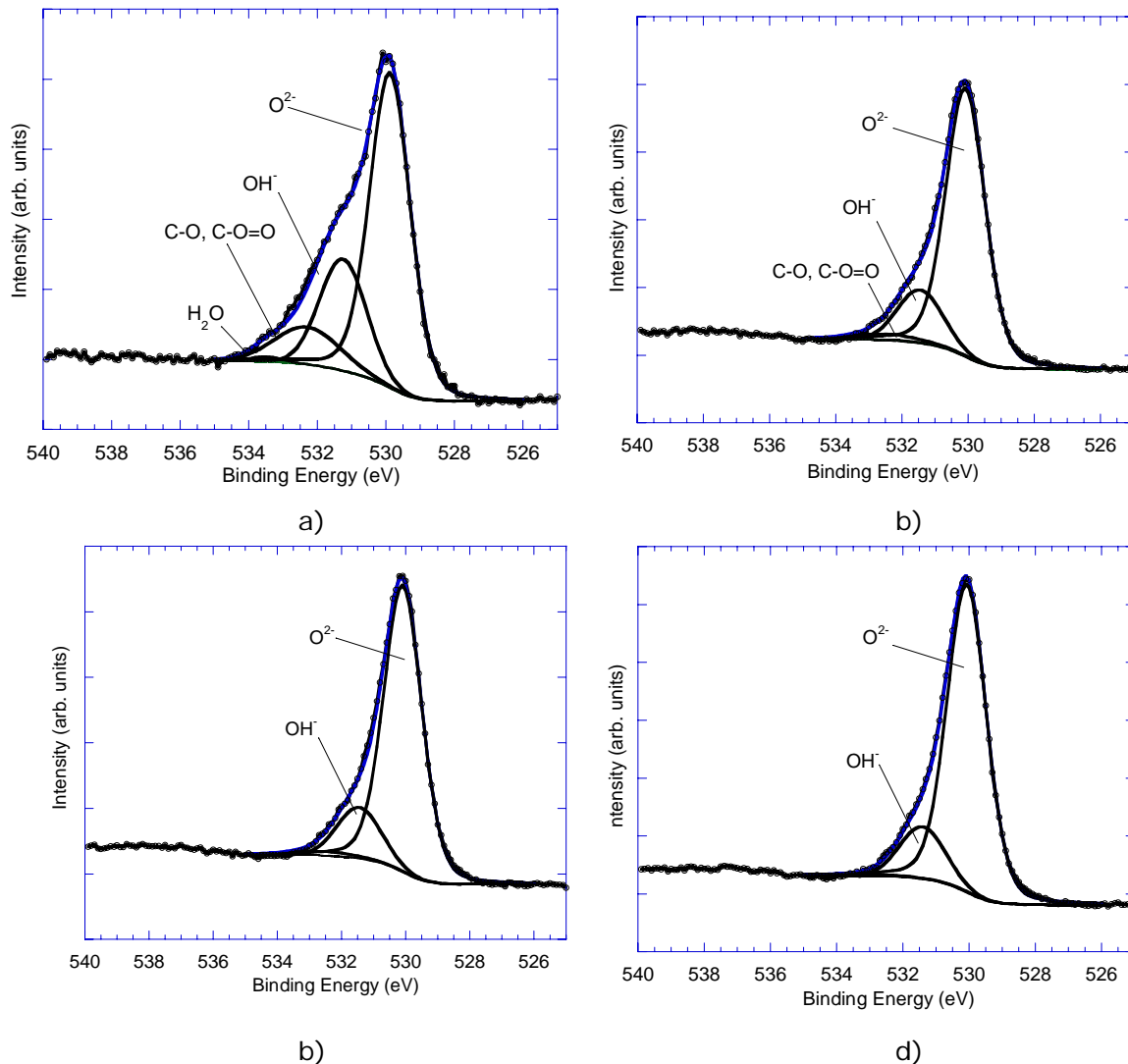


Figure 4. O_{1s} core-level before (a) and after argon sputtering during 2 (b), 3 (c) and 15 (d) minute

Following argon sputtering the peak at 533,7 eV corresponding to H_2O disappears after 2 minutes.

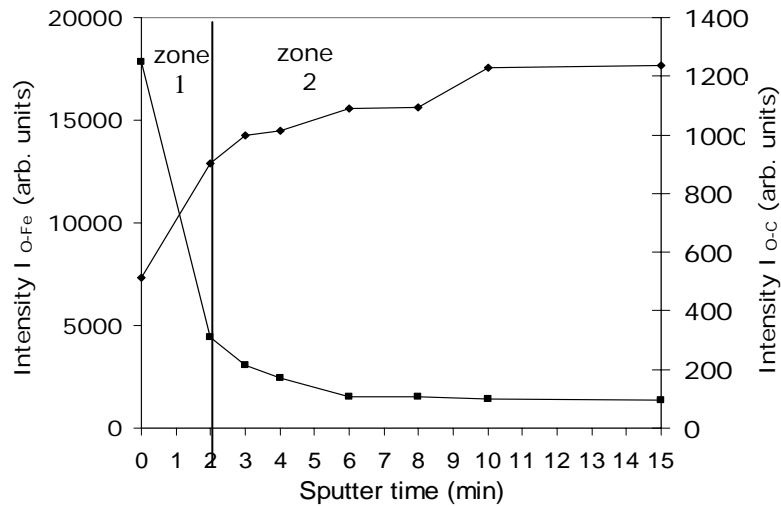


Figure 5. Variation in the intensity of the O-Fe and O-C contributions with sputtering time

In figure 5, we can see that up to 2 minutes of argon sputtering, the etch speed is high (zone 1) while in the zone 2 the quantity of eliminated carbon per unit time decreases. In another experience taking off all the iron oxide, we have determined the cleaning speed which was equal to 0,07 monolayer/minute. That is close to the speed found by Brundle C.R. and Leygraf [5,6]. This slow speed is due to the high atomic bond in the Fe₂O₃ compared to the bond of carbon species that are only physisorbed. Thus the zone 2 is corresponding to a 1 monolayer of oxide.

A three-layer theoretical model (contamination, oxide layer and substrate-figure 1) was used for the determination of the thickness of the carbon contamination layer formed in atmosphere exposure. We consider in the model that carbon contamination layer cover all the surface of oxide layer.

The intensity of the C_{1s} peak due to carbon contamination is given by relation (2) [7]:

$$I_C = i_C \cdot \frac{1 - \alpha_{C(C)}^n}{1 - \alpha_{C(C)}} \quad (2)$$

where $i_C = F \cdot \sigma_C \cdot D_C \cdot T \cdot \lambda_C(E_C)$ is the photoelectron intensity of one atomic monolayer of carbon, where F is the x-ray flux, σ_C is the cross-section for photoionization, D_C is the atom density of the scattering atom (carbon) in atoms/cm³, T is the transmission function of the spectrometer and $\lambda_C(E_C)$ is the inelastic mean free path of the carbon photoelectrons in the carbon monolayer at kinetic energy E_C ,

$\alpha_{C(C)} = \exp(-d_C / \sin\theta \cdot \lambda_{C(C)})$ is the attenuation coefficient of C_{1s} photoelectrons by one monolayer where d is the thickness layer, θ is the take-off angle (measured from the sample surface),

n is the number of monolayers of carbon.

Similar expression was deduced for Fe_{2p} peak too (relation 3) [7]:

$$I_{Fe} = i_{Fe}^\infty \cdot \alpha_{Fe}^n \quad (3)$$

where i_{Fe}^∞ represents the photoelectron intensity of a pure iron substrate covered by Fe₂O₃.

Further, the I_C/I_{Fe} ratio was calculated.

Figure 6 shows the comparison theory-experience of the ratio I_C/I_{Fe} . By this way we found that 7 monolayers of carbon were present on the sample surface.

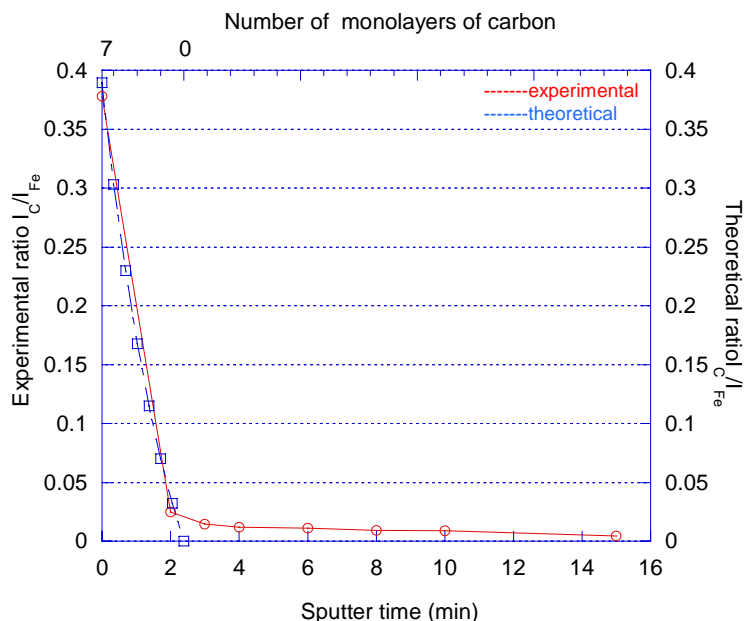


Figure 6. Comparing experimental and theoretical data for I_C/I_{Fe} ratio

4. CONCLUSIONS

Regarding to the high decrease of the ratio I_C/I_{Fe} , we can conclude that after this cleaning the quantity of carbon was reduced at approximately 7%.

The formation of the contamination layer in this study occurs in ambient atmosphere under normal conditions. It can be concluded that after 2 minutes of argon sputtering the quantity of carbon contamination on the steel samples surface has totally disappeared.

The theoretical evolution line of signals coming from the carbon and iron atoms were used in order to determine precisely the thickness of the contamination layer (7 monolayers).

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