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STUDY OF DEPTH CHEMICAL COMPOSITION  
CHANGES BY THE MEANS OF XPS/ESCA

Key words  
XPS, binding energy, XPS spectrum, sputtering, concentration of the elements.

Abstract  
X-ray photoelectron spectroscopy (XPS) is a dedicated surface characterisation spectroscopy. It reveals which chemical elements are present at the surface, it informs us about the chemical bound nature which exists between these elements. An appropriate data processing leads to the specimen elemental composition.

A sample of steel disc was prepared by ball on disc tribology test. The test was conducted in the presence of lubricant containing fluoride. The surface of steel disc was examined by means of XPS technique, and its chemical composition was determined accordingly to location of photoelectron peaks on the binding energy axis on XPS spectra. Depth profiling after 9 sputtering cycles was also conducted.

Introduction  
X-ray Photoelectron Spectroscopy known as XPS or ESCA (Electron Spectroscopy for Chemical Analysis) has been developed by K. Siegbahn in the 1960’s. In 1981 Siegbahn was awarded for his work with Nobel Prize in Physics.
The most interesting thing with this technique is its ability to measure binding energy variations resulting from their chemical environment.

Photoelectron spectroscopy is based on Einstein’s photoelectric effect. The principal of this technique involves measuring the kinetic energy of electrons (called photoelectrons) emitted by the substance as a result of the photoelectric effect (Fig. 1). Photoelectric effect is a physical phenomenon involving the transfer of energy quanta of electromagnetic radiation – photons to electrons located in different substances. This phenomenon depends on the ejection of electrons from the surface of the solids irradiated by sufficiently high energy photons [1].

\[ E_b = h\nu - E_{kin} - W \]  

where:
- \( h\nu \) – photon energy,
- \( E_{kin} \) – kinetic energy of the electron,
- \( W \) – spectrometer work function,
- \( E_b \) – binding energy.

Emitted electron acquires the energy of the incident photon and its energy is reduced by the ionization energy. Knowing the incident photon energy and the kinetic energy of the photoelectrons in individual orbitals, binding energy can be determined. This energy is a characteristic of an electron of an element and can be used for identification. In addition, the size of the binding energy is dependent on the method of binding the molecule electron-emitting atom. Therefore, the electron energy spectrum information can be obtained not only on the composition but also on the chemical environment of the atom, as each type of binding in the atom affects the binding energy of electrons [1, 2].

The energy spectrum of the ejected electrons is displayed as plot of the number of electrons versus electron binding energy. The analysis of the spectrum may be quite problematic due to some disruptions. All information on the spectrum is a combination of an overall trend due to transmission
characteristics of the spectrometer, energy loss processes within the sample and resonance structures that originate from electronic states of the material under analysis. Besides Photoelectron Lines (peaks) on the spectrum other lines are detected, such as X-ray Ghost Lines, X-ray Satellites, Shake-up Lines, Multiplet Splitting, Energy Loss Lines, Valence Lines and Bands and finally Auger lines, which are the result of the technique principle [3].

Interpretation of XPS spectrum generally is accomplished first by identifying the lines that are most likely to be present (those of C and O). Secondly by identifying major lines and associated weaker lines and finally by identifying the remaining weaker lines. The following step-by-step procedure simplifies data interpretation [3]:

1. The C 1s, O 1s, C (KLL) and O (KLL) lines are usually present in any spectrum. Identify these lines first together with all derived X-ray satellites and energy loss envelopes.

2. Identify other intense lines present in the spectrum, then label any related satellites and other less intense spectral lines correlated with identified elements. Be aware of possible overlapping lines from serious interferences.

3. Identify any remaining minor lines. In doing that expect they are the most intense lines of an unknown element. If not, they should already have been identified in the previous steps. Small lines that seem unidentifiable can be ghost lines.

4. Check the conclusions by noting the spin doublets for p, d and f. They should have the right separations and should be in the correct intensity ratio. The ratio for p lines should be about 1:2, d lines 2:3 and f lines 3:4.

Complete identification of elements on the spectrum is accomplished by deconvolution of all significant photoelectron peaks. The term “deconvolution” is used for an algorithm-based process of resolving or decomposing a set of overlapping peaks into their separate components by the technique of iterative least-squares curve fitting of a presumed peak model to the data set [4, 5].

1. Experimental

A sample of steel disc was prepared by ball on disc tribology test. The test was conducted in the presence of lubricant containing fluoride additives. Before sample mounting the sample and sample holder were separately cleaned in isopropanol using ultrasonic cleaner for 3 minutes.

The composition of the surface of steel disc was determined from XPS spectra.

Depth profiles of the elements were measured using PREVAC UHV-XPS system (with base pressure <3x10^{-9} mbar). The system is equipped with standard dual aluminum/magnesium anode. XPS measurement and sputtering parameters were presented in Tab. 1.
<table>
<thead>
<tr>
<th>XPS Measurement information</th>
<th>Sputtering information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use of X-ray Monochromator</td>
<td>No</td>
</tr>
<tr>
<td>Excitation Energy (eV)</td>
<td>1486.6</td>
</tr>
<tr>
<td>Energy (kV)</td>
<td>4.0</td>
</tr>
<tr>
<td>Anode type</td>
<td>Aluminium</td>
</tr>
<tr>
<td>Data acquisition mode</td>
<td>Sweep</td>
</tr>
<tr>
<td>Energy (mA)</td>
<td>2.3</td>
</tr>
<tr>
<td>Data acquisition mode</td>
<td>Sweep</td>
</tr>
<tr>
<td>Pass energy (eV)</td>
<td>200</td>
</tr>
<tr>
<td>TPD (ms)</td>
<td>10.0</td>
</tr>
<tr>
<td>X-ray power (W)</td>
<td>200</td>
</tr>
<tr>
<td>Angle of incidence (°)</td>
<td>50</td>
</tr>
<tr>
<td>Survey spectra step size (meV)</td>
<td>1000</td>
</tr>
<tr>
<td>Detailed spectra step size (meV)</td>
<td>200</td>
</tr>
<tr>
<td>Time of 1÷8 cycles (min)</td>
<td>60</td>
</tr>
<tr>
<td>Angle of incidence (°)</td>
<td>50</td>
</tr>
<tr>
<td>Time of 9th cycle (min)</td>
<td>120</td>
</tr>
</tbody>
</table>

Data processing was carried out by means of CasaXPS software. Charge correction was carried out using C 1s peak. The carbon peaks were curved fitted by a computer. All spectra of interest were contained in one file with extension “.vms”. To obtain proper data each spectrum was processed individually.

Although data processing of spectra is computer aided, most operations are performed and vast parameters are selected manually by the operator:

1. The number of peaks to be deconvoluted (Auger peaks, satellite lines, etc. are not processed).
2. The range of the peak for background subtraction.
3. Straight line (L), Tougaard (T) or the Shirley (S) background subtraction method.
4. GL ratio (the ratio of Gaussian and Lorentzian contribution to the peak shape (GL(30) means 30% of Lorentzian and 70% of Gaussian).

In order to receive comparable data a certain method of data processing was developed as follows:
1. Determine the position of C 1s transition and calibrate the peak to energy of 284.8 eV.
2. Identify the most prominent lines in the spectrum, along with all derived X-ray satellites and energy loss envelopes.
3. Identify all remaining lines, including position determination of Auger peaks in kinetic energy range.
4. Determine the background subtraction region and background type (for quantity analysis the same range of regions is advisable).
5. Create and adjust synthetic compounds according to previously set calibration.
6. If data seems out of place perform a correction in the calibration until synthetic peaks seem correct (in every spectrum maintain the same calibration).

In the present study for Fe 2p, F 1s, O 1s, C 1s and Si 2p Shirley-type background subtraction was chosen along with GL ratio of 30.
The concentration of elements was determined as follows:
1. Calibrate all spectra to the same value of binding energy.
2. Determine and implement the same range and position of background subtraction regions to all spectra when possible.
3. Perform data processing in CasaXPS software for regions quantification.
4. Export quantification data to “.txt” file format.
5. Import quantification data to spreadsheet for data analysis and organisation.
6. Organise data in tables and appropriate charts for visualization purposes.

2. Results and discussion

After peak fitting procedures of all the spectra was concluded a comparison of spectra was made. The results show that sputtering was successful. Especially the first sputtering brought a significant change in the concentration of fluoride compounds (peak F 1s). Next cycles of sputtering also changed the concentration but more to other elements.

Figure 2 presents peak identification on XPS survey spectra of: (1) – raw sample, which means a sample that hasn’t been subjected to any sputtering processes and (10) – the same sample but after 9 cycles of sputtering (600 minutes).

![Fig. 2. XPS survey spectra of (1) raw sample and (10) sample after 9 cycles of sputtering](image)

Although ten XPS scans were performed for this study purposes, for visibility reasons only two spectra were compiled in the Fig. 2. It is apparent
that fluoride compounds were covering the very top of the surface of the steel sample.

Figure 3 illustrates the results of depth profiling process for ten consecutive XPS scans.

In Fig. 3 the doublet Fe 2p peak on the spectrum nr 1 is almost flat, which means that Fe is detectable but very little amount of it is present on the examined surface. In scans after sputtering the doublet Fe 2p peak becomes more visible. F 1s peak on the spectrum nr 1 is very significant comparing to Fe 2p doublet peak, yet not as big as final Fe 2p peak after 9th sputtering cycle. With the increase in the number of sputtering cycles the size of F 1s peak decreases.
Table 2. Comparison of concentration changes in the sample before and after sputtering

<table>
<thead>
<tr>
<th>Sputtering time [min]</th>
<th>Fe 2p, 3s and 3p</th>
<th>F 1s</th>
<th>O 1s</th>
<th>C 1s</th>
<th>Si 2p and 2s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.08</td>
<td>38.16</td>
<td>24.84</td>
<td>21.49</td>
<td>9.42</td>
</tr>
<tr>
<td>60</td>
<td>24.7</td>
<td>21.66</td>
<td>27.73</td>
<td>18.99</td>
<td>6.93</td>
</tr>
<tr>
<td>120</td>
<td>49.42</td>
<td>14.28</td>
<td>19.91</td>
<td>11.2</td>
<td>5.19</td>
</tr>
<tr>
<td>180</td>
<td>57.06</td>
<td>12.11</td>
<td>16.78</td>
<td>9.37</td>
<td>4.69</td>
</tr>
<tr>
<td>240</td>
<td>62.04</td>
<td>10.96</td>
<td>14.27</td>
<td>9.01</td>
<td>3.68</td>
</tr>
<tr>
<td>300</td>
<td>67.03</td>
<td>9.02</td>
<td>12.53</td>
<td>8.08</td>
<td>3.33</td>
</tr>
<tr>
<td>360</td>
<td>66.68</td>
<td>8.26</td>
<td>13.13</td>
<td>8.74</td>
<td>3.18</td>
</tr>
<tr>
<td>420</td>
<td>69.64</td>
<td>7.38</td>
<td>12.45</td>
<td>7.44</td>
<td>3.08</td>
</tr>
<tr>
<td>480</td>
<td>72.14</td>
<td>6.58</td>
<td>10.99</td>
<td>7.36</td>
<td>2.92</td>
</tr>
<tr>
<td>540</td>
<td>75.72</td>
<td>5.94</td>
<td>10.63</td>
<td>6.09</td>
<td>2.62</td>
</tr>
</tbody>
</table>

After data acquisition, depth profiles were compared in order to calculate quantity relationships between all XPS scans (Fig. 4 and Tab. 2). Although during quantification procedure every photoelectron peak was quantified separately, i.e. Fe 2p, Fe 3s and Fe 3p, for more adequate concentration calculations data from all Fe peaks were collected in one column representing Fe concentration on the surface in tab. 2, the same happened to Si peaks.

As shown in the tab. 2 and on the fig. 4 with every sputtering cycle the amount of Fe increased, while the concentration of Si, F, O and C decreased. The concentration of F 1s decreased more than 7.5 times after 9th sputtering cycle. Concentration of O 1s decreased about 2.3 times, and C 1s and Si decreased 3.5 times each. During sputtering the amount of Fe was increasing and reached finally 12.5 times the amount, from before sputtering.

All spectra were first analysed using CasaXPS software [6]. Peak shifts due to apparent charging were normalised with the C 1s peak set to 284.8 eV. Curve fitting was carried out for F 1s peak as shown in Fig. 5 with the aid of computer software.
Figure 5 compares peak fitting results and relation between synthetic components maxima for fluoride compounds. The F 1s photoelectron peak in spectrum b-1, nr 1, appears near 686.0 eV, and number 2 from sputtered sample is near 685.3 eV. On the Fig. 5 a) there is a clearly visible shift on the binding energy scale to the right and change in size of the peak after sputtering. Curve fitting was carried out for C 1s peak as shown in Fig. 6 with the aid of computer software.

Figure 6 b) compares peak fitting results and relation between synthetic components maxima for carbon compounds. The C 1s photoelectron peak in spectrum b-1 was deconvoluted with a result of three synthetic peaks: 1 – 284.8 eV; 3 – 288.1 eV and 5 – 292.6 eV. The C 1s photoelectron peak in spectrum b-2 was deconvoluted with a result of two synthetic peaks: 2 – 284.4 eV and 4 – 286.6 eV. All synthetic compounds from C 1s peaks on both spectra were assigned according to Moulder J.F. et al. Peaks number 1 and 2 present at 284.8 eV and 284.4 eV respectively were attributed to carbon (C) and peaks number 3, 4 and 5 were assigned to CHF [3]. On the Fig. 6 a) there is a clearly visible change in the size of photoelectron peak after sputtering. Curve fitting was carried out for O 1s peak as shown in Fig. 7 with the aid of computer software.

On the Fig. 6 a) there is a clearly visible change in the shape and size of photoelectron peak after sputtering. Figure 7 b) compares peak fitting results and relation between synthetic components maxima for oxygen compounds. The O 1s photoelectron peak in spectrum b-1 was deconvoluted with a result of two synthetic peaks: 1 – 531.8 eV and 3 – 529.4 eV. The O 1s photoelectron peak in spectrum b-2 was deconvoluted with a result of two synthetic peaks: 2 – 531.6 eV and 4 – 529.2 eV. The highest O 1s peak in the first and second spectra found at 531.8 eV±0.2 eV and 531.6 eV±0.2 eV respectively could be attributed to adsorbed atomic oxygen, according to Grosvenor A.P. et al. [7]. The second
set of O 1s peaks in spectra b-1 and b-2 found at 529.4 eV±0.2 eV and 529.2 eV±0.2 eV respectively could be attributed to iron oxides, like Fe$_2$O$_3$ or Fe$_3$O$_4$, according to Braindard W.A. et al., McIntyre N.S. et al. and Brion D. [8, 9, 10]. This identification of iron oxides which are increasing in the amount in the second spectrum clearly is a result of sputtering. Curve fitting was carried out for Fe 2p doublet peak as shown in fig. 8 with the aid of computer software.

Fig. 7. Compilation of XPS spectra a) 3D visualisation of sputtering results for O 1s photoelectron peak; b) Comparison of high resolution spectra of O 1s photoelectron peak from raw sample (b-1) and after 9 cycles of sputtering (b-2)

Fig. 8. Compilation of XPS spectra a) 3D visualisation of sputtering results for Fe 2p doublet photoelectron peak; b) Comparison of high resolution spectra of Fe 2p doublet photoelectron peak from raw sample (b-2) and after 9 cycles of sputtering (b-1)

Figure 8 b) compares peak fitting results and relation between synthetic components maxima for iron compounds. The Fe 2p3/2 photoelectron peak in the first spectra was deconvoluted with a result of three synthetic peaks: 1 – 707.8 eV; 2 – 705.5 eV and 3 – 704.4 eV. The Fe 2p3/2 photoelectron peak in the second spectra was deconvoluted with a result of two synthetic peaks: 4 – 708.9 eV and 5 – 706.2 eV. On the Fig. 8 a) there is a clearly visible change in the shape and size of photoelectron peak after sputtering. After performing the peak fitting and analysing the data some identification were estimated. Peaks
number 1 and 5 present at 707.8 eV ±0.1 eV and 706.2 eV±0.3 eV respectively could be attributed to iron (Fe), according to Shabanova I.N. et al. [11] and Hawn D.D. [12]. The peak at 708.9 eV±0.1 eV according to Brainard W.A. et al. could be assigned to Fe$_3$O$_4$ [8].

**Conclusions**

XPS scans provided enough data to identify chemical states of elements present on the sample surface. Binding energy of C 1s synthetic peaks indicate on the presence of carbon and CHF components. Binding energy of O 1s synthetic peaks was assigned to metal oxides, such as iron oxides. This was confirmed after Fe 2p synthetic peaks fitting, which also indicate on the presence of iron oxides. The analysis of spectra before and after sputtering gave both visual and numerical (concentration) confirmation of the influence of sputtering on the surface chemical composition. The concentration of F 1s decreased more than 7.5 times after 9th sputtering cycle. Concentration of O 1s decreased about 2.3 times, and C 1s and Si decreased 3.5 times each. During sputtering the amount of Fe was increasing and reached finally 12.5 times the amount from before sputtering. However, most change was made during first hour. This proves many of advices found in the literature about proper sample handling. The surface of samples is very prone to contamination from the environment. Even very short duration of exposition to air creates substances which may mislead the analyst. That is why a sample should undergo a first cleaning sputter prior to XPS analysis. This information gave a possible direction to our future methodology modification and further XPS analysis.

Future experiments will involve adjustments in sputtering time and parameters.

**Acknowledge**

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**References**

Badanie zmian składu chemicznego materiałów za pomocą techniki XPS/ESCA

Słowa kluczowe

XPS, energia wiązania, widmo XPS, sputtering, stężenie pierwiastków.

Streszczenie

Rentgenowska spektroskopia fotoelektronowa jest techniką analizy powierzchni. Polega na analizie rozkładu energii kinetycznej fotoelektronów emitowanych w wyniku wzbudzenia próżni charakterystycznym promieniowaniem rentgenowskim. Pozwala na uzyskanie informacji o obecnych pierwiastkach oraz o wzajemnej relacji poszczególnych wiązań chemicznych.

Do badania wykorzystano stalową próbkę w postaci teściwa ball-on-disc, który został przeprowadzony w środowisku smaru zawierającego związki fluoru. Powierzchnia stalowego dysku została przebadana za pomocą techniki XPS, a skład chemiczny został ustalony na podstawie położenia pików fotoelektronowych na osi energii wiązania na widmach XPS. Przeprowadzono również analizę wglądą po 9 cyklach sputteringu za pomocą jonów Ar⁺.