Anita BEDNARSKA, Edyta OSUCH-SŁOMKA, Marian GRĄDKOWSKI
Institute for Sustainable Technologies – National Research Institute, Radom
anita.bednarska@itee.radom.pl, edyta.slomka@itee.radom.pl,
marian.gradkowski@itee.radom.pl

A METHODOLOGY FOR IDENTIFYING THE CHEMICAL COMPOSITION OF THE SURFACE OF SOLIDS USING THE XPS AND SEM/EDS TECHNIQUES

Key words

SEM/EDS, XPS/ESCA, sputtering, vertical profile.

Abstract

In many fields of science and technology, it is necessary to apply non-destructive methods of analysis. Such non-destructive methods include scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM/EDS) and X-ray photoelectron spectroscopy (XPS), and the results obtained with this set are often regarded as complementary. These methods were used in this study to research the chemical composition of the top layer of a model made with gold on a ceramic coating produced by the PVD technique on the surface of steel. The gold layer was ion sputtered until its complete removal and was studied by means of X-ray photoelectron spectroscopy and X-ray micro-analysis. It was found that the analytical data for an identical specimen obtained by SEM/EDS and XPS might differ significantly. This necessitates very careful consideration in treating these techniques as

complementary, and during the interpretation of the results, one should take into account the physical essence of each method.

Introduction

In materials engineering and in many other areas of technology, the knowledge of the physical and chemical structure of the material is important. In some cases, the data on the outer layers of the material alone is of critical importance, since they determine its functional properties. In surface engineering, the data properties that are important concern the coating and the surface layer of solids on the nanometric and even molecular level. Moreover, it is important that the testing is non-destructive and the specimen properties are not changed. Particularly useful in this regard are spectroscopic techniques. In materials testing, the application of scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM/EDS) and X-ray photoelectron spectroscopy (XPS) has become widespread. The basic data describing techniques are shown in Table 1. These data show the boundary capabilities of each individual technique resulting from the laws of physics and the development of technology. The actual parameters of a particular device depend on its design and are often lower than those given in Table 1.

Table 1. Comparison of parameter and detection limits of used analytical techniques [2]

Technique	Parameter limits						
	Range of elements	Detection limits	Quantitative accuracy	Analysis area (radius)	Minimum film thickness	Depth of information	The type of data
SEM/EDS	B-U	0.1 atom. %	±10%	>0.5– –4 μm	500 nm	500– –3000 nm	qualitative and quantitative
XPS/ESCA	Li-U	0.1 atom. %	±10%	>15– –500 μm	5 nm	1– –10 nm	+ chemical status of elements

The SEM/EDS and XPS techniques are based on an analysis of the electron energy emitted from the specimen. The main difference consists in how the excitation is induced in the specimen: In SEM/EDS, it is an electron beam with an established energy, and in XPS, it is monochromatic X-ray radiation. In the first case, it is a result of an elastic collision of the electrons. In the second case, it is an external photoelectric phenomenon. In consequence, for each technique, there is a characteristic energy of the electron leaving the specimen and the information it carries [1]. There are also important differences in the size of the excitation area and thus in the planar and vertical resolution. SEM/EDS is characterized by a greater planar but a smaller vertical resolution than XPS. The advantage of XPS over the SEM/EDS is the possibility of ion sputtering of the

test specimen (Ar^+) and, thanks to the high vertical resolution, creating depth profiles of the chemical structure of the test material. In summary, both methods provide data with different levels of detail, and in many cases, they can be complementary.

The analytical information from SEM comes from the surface layer, but the thickness of the layer significantly depends on the atomic mass of constituent elements. The depth of the analysis for selected elements is shown in Figure 1, where the larger the atomic mass, the shallower is response of the element.
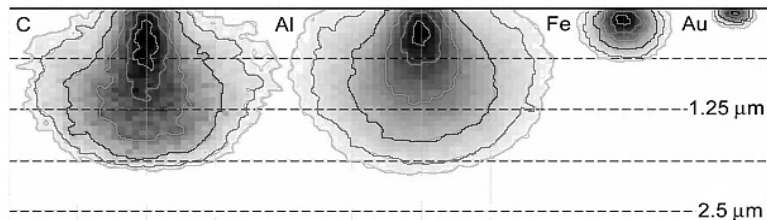

Fig. 1. Monte Carlo simulation of energy distribution in SEM imaging: Energy distribution depends on the material and acceleration voltage, which was 15 kV in this visualisation. Contour lines illustrate the amount of energy: 5% (outside line), 50% (bright line), 90% (centre) [3]

The XPS technology exemplifies the wave-particle theory of matter. It applies only to the elements that are located sufficiently shallow in the surface layer, so that it is possible for the electrons excited by monochromatic X radiation to leave freely [4]. The kinetic energy of the electron (KE) is the sum of the binding energy (BE) and energy of the "taken over" X-ray quantum (hν). Thus, by measuring the KE, we can determine the electron energy before its "impact" with the X-ray quantum, which is the binding energy BE in the atom. This energy is dependent on the atomic number and on the position of the electron in the atom (the atomic orbital) [5]. When determining BE, a coefficient should be taken into account that compensates for the difference between the electron exit energy from the specimen and the spectrometer [6]. The KE measurement is obtained using the analyser, which is a part of the XPS apparatus. As a result of the counting of the number of electrons at a specific KE in a unit of time, a photoelectronic spectrum is created [7].

In XPS analysis, it is usually assumed that the test surface is flat and homogeneous. However, in vertical resolution at the level of the single nanometres, the shape of the surface is essential because of the change in the analytical signal to the background signal [8]. This is particularly important in the study of thin layers.

The aim of this study was to develop a methodology of ion sputtering and the identification of the chemical composition of the surface layer using the XPS technique by creating depth profiles, analysing the structure of the functionally

coated materials, and verifying the data obtained by SEM/EDS technique and correlating and comparing the data obtained in each method.

1. Research object

The object of study was a steel disc, 25.4 mm in diameter, with a functional ceramic coating embedded in it by using the PVD method, which was covered in a layer of gold with a nominal thickness of 20 nm, determined based on the sputtering parameters using the BAL-TEC SCD 050 Sputter Coater [9]. Covering the surface of the specimen with a layer of gold with a known thickness makes it possible to link the parameters of ion milling with the characteristics of the specimen layers being uncovered. The specimen was fixed in the holder of the XPS using conductive graphite tape.

2. Research method

The SEM images and the X-ray EDS microanalysis were performed using a scanning electron microscope with a Schottky type thermal field emitter (model SU-70 by Hitachi) in conjunction with an X-ray microanalyser by Thermo Scientific, enabling the detection of elements from beryllium to uranium. The analyses were carried out in a vacuum at 1×10^{-8} Pa, with an accelerating voltage of 15 kV. The angle of the reception of secondary electrons (SE) was 30.4°. During the EDS analysis, spectra were recorded for selected portions of the surface along the selected lines or points of 10 x 10 nm.

The XPS analysis was carried out using a spectroscope by PREVAC. In order to remove from the surface of the specimen the adsorbed foreign substances and products the oxidation, initial surface cleaning of the specimen was conducted using the ion mill Ar^+. To induce excitation in the specimen, an X-ray lamp equipped with the standard achromatic source of X-rays, accompanied by a double anode Al/Mg, were used. The main ion sputtering (for creating depth profiles) was conducted with 5 kV beam, with a current of 10 mA, and current density at 147 µA/cm^2. Survey analyses after each cycle of ion sputtering were conducted using radiation Al Kα energy 1486.6 eV, with a transition energy of 200 eV and an increment of 200 meV. The parameters for creating a detailed spectrum for each element were selected individually, taking into account the power of the X-ray excitation, the element, sampling density, transition energy, and slits of the analyser lenses. These parameters were set in such a way so that the quality of the obtained spectra was the highest. The recorded spectra were subjected to a detailed digital analysis, based on which the quantitative composition of elements in subsequent layers was established.

3. Test results-discussion and conclusions

Figure 2 shows a survey of the XPS spectra of the specimen surface before gold coating (a), after the gold coating (b), and after ion sputtering of the gold (c). As can be seen from the data in Figure 2, after coating the surface with gold, all of the signals of all specimen elements were "covered," except for carbon. The spectrum (b) spectrum was registered after an initial 30-minute cleaning of the surface of a specimen with an argon ion beam. Spectrum analysis showed that, after this operation on the surface of the specimen, carbon remained at about 16%. The gold layer level not containing carbon was reached after up to 50 minutes of further cleaning. It is therefore necessary to monitor the effectiveness of the initial surface cleaning of the specimen and, if necessary, carry it out with greater intensity.
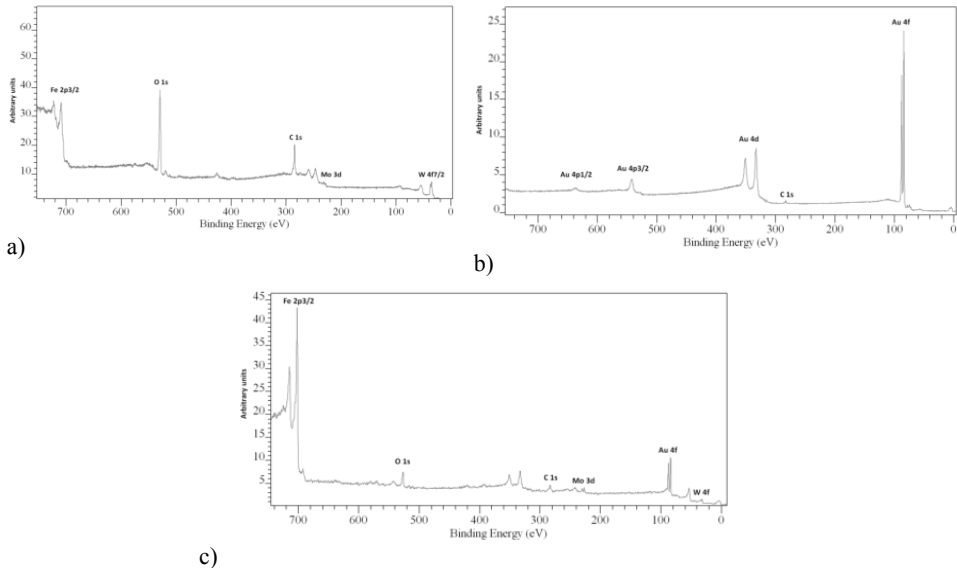

Fig. 2. XPS survey spectra: a) specimen before coating – without gold, b) specimen after gold coating, c) specimen after gold coating and ion sputtering

Figure 3 shows the depth profile of the content of each of the elements in the layers being uncovered after consecutive cycles of ion sputtering, between which XPS data acquisition was carried out. After each test, a detailed analysis of each of the peaks was conducted (Figure 4) in order to determine the atomic concentration of all elements. When quantifying the XPS spectra, in order to adjust the size of the measured area under each peak for each of the elements, the relative sensitivity coefficient RSF was taken into account [10]. In the first 300-minute milling phase with the XPS technique, no elements other than gold were detected. After this time, iron appeared and its content steadily increased,

and then tungsten, carbon, oxygen, and molybdenum. This indicated the gradual revealing of the substrate coated by gold (analysis of the composition of the substrate was not the aim of the testing). The milling was completed after 1,230 minutes, because cycles after 1,110 min did not reduce the participation of gold in the composition of the milled material. Despite the extended time of ion milling, there was gold content in the tested layer. This may be related to the fact that the used XPS spectrometer is not equipped with a monochromator; therefore, concentrating the excitation radiation beam is possible only within the area around 1 mm^2. As a result, the analysis might have included a fragment of the specimen lying outside the milled surface.

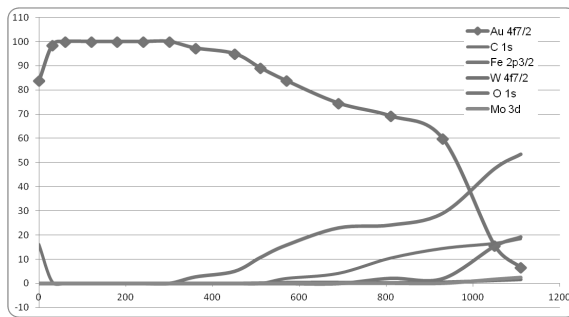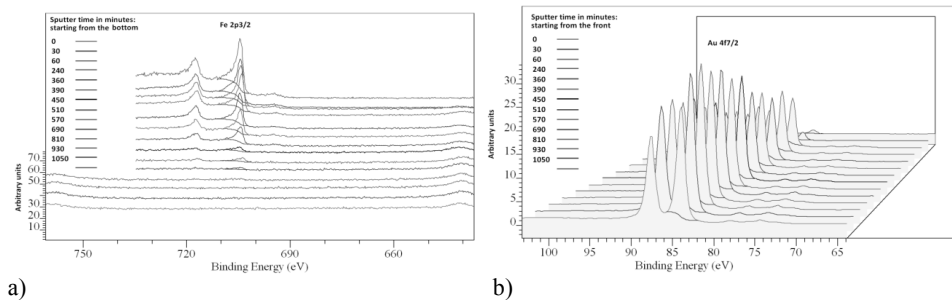Fig. 3. Depth profiles of elements atomic concentration in gold coated specimen

a)   b)

Fig. 4. Detailed spectra of selected elements in consecutive layers of examined specimen: a) 2D XPS spectra compilation of Fe2p3/2 peak before and after ion sputtering; b) 3D XPS spectra compilation of Au 4f7/2 peak before and after ion sputtering

Since optical examination of the specimen showed no presence of gold in the place of sputtering, it was decided to subject it to the SEM/EDS test. The results of SEM observations and EDS analyses of the specimen surface layer after gold coating and after sputtering is shown in Figs. 5 and 6. As can be seen from the SEM image shown in Fig. 5a, the surface of the specimen is not

homogeneous; the same case is for this this material before coating it with gold. This is characteristic of the coating that constituted the substrate. Due to the much greater depth of analysis of the EDS technique (≥500 nm) than XPS (~1 nm), in EDS spectra (Fig. 5b) in addition to gold, there are also elements of the substrate. Local analysis of this surface (Table 1) illustrates the chemical composition of the coating with gold deposition rather than a gold layer (XPS analysis – 100% gold at this point). Figure 7a shows a SEM image of the same specimen after ion sputtering. Characteristic is the "dispersed" of globular structures (Fig. 6a) located on the surface of the specimen, in the opposite direction to the direction of the Ar^+ ion sputtering. As a result of sputtering, there has been a significant change in the surface structure of the specimen. An EDS analysis (Fig. 6b) has not, however, found the presence of gold on the surface, in contrast to the analysis of XPS. Since the planar resolution of the EDS is much greater than of the XPS, the hypothesis is that the results of the XPS analysis were influenced by too large an analytic field can be considered verified. However, one should also bear in mind the potential impact on the outcome of the depth from which the analytical information in both methods is taken and the deformation of spherical structures on the surface of the specimen. However, the most likely option is that the SEM/EDS technique proved insufficiently sensitive for gold under the conditions of the experiment.

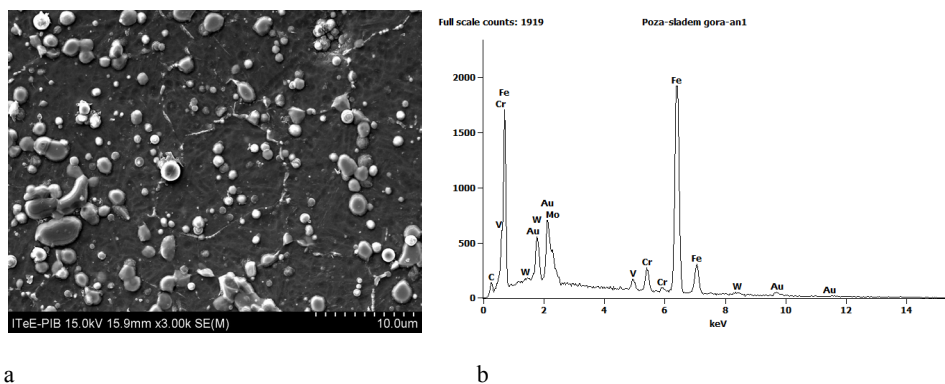a   b

Fig. 5. SEM images (a) and EDS results (b) of the surface of the layer covered with gold

Figure 7 shows the SEM images correlated with the results of the linear gold content analysis used in the EDS technique on the boundary between the sputtered and un-sputtered surface (left). As the data in Fig. 7 indicates, the proportion of gold in the surface layer decreases along the lines of analysis; however, traces of the gold signal disappear entirely after crossing the sputtering boundary, indicating that gold is absent (right).
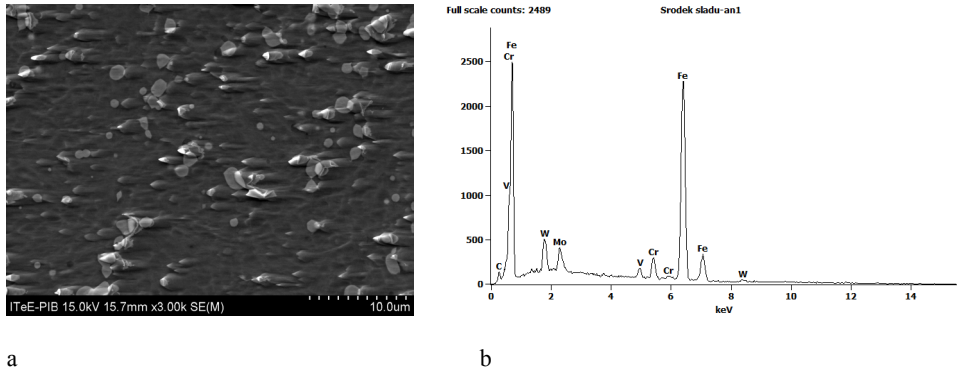
a   b

Fig. 6. SEM images (a) and EDS results (b) of the surface of the layer covered with gold after ion sputtering with Ar^+

Table 2. Atomic concentration of main components before and after sputtering (EDS)

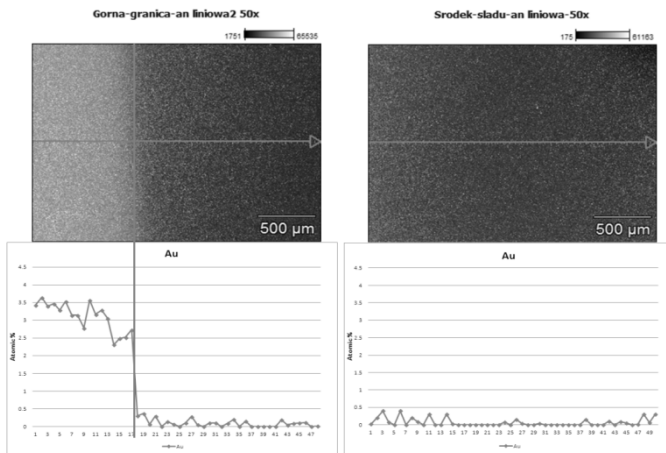| Element	Atomic concentration [%]	
	Before sputtering	Middle of the sputter spot
Au	3.4	0.1
C	7.1	5.1
Fe	76.6	83.0
W	2.5	2.4
O	0.7	0.0
Mo	2.8	2.6
V	2.4	2.2
Cr	4.5	4.7

Fig. 7. Linear EDS analysis results correlated with SEM images for the boundary of sputtering spot (left) and for the middle of the spot (right)

The study has shown that quantitative data derived the SEM/EDS and XPS techniques for the same object may vary significantly. It also demonstrated the importance of the surface structure of the specimen to the process of ion sputtering in XPS. These facts should be taken into account, both when planning research, and during the interpretation and correlation of results obtained with these methods. The data presented will facilitate the planning and implementation of research techniques for SEM/EDS and XPS of materials with ceramic coatings, including multilayer coatings.

Summary

This study compared the results of the chemical composition testing of surface layers in the coating material using the SEM/EDS and XPS spectral techniques. Both techniques rely on the properties of electrons "escaping" from the specimen and provide qualitative and quantitative analyses of elements. The XPS technology enables ion sputtering of the surface of the specimen and the creation of depth profiles of the chemical structure of successive layers of material. It was found that the qualitative and quantitative data obtained for the same object of research converge for both methods if the material is homogeneous. In the case of heterogeneous materials, the results of qualitative analysis and particularly the quantitative analysis of the two methods can essentially differ. The key importance lies in the structure of the tested material and, above all, in the ratio of the thickness of the layers of different composition in the vertical structure of the material to the depth of electron output. Therefore, the methods of SEM/EDS and XPS cannot be considered complementary in all cases.

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Metodyka identyfikacji składu chemicznego powierzchni ciał stałych technikami XPS i SEM/EDS

Słowa kluczowe

SEM/EDS, XPS/ESCA, sputtering, profil głębokościowy.

Streszczenie

W wielu dziedzinach nauki i techniki niezbędne jest zastosowanie nieniszczących metod analizy. Do takich metod należy skaningowa spektroskopia elektronów sprzężona z mikroanalizą rentgenowską (SEM/EDS) oraz rentgenowska spektroskopia fotoelektronów (XPS), a wyniki uzyskiwane za ich pomocą często są traktowane jako uzupełniające się. W pracy zastosowano te metody do badania składu chemicznego modelowej warstwy wierzchniej, utworzonej ze złota na podłożu powłoki ceramicznej wytworzonej techniką PVD na powierzchni stali. Warstwę złota trawiono jonowo aż do jej całkowitego usunięcia i badano za pomocą rentgenowskiej spektroskopii fotoelektronów oraz mikroanalizy rentgenowskiej. Stwierdzono, że dane analityczne dla identycznej próbki uzyskiwane metodami SEM/EDS oraz XPS mogą dość istotnie różnić się. Oznacza to konieczność dużej ostrożności przy traktowaniu tych technik jako komplementarne, podczas interpretacji wyników należy uwzględniać fizyczną istotę obydwu metod.