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OXIDE NANOMETRIC PELLICLES FORMATION BY APPLYING ELECTRICAL DICHARGES IN INPULSE

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Abstract. The paper presents the results of theoretical and experimental investigations of phenomena that accompany the formation of nanometer oxide and hydroxide pellicles by applying electrical discharges in impulse (EDI). The chemical content of processed surface analysis (EDX – Energy Dispersive X-ray analysis) attests the presence of oxygen that reaches up to 60% at. for steel surfaces, 30-35% at. for those made of titanium alloys, up to 20% at. for those made of aluminum alloys, and up to 50% at. for those made of copper alloys. The presence of considerable amounts of nitrogen is found only in titanium and iron alloys (and constitutes about 15% at), while in aluminum and copper alloys its presence is not significant. The superficial phase analysis (XPS - X-ray Photoelectron Spectroscopy) of the oxygen allowed us to state that the oxygen in pellicle forms three base structures: $-O^{-2}$ (oxide), $- OH^{-}$ (hydroxide), and structures of the type O-C and O-C=O. The chemical analysis showed that the concentration of each of the three components is 0.89:1.00:0.50.

Keywords: *electrical discharges in impulse, oxide pellicle, "cold" electrode spot, micro-hardness, surface roughness*

Introduction

Oxidation of metal surfaces has found applications in various fields of technology for corrosion protection [9] and to change the electrical properties of surfaces in electrical and radio engineering [6, 7]. For this purpose, the method of electrolytic deposition of thermodynamically stable pellicles on some metal surfaces is applied [4], which can be obtained only at the so-called fed metals, which include aluminum, titanium, tantalum, niobium, etc. The spark-anodic electrolysis, also known as micro-plasma or micro-arc oxidation, has been developed [2, 3]. Depositions formed by this method are a large range of structural, technological and operational requirements: micro-hardness, wear resistance, low coefficient of friction, and ability of electro-isolation, erosion resistance, and high adhesive properties. An important advantage of such depositions is that their properties are of complex operational character.

Low-alkaline and acidic electrolytes and metal salt solutions are used to realize this process. Deposition properties depend on the chemical composition of the alloy, concentration, composition and temperature of the electrolyte, electrical regimes of the process and its duration, etc. Coverings mainly consist of solid crystalline phases in the matrix of softer oxide phase of metals that form part of the alloy and the electrolyte. This structure provides a high micro-hardness, wear-proof and corrosion resistance, heat protection and electro-isolation properties of the covering. The application of this technology implies the use of special devices for electrolytic processes and the adoption of measures required to ensure safe working conditions for staff.

From the moment of application the electrical discharges in impulse (EDI) for technological purposes in dimensional processing [11], in deposit formation of compact and powder materials [1, 5], the micro-metallurgical processes that occur in the surface layer of the work-piece in both liquid and solid phases were studied. It has been established that the formation of new alloys in the processed surface is accompanied by convective mixing of the components in the liquid phase and the diffusion of elements in the substrate from the liquid phase of the deposition. In the work [1] it has been shown that for the interstice greater than 0.03 mm, the interaction of EDI plasma channel with the processed surface is manifested by the appearance of an indent consists of a central zone that represents a crater with liquid phase and a heat-affected zone of freshly etched metal color. For certain sizes of the interstice, the central zone disappears, and the processed surface represents only a heat-affected zone where phenomena of quenching and enriching piece material with elements from the work media occurs.

Recently, a number of works [6-10] has been published where the results on the electro-discharge oxidation of metal surfaces under ordinary conditions are presented. Coverings obtained by this method have usually a dual structure. It consists of an inner base layer on the edge of the metal-coating and external outer layer (coat).

The base layer is fine-porous, has a crystalline structure and constitutes 60...90% of the covering thickness. The outer layer coating is less hard, more porous, has an amorphous structure and takes on the 40...10% of the thickness.

The coating under the oxidation process is able to germinate in metals in about 10 to 60% of the total thickness of the coating in the depth and consists mainly of oxides of the elements contained in the machined alloy and elements from the interstice.

The following chemical reactions are produced on the surface of the electrodes [10, 12]:

- on the anode:

$$\begin{gathered} xMe + yO^{-} \rightarrow Me_xO_y + (y-x)e^{-}; \\ xMe + yO^{3-} \rightarrow Me_xO_y + O_2 + (y-x)e^{-}; \\ xMe + yOH^{-} \rightarrow Me_x(OH)_y + (y-x)e^{-}; \\ xMe + yN^{-} \rightarrow Me_xN_y + (y-x)e^{-} \text{ and so on.} \end{gathered} \tag{1}$$

- on the cathode:

$$\begin{gathered} xMe + yO^{+} + (y-x)e^{-} \rightarrow Me_xO_y; \\ xMe + yO^{3-} + (y-x)e^{-} \rightarrow Me_xO_y + O_2; \\ xMe + yH_2O + (y-x)e^{-} \rightarrow Me_x(OH)_y + H_2; \\ xMe + yN^{+} + (y-x)e^{-} \rightarrow Me_xN_y \text{ and so on.} \end{gathered} \tag{2}$$

EDI method allows to form coverings on pieces of complex shapes and of any configuration, including the internal surface of pipes [9].

The process operates at room temperature, which positively affects the constancy of the base metal physical properties.

The main characteristics of coverings formed by applying the EDI method are the following: layer thickness – up to 240 nm, micro-hardness – up to 2000 HV, approaches the hardness of corundum; surface roughness of coatings after oxidation – Ra = 0.05...0.10 μm.

The analysis of the operational properties of coatings obtained by EDI oxidation shows that these properties are closely related. Total thickness of covering, taking into account the number of electricity spent on it, demonstrates the high performance and efficiency of the process. The boundary between the main piece material and covering relative to its original size is essential both for the adoption of constructive decisions on the use of pieces with EDI coverings and for the design of technological process of manufacturing such pieces.

The purpose of this paper is the analysis of results of theoretical and experimental investigations of phenomena that accompany the formation of nanometer oxide and hydroxide pellicles by applying electrical discharges in impulse and their possible application in practice.

Methodology of experimental investigations

The main challenge for the stage of preliminary research of EDI coatings was to search for a technological regime of the oxidation that contributes to the formation of oxide pellicles with high operational properties on the pieces made of metallic materials and their alloys. The chemical content of machined pieces materials were taken into account during the EDI (Table 1).

Table 1

Chemical content of machined pieces materials

Alloy	Chemical content
Iron alloy	
Steel C45	0.42-0.50 % C; 0.17-0.37 % Si; 0.5-0.8 Mn; ≤0.25 % Cr; ≤0.04 % S; ≤0.035 % P; ≤0.25 Cu; ≤0.25 % Ni; ≤0.08 % As; the rest (basis) – Fe
Titanium alloy	
TiAl6Mo4	5.8-7.0 % Al; 2.8-3.8 % Mo; ≤0.5 % Zr; 0.2-0.4 % Si; ≤0.30 % Fe; the rest (basis) – Ti
Aluminum alloy	
AlCu4Mg1	3.8-4.9 % Cu; 1.2-1.8 % Mg; 0.3-0.9 Mn; ≤0.5 % Fe; ≤0.5 % Si; ≤0.1 % Ni; ≤0.30 Zn; ≤0.1 % Ti; the rest (basis) – Al
Copper alloys	
Technically pure copper M0	Basis – 99.95 % Cu, impurity - ≤0.05 %
Brass Cu63Zn37	Basis – 62.0-65.0 % Cu; 34.5-37.5 % Zn; impurity - ≤0.5 %
Bronze Cu95Al5	3.5-6 % Al; impurity - ≤0.5 %; the rest (basis) – Cu

To realize the EDI process the piece surface was processed in a sub-excitation regime, in which the processing occurs by "cold" electrode spots without surface layer melting of the processed material. The condition of the energy balance, in this case, takes the form [12]:

$$Q = \frac{4W_S}{\pi d_c^2 S} < Q_{melt}\,, \tag{3}$$

where Q is the heat emitted on the surface of electrodes per volume unit, J/m^3; $W_S = \int_0^{\tau} u(t)i(t)dt$ is the energy emitted in the interstice, J; u(t) is the voltage on the interstice at the discharge, V; i(t) is the instantaneous value of the current in the interstice, A; τ is the duration of the discharge impulse, s; d_c is the diameter of the plasma canal, m; S is the distance between the electrodes (the gap value), m; $Q_{melt} = q_{melt} \cdot \rho_{melt}$ is the volumetric melting heat of the processed piece, J/m^3; q_{melt} is the specific melting heat of the processed piece, J·kg^{-1}; ρ_{melt} is the material density at the temperature of melting, kg·m^{-3}. So, for the EDI of construction steel, the energy emitted in the interstice of 1-2 mm will not exceed 6-10 J.

The impulse current generator [8, 9] with voltage block for interstice pre-ionization was used as a source of energy. The discharge energy emitted in the interstice constitutes 1-6 J. And, thus, establishing the generator energy regime, the superficial piece oxidation for indicated materials without melting of the processed surface can be produced.

The thickness of the oxide pellicle subjected to the condition of the energy balance and according to Palatnik's criterion [11], is directly proportional, respectively, to the quantity of heat and the energy emitted on the electrode surfaces:

$$\begin{aligned} &\delta \sim Q; \\ &\delta \sim W_S. \end{aligned} \tag{4}$$

The power of electrical discharge:

$$P = \frac{dW_S}{dt} = \frac{W_S}{\tau} \tag{5}$$

where τ is duration of electrical discharge.

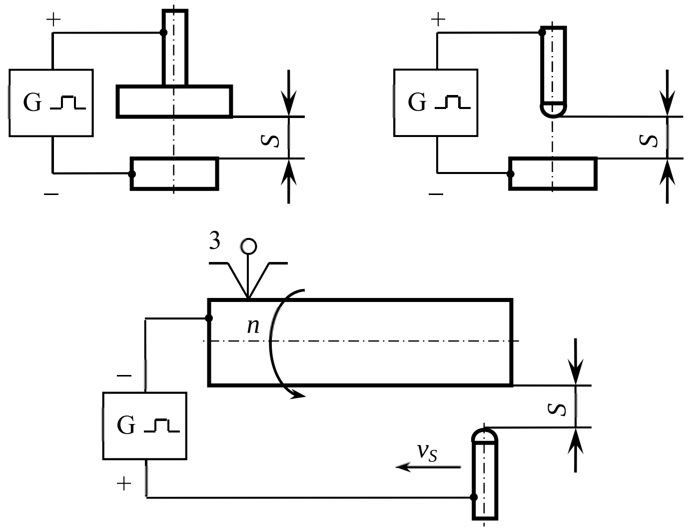
From the other point of view, the thickness of the oxide pellicle depends on the physical properties of processed surface material [5]:

$$\delta \sim \sqrt{\rho \cdot c \cdot \lambda}\,, \tag{6}$$

where ρ is material density, kg/m^3; c is specific thermal conductibility, W/(m·K); λ is specific melting heat, J/kg.

Thus, the thickness of the oxide pellicle is directly proportional to the power of electrical discharge emitted in the interstice and depends on the physical properties of processed surface material.

Technological schemes used in the formation of the oxide pellicles by applying EDI are shown in Figure 1. The work-piece was connected in the discharge circuit as a cathode, and the tool-electrode – as an anode.



a) b) c)

Figure 1. Technological schemes of the oxide pellicle formation by applying EDI: a) on the plane surface with plane tool-electrode; b) on the plane surface with a semi-circular tool-electrode; c) on the external cylindrical surfaces

The direct determination of operating properties that affect the functionality of pieces has required intensive investigations. Therefore, this task has been allocated for the performance that best suits the peculiarity of the work and does not require the use of lengthy and expensive techniques and equipment.

For evaluating and determining the operating properties of oxide coverings that characterize corrosion resistance, active surface resistance and other properties, the results of measuring the following characteristics of the coverings are presented: surface morphology (SEM), chemical (EDX) and phase (XPS) composition of coverings, the total pellicle thickness (Nanoscale Profilometer).

Results of experimental investigations and their analysis

The results of SEM and EDX analysis of investigated sample surfaces are represented in Figures 2 - 7 and in Table 2.

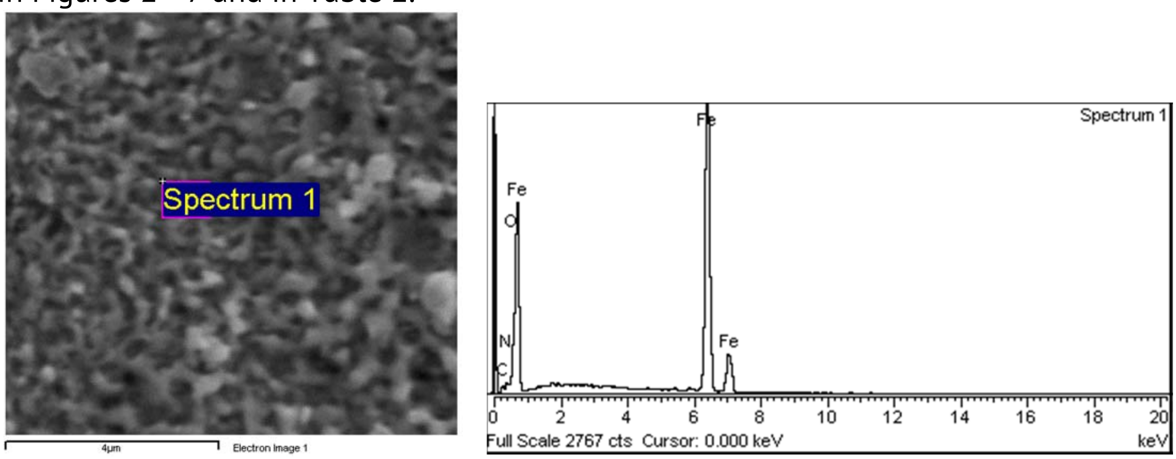


Figure 2. SEM and EDX analysis of steel C45 sample surface [6, 7]

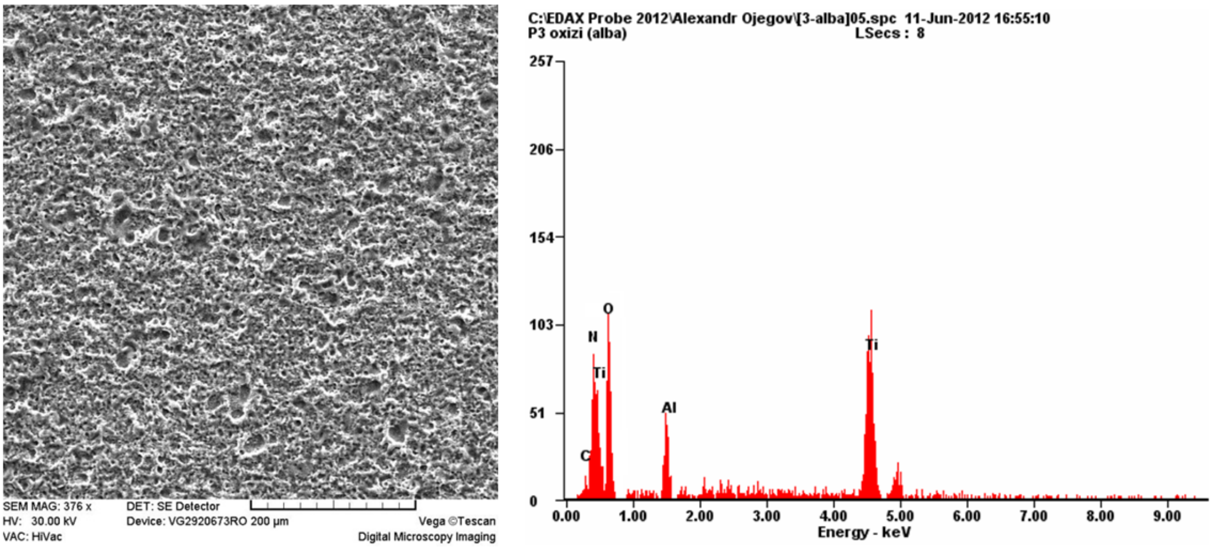


Figure 3. SEM and EDX analysis of TiAl6Mo4 titanium alloy sample surface

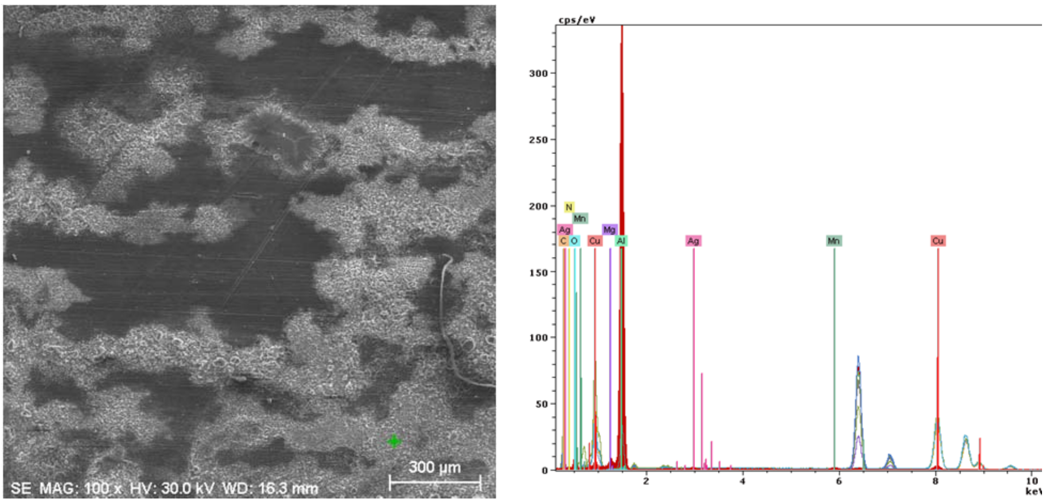


Figure 4. SEM and EDX analysis of AlCu4Mg1 aluminum alloy sample surface

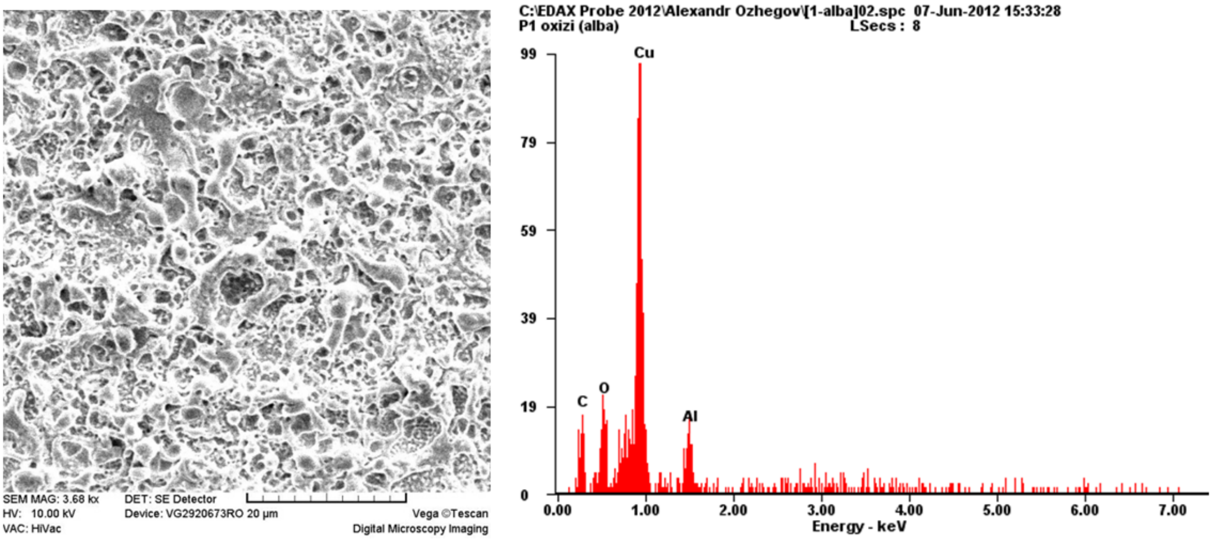


Figure 5. SEM and EDX analysis of M0 copper alloy sample surface

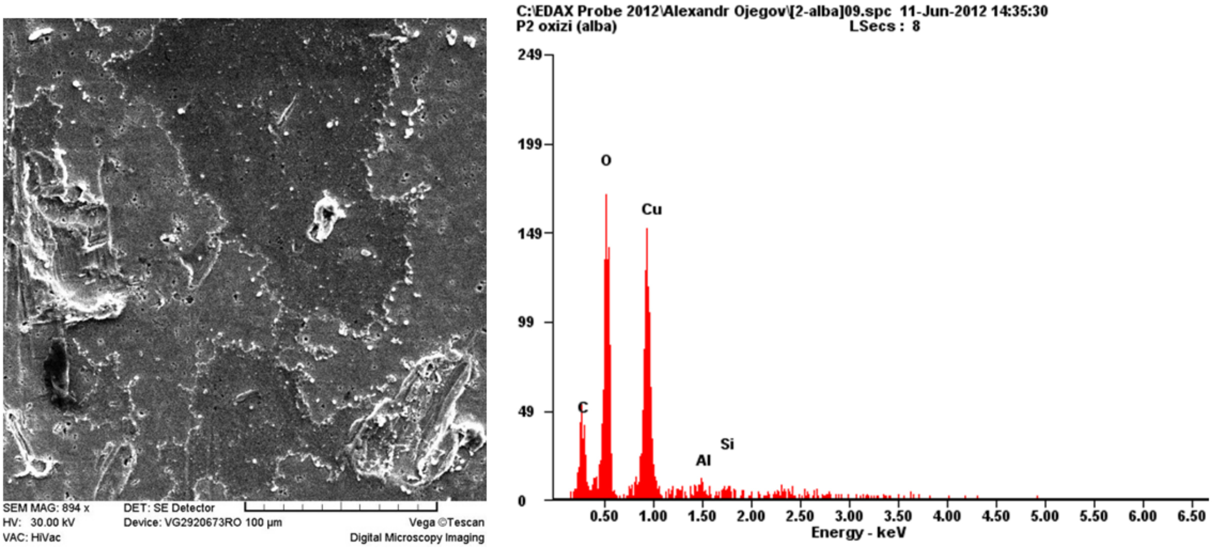


Figure 6. SEM and EDX analysis brass Cu63Zn37 sample surface

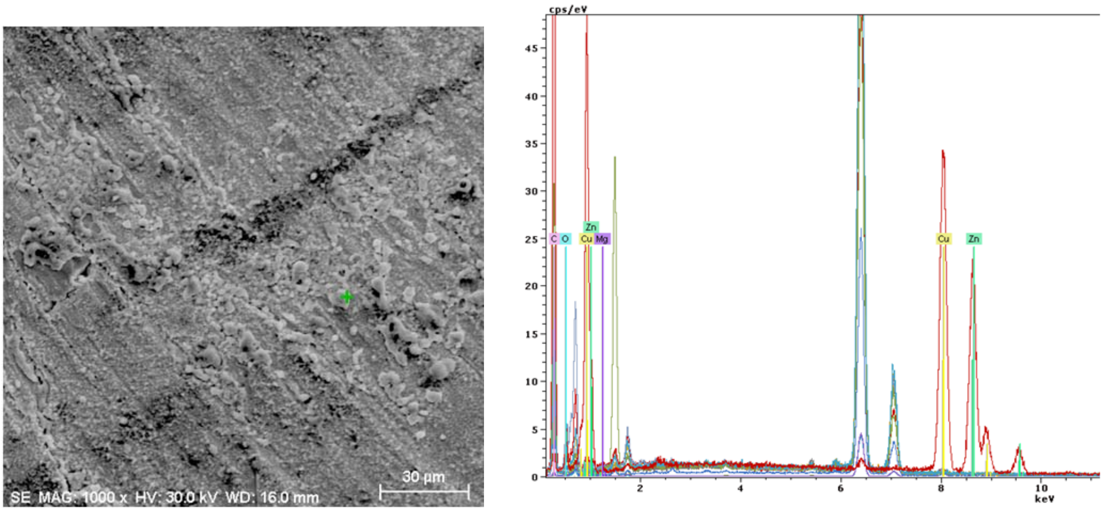


Figure 7. SEM and EDX analysis bronze Cu95Al5 sample surface

As we can see out of these results, the abnormal dissolving oxygen in metals is observed when processing metal surfaces by this method [6]. It is demonstrated that the desolation of the oxygen when processing the samples made of construction steel reaches 60% at, those made of titanium alloys – 30-35% at, the ones made of aluminum alloys – up to 20% at and those made of copper alloys – 50% at. The superficial layer of steel and titanium alloy surfaces includes, beside the oxygen, the nitrogen too.

Table 2

The EDX analysis of sample element content

Basis material of the sample	EDX element content of processed surface		
	Element	[norm. wt.%]	[norm. at.%]
Steel C45	Carbon	1.89	4.32
	Nitrogen	7.82	12.43
	Oxygen	29.77	58.74
	Iron	60.52	24.51

Table 2 Continuation

Titanium alloy TiAl6Mo4	Carbon	00.41	01.38
	Oxygen	30.33	33.27
	Nitrogen	03.38	09.56
	Aluminum	05.84	08.57
	Titanium	60.04	47.22
Aluminum alloy AlCu4Mg1	Aluminum	66.84	55.68
	Oxygen	13.95	19.60
	Magnesium	2.49	2.30
	Carbon	1.82	3.40
	Copper	2.42	0.86
	Manganese	0.55	0.23
	Silver	0.86	0.18
Technically pure copper M0	Copper	59.5	25.55
	Oxygen	29.53	50.50
	Carbon	10.22	23.20
	Aluminum	0.75	0.76
Bronze Cu95Al5	Copper	52.97	21.18
	Oxygen	26.66	42.34
	Carbon	14.83	31.38
	Aluminum	02.66	02.50
	Silicate	02.87	02.60
Brass Cu63Zn37	Copper	42.30	23.25
	Zinc	32.89	17.57
	Oxygen	16.72	36.50
	Carbon	7.52	21.86
	Magnesium	0.57	0.82

Signal XPS analysis (Figure 8) revealed the presence of oxygen O-1s in three types of chemical bonds (collectively called components). These are: component O^{-2} (which contains oxygen atoms of the metal oxides, in the sample is labeled number 3 in Figure 8, with the specific energy 529.6 EV); component OH^- with the specific energy 531.5 EV (indicated by the numeral 2 in Figure 8); the relationship of O-C and O-C=O type (with the specific energy 533.4 EV, the curve no. 4 in Figure 8).

The chemical analysis showed the concentration of each of the three components (C) (a): (C) (b): C (c) = 0.89: 1.00: 0.50. Additional studies have shown the possibility of the existence of the fourth component of oxygen within the context of type $O\text{-}H_2$, however, the relative concentration of the component value is assumed to be not greater than 0.15.

Studies have proven that when applying the EDI method for the formation of oxide pellicles there is no change in the geometry of the original surface. This makes it possible for us to recommend this method for surface processing of completed parts. The thickness of films is between 10-240 nm [10], which allows us to include it at the level of nanotechnology.

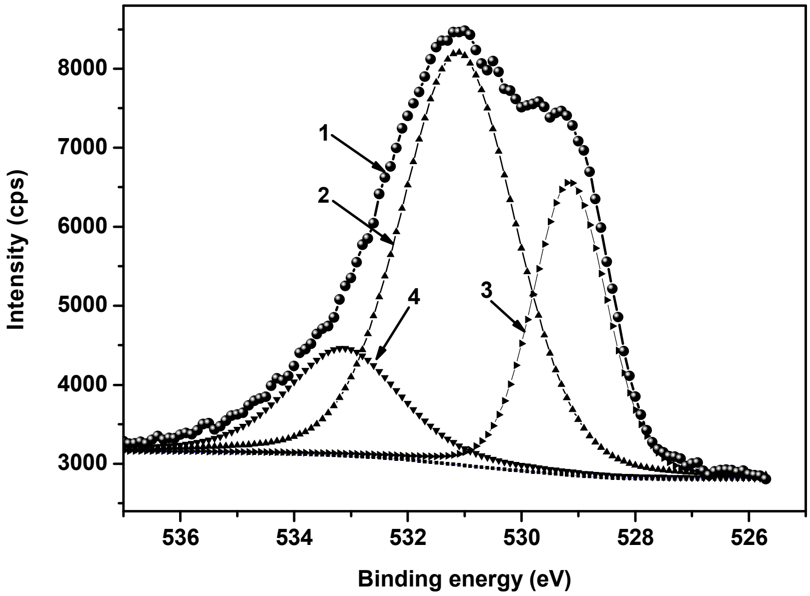


Figure 8. The phase composition (by XPS analysis) of oxide pellicles on samples of steel 45 (spectrum of oxygen on the surface) [12]: 1 – total spectrum; 2 – OH^- component; 3 – O^{2-} component; 4 – components of O-C and O-C=O types

Oxides of metals in the pellicle are in amorphous state. This probably explains why the surface electrical resistance for steel pieces increases up to 10^6 Ω/mm [7], the potential to corrosion increases by 10 or more times, and the corrosion speed is reduced by 2...4 times [6, 7].

Conclusions

– the obtained results allow to recommend the ESO method for processing the internal and external surfaces of pieces made of iron, aluminum, copper and titanium alloys and to indicate the possibility of applying the method in anticorrosive protection of machine pieces, in surface passivation of pieces in the chemical industry;

– when processing the samples made of construction steel the desolation of the oxygen reaches 60% at, those made of titanium alloys constitutes 30-35% at, the ones made of aluminum alloys – up to 20% at and those made of copper alloys – 50% at.;

– XPS analysis of steel 45 samples' surfaces shows the presence of three types of oxygen components: OH^- component; O^{2-} component and the components of O-C and O-C=O types. The concentration of each of the three components is (C) (a): (C) (b): C (c) = 1.00: 0.89: 0.50;

– the superficial layer of steel and titanium alloy surfaces includes the nitrogen beside the oxygen;

– each compound formed while processing by electrical discharges in impulse is in amorphous non-stoichiometric state;

– maximal depth of oxide pellicles reaches up to 250 nm depending on energy regime and material of samples.

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