PROCEDEE TEHNOLOGICE DE MICRO ȘI NANO STRUCTURARE A MATERIALELOR CU APLICAREA PLASMEI DESCĂRCĂRILOR ELECTRICE ÎN IMPULS

MICRO- AND NANO-TECHNOLOGICAL POCEDURES OF MATERIAL PROCESSING BY APPLYING PEDM

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Micro- and nano-technology is nowadays a field of production that grows up vigorously and attempts to solve the material and energy crisis that has affected all mankind on the one hand, and, on the other hand, it comes with new solutions in miniaturization of the technique and solving the problems faced by the compatibility of existing materials with the living matter, i.e. it comes with apply for a better life. The recent studies regarding the interaction of surface materials with plasma pulsed electrical discharges caused by a solitary discharge have shown that under the action of PEDM the active surfaces of the parts applied in machine building, electronics, chemical industry, food industry, medicine, etc. micro-modifications of these surfaces can take place, along with the formation of 3D-structured carbon films with micrometric thicknesses, synthesis of amorphous films of oxides and hydroxides of nanometres thicknesses. The application of surface micro-geometry modifications ensures the increase of the thermoelectric current of the electrons up to 10 times, the surface-active resistance by 10^7 times, the resistance to corrosion in the aggressive media from 2 to 100 times.

Micro- și nanotehnologia este astăzi un domeniu de producție care crește viguros și încearcă să rezolve criza materială și cea energetică care a afectat întreaga omenire, pe de o parte, iar pe de altă parte, vine cu soluții noi în miniaturizarea tehnicii și rezolvarea problemelor cu care se confruntă știința, compatibilitatea materialelor existente cu materia vie, adică vine cu aplicarea științei pentru sporirea calității vieții. Studiile recente privind interacțiunea suprafeței materialelor cu plasma descarcărilor electrice în impuls (PDEI) au demonstrate, că sub acțiunea acestora pot avea loc micro- și nano modificări ale suprafețelor pieselor aplicate în construcția de mașini, electronică, industria chimică, industria alimentară, medicină, etc. Modificările în suprafețele pieselor sunt însoțite de formarea filmelor: de carbon structurate 3D cu grosimi micrometrice și sinteza filmelor amorfe de oxizi și hidroxizi de grosimi nanometrice. Aplicarea modificărilor microgeometriei suprafeței asigură creşterea curentului termoelectric de până la 10 ori, peliculele de oxizi cauzează creşterea rezistenței active de suprafață de 10^7 ori, rezistenței la coroziune în mediile agresive de la 2 la 100 de ori.

Keywords: *micro-, nanotechnologies, pellicle, film, corrosion, emission, resistance*

1.Introduction

At present, a vertiginous development has known at the beginning the field of micro, followed quickly by that of nanotechnologies. They come to solve a multitude of problems faced by all of humanity, among which the crisis of materials and energy can be highlighted.

Micro- and nanotechnology comes with new solutions in the miniaturization of technology, thus solving the problem of the material crisis, and finally solving the problems faced by the compatibility of existing or artificially created materials with living matter, that is, it comes with solutions regarding the improvement of the quality of life. It applies a whole range of phenomena of physics, chemistry, biology and comes in turn with new knowledge and legalities obtained in the process of scientific research. Of particular interest is the physical methods of nanotechnology and especially those of plasma interaction with material surfaces or with material particles of different origins. Plasma as the fourth form of existence of matter is most often obtained by electrical discharges [1-3].

In this context, it is important to mention that the most widespread method of obtaining plasma is electrical discharges [1, 2]. In the case of electric discharges, plasma formations interact with the working environment and with the surfaces of the electrodes, causing important changes in composition, structure and, as a result, in properties.

Recently, a series of scientific papers have appeared that attest to the application of plasma in various nano-technological processes for obtaining nanoparticles and nano-films [1-3]. In these works, plasma is cautious as a highly ionized gas that interacts with highly ionized processed surfaces, which causes a whole host of effects. These effects do not find their real explanation, but only remain, as documented experimental findings and applied in practice, without penetrating deep into their scientific essence.

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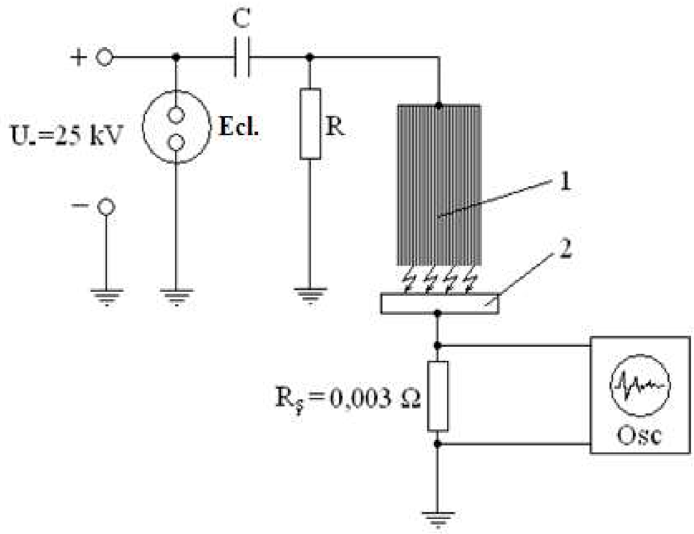

Fig. 1 - Schematic presentation of the experimental stand / *Schema standului experimenal*

2. Research methodology

For the research of the phenomena related to the electrical discharge in gases and its interaction with the surfaces of the electrodes, a construction made of two electrodes is used, placed at a certain gap in which the gaseous medium is located at different values of its pressure.

New technological processes in which plasma serves as a tool for processing metal surfaces is not possible without real knowledge of how it interacts with processed surfaces and the working environment, in order to confer new permanent or temporary functional properties

The component of the equipment assembly applied in the research is shown in fig.1. It consists of the following [1, 2]: ge power supply at voltage U = 25 kV, arrester (Ecl.), capacitor battery (C), current-limiting resistance (R), electrode-anode (1) and part-cathode (2).In order to measure the pulse current intensity and its duration in the discharge circuit, a coaxial shunt with active resistance R=0.003Ω is inclined, parallel to which the oscilloscope (OSC) is connected.

The tool electrode (anode) is composed of several wires (elimentary electrodes) with one and the same active resistance. Such a construction ensures uniform division of the discharge current through all elimentary electrodes. Thus, in the interstitium between the electrode-anode and the electrode-cathode, several condictivity channels are formed simultaneously for a solitary impulse electrical discharge. It ensures homogeneous and sufficiently high current densities in the interstitium and determines an increased efficiency of using the energy of solitary electric discharge and, last but not least, the homogenization of plasma in the interstitium.

Before processing, the samples were prepared by fine sanding to the mirror state. After processing plasma pulsed electrical discharges [5], on their surfaces have certain changes have been attested: areas of thermal influence where the surface of the sample had the color of freshly pickled metal (the surface was enriched with elements contained in the plasmogenic medium) and areas where plasma caused melting of metal (erosion craters or conical roughness extracted from craters and frozen on the surface were observed in them).

The study of the surface of samples after processing and recording information about their condition was performed with the help of metallographic microscope type XJM600T. Equipping this microscope with the digital information recording system allowed it to be stored and processed on the computer.

The study of surface geometry was performed by electron microscopy (SEM) method and the determination of chemical composition by EDX analysis of the surface layers of processed samples. The research was conducted with the TESCAN microscope from the National Center for the Study and Testing of Materials, which operates under the Technical University of Moldova in the Republic of Moldova.

3.Technological processes of micro and nano processing with PEDM

3.1. Extraction of conical asperities from metal surfaces

The authors of this work support the hypothesis that the contact between the plasma of electric discharges and the surfaces of the electrodes takes place through "cold" and "hot" electrode spots. When pulsed electrical discharges interact with electrode surfaces via "hot" electrode spots, they generate heat fields with temperature $T\sim4\cdot10^4$ K and simultaneously generate strong electric fields ($E=10^6\div10^8$ V/m).

The authors of the papers [3, 5, 7, 10] put forward and defended the hypothesis, according to which thermal phenomena in the material of the processed surface are caused by the high temperature field, and surface erosion phenomena are caused by electric fields developed by electrode spots. They argue that material sampling [3, 7, 12] is caused by the development of capillary waves on the surface of liquid metal under the action of strong electric fields generated by electrode spots

We consider that on the liquid metal in the surface attacked by the plasma of the electrodes, acts: the pressure force of the ion and electron beams, the pressure force caused by the metal vapor and the surface tension force of the liquid.

Taking into account the scientific findings of the authors of the papers [6,7], they performed the extraction and freezing of Taylor cone roughness (Fig.2) from the processed surfaces. These roughness [7,10,13] confers new functional properties to the processed surfaces: changing the surface relief, significantly increasing the active surface area of the part, increasing the electronic thermoemission capacity and could be applied to the construction of microobjects (console for AFM).

The authors of the papers [8,10, 11, 13] through a wide range of experimental studies have determined, that in order to extract from the surface and freeze on it roughness such as Taylor cone by applying PEDM, it is necessary to satisfy the conditions imposed by the processing process.

The first of these would be to provide local melting of the surface of the workpiece. This condition can be satisfied if the inequality (1) deduced by the authors [8, 10] is satisfied:

$$Q = \frac{4W}{\pi d_c^2 S} \geq Q_{melt}\,, \qquad (1)$$

where: Q - the amount of heat released into the gap at a solitary electrical discharge; W – the energy released into the plasma jet in the interstitium I DC – the diameter of the liquid phase surface portion obtained on the surface of the cathode piece at a solitary discharge; S – size of the interstitium; Qmelt - is the volumetric density of the melting heat of the workpiece material. It is dependent on the performance of the material of execution of the part and is calculated with the relation:

$$Q_{melt}=q_{melt}\cdot\rho;, \qquad (2)$$

In the last relationship $\mathbf{q_{melt}}$ is the specific melting heat of the workpiece and ρ its density.

In order to extract conical roughness from the molten metal surface, it is necessary, in the interstitium, to act on the electric field with the intensity of 10^8 V / m [9, 19].. It is mandatory to take into account that the liquid on the surface of the part is subject to the actions: electrodynamic force (generated by electrode stains), surface tension and weight force (this component was neglected by the authors [13]

Since both the heating and melting of the surface of the part and the disturbance of the surface accompanied by the development of

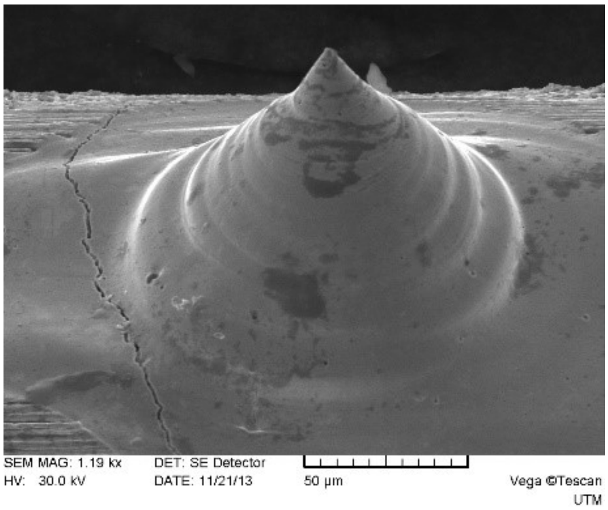

Fig.2 - Conical meniscus view extracted from anode executed from W+10%Re (energy released into the gap W = 3,04J, capacitor battery capacity of generator C = 200µF, gap size S = 0,3 mm, diameter of machined surface area d = 0,25 mm, number of electrical discharges applied to surface portion n = 1) / *Aspertate conică extrasă din suprafața anodului executat din aliajul W+10%Re*

capillary waves on the surface of the liquid occur under the action of the electric and thermal fields generated by the electrode spots, the following relationship will be applied to calculate the strength of the critical electric field [8,12,13]:

$$E_{cr} = \sqrt[4]{64\pi^2 \rho g \gamma \times 3 \times 10^4}\,, \qquad (3)$$

where: E_{cr} is the critical electric field strength in the cathode (or anode) layer; ρ – density of the workpiece material at melting temperature; g – acceleration of universal free fall; γ – surface tension coefficient of liquid material (critical values of the electric field are: 16.1·106 V/m – for W(tungsten), 12.7·106 V/m – for Fe, 8.6·106 V/m – for Ti, 13.2·106 V/m – for Mo).

Another necessary condition to be satisfied according to the authors of the papers [8, 10-13-], is the accumulation of the critical amount of charge (σcr) on the liquid surface of the metallic material subjected to interaction with pulsed electric discharge plasma, which can be determined with the relationship:

$$\sigma_{cr} = \sqrt{\frac{g\rho\gamma}{4\pi^2}}\,, \qquad (4)$$

In order for the surface of the workpiece to melt, it is necessary that the gap is covered by an electric current of critical intensity and density. Since during discharge the current changes value, its critical density will be calculated for the value of its amplitude in solitary discharge, with the relation [12]:

$$j = \frac{4I_{max}}{\pi d_{cr}^{2}}, \qquad (5)$$

where: ***j*** is the current density in the interstitium at a solitary discharge; Imax – impulse current amplitude value; dcr – diameter of plasma footprint on the machined surface of the workpiece (experimental measurements have shown that the critical density required by current for melt formation for some metals is: for Fe it is 129.6 , for Ti – 160.4 and for Cu – 369 A/mm^2).

Experimental research has allowed to establish that the height of the conical meniscus is dependent on: the energy of the electric discharge released in the interstitium, the duration of the pulse, the properties of the electrode-anode execution material, the intensity of the electric and magnetic fields applied to the interstitium [10].

The tests on increasing the thermo-electronic emission capacity of cathodes made of W+10%Re alloys [13] demonstrated that for the same operating regime, in the case of applying only a single conical asperity on its active surface, the intensity of the emission current increases by 10 times

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3.2. Extraction of nanowires from surfaces of cathode parts made of aluminium alloys

Thus, the authors of the works [14,15], have experimentally verified the possibility of extracting nanowires for the case when the electrode manufacturing alloy subjected to PEDM processing presents in a solid state a mechanical mixture of the crystals of the chemical elements in the composition.

The authors of the papers [14,15,16] obtained SnO_2 nanowires extracted from the surfaces of the executed samples, well-being alloys of the Al-Sn group. The nanowires were extracted from the cathode-skin surfaces under the action of PEDM plasma in air medium in normal tails (see Fig. 3)

Following SEM/EDX measurements, the chemical composition of these nanowires was determined, containing:: Al -19,1%, Sn-61,5%, O-11,5%, N- 4,9% and C-3%

It can easily be seen that the concentration of Sn is considerable. The analysis of the composition of the nanowires proves that it is basically tin dioxide. It is natural to form oxides given the fact that the processing takes place in the atmosphere under ordinary conditions, and the components of the electrode execution alloy have an avidity for oxygen.

The explanation of the physics of the formation of nano-wires interpreted by the authors [16,17] is not a plausible one, given the fact that they put forward the hypothesis only emerging from those "as the alloy from which the part is made covers an aluminum matrix in which the tin is dissipated, which melts being thrown into the interstitium in the form of a drop, and it is deformed

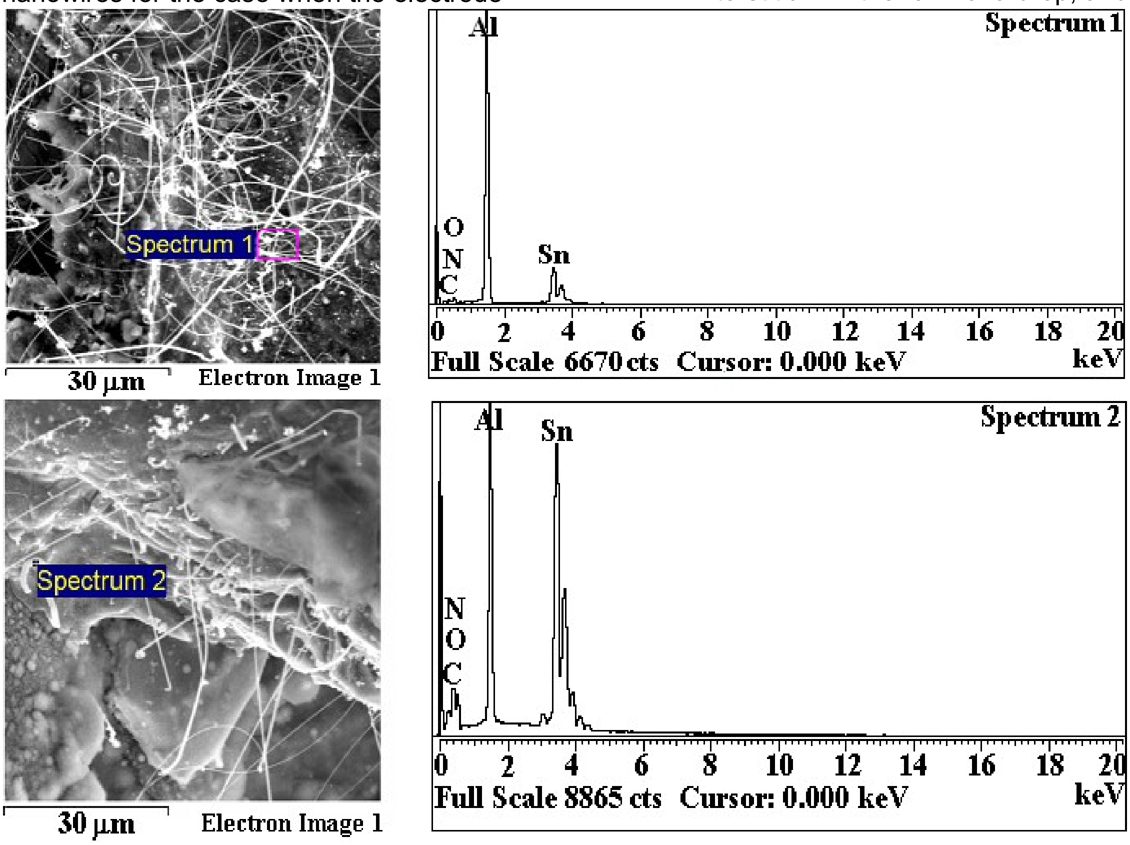


Fig. 3 - Morphology and EDX spectra of the electrode-anode and workpiece-cathode surfaces after processing
Morfologia și spectrul EDX a suprafeței electrodului-anod și piesei-catod după prelucrare

under the action of the electromagnetic field, up to the state of nanowires".

From our point of view [18.19], this is not the case, as the authors considered [14:15,16]. If we take into account that melting occurs under the action of electrode spots, which, according to [7,12], present concentrated sources of both heat and strong electric fields (106÷108 V/m), these being distributed according to the radius vectors of the point source, we could have the argument that the obtained wires have a cylindrical shape. Their considerable length is due to melting and ionization of the processed surface under the action of "warm" electrode spots. Also under the action of "warm" electrode stains.

Nanowires are extracted, which have a migratory character of movement at a speed of about 30 m / s and drive molten and ionized metal. In this way, nanowires of considerable lengths can be obtained, as shown in fig. 3. The distribution of the wires on the processed surface attests to this, having a configuration characteristic of the trajectory of the displacement of the electrode spots! The length of the wires can be obtained only due to the movement of the electrode spots (v=30 m/s) and in no case of the electrodes, which for the deposition formation installations is v=10^{-2} m/s and the duration of a discharge is the order of 10^{2} μs.

It is obvious that in this situation, melting Sn occurs at deeper depths

Tin (Sn) is located in the still solid matrix of aluminium, which in turn undergoes expansion and thus facilitates the process of extracting nanowires under the action of electric fields generated by electrode stains.

The nanowires generated by this method are relatively cheap and could solve the problem of electrical conductors for contemporary electronics.

3.3. Generation of fullerenes and carbon nanotubes

The deposition of carbon layers of micro and nanometer thicknesses on the surfaces of Steel-30 and Steel-45 parts also causes diffusion of carbon atoms in the part surface of the part, accompanied by the formation of cementite high hardness and, as a result, the wear resistance of this layer increases proportionally [20-22].

Superficial processing with the deposition of carbon films by the PEDM method, conditions in all cases reducing roughness on the processed surface. According to the experimental results of checking parts for operation in kinematic couples by the authors [22,23-28], the application of carbonaceous films, conditions an approximately 3-fold decrease in friction force for component parts of kinematic couplings.

In order to elucidate the effects and transformations that occurred on the surface and inside the machined layer of the anode-piece and cathode-electrode, a lot of SEM research of their surfaces and sections was expectorated.

Morphology, chemical composition and micro geometry surfaces as a result of SEM research of surfaces subject to interaction with plasma are shown in Fig. 4. and Fig. 5. Through SEM measurements, the geometry of surfaces was determined and measured, also the chemical composition of the electrode-cathode execution material. From these we can obsess on the surface of the catode-electrode, the formation of spherical globules in groups (fig.5) If we refer to the chemical composition, it presents 100% carbon, due to the fact that they are made of pyrolytic graphite.

There are a number of important changes in the micro geometry of the surface as a result of the action of plasma in the interstitium. At the same time, the active surface of the electrode-cathode is bombarded with plasma ions. It has undergone micro geometry changes. Nanometer-sized globular carbon formations have been attested on this surface (Fig. 5)

The generation on the surface of the cathode-tool of carbon globular formations can be explained as a result of simultaneous and concurrent action: melting and vaporization of

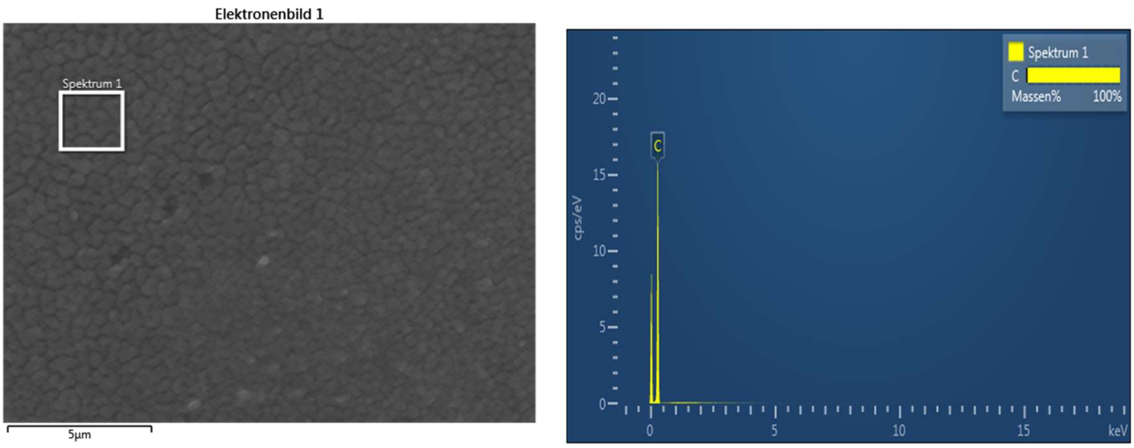


Fig.4 - Surface morphology of tool electrode (a) and chemical composition of tool material (b)

. Morfologia suprafeței electrodului-piesă (a) și compoziția chimică a acestuia (b)

carbon, followed by its recrystallization. All this occurs under the action of strong thermal and electric fields generated by electrode spots. An additional source of energy is the bombardment of its surface with ions from plasma and the workpiece. The generation of special carbon structures occurs under the influence of strong electric fields and in the presence of iron ions.

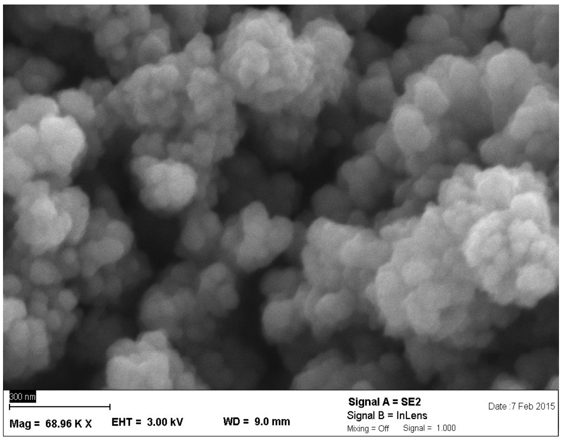


Fig.5 - Micro surface geometry of the tool-electrode (made of pyrolytic graphite) after interaction with pulsed electric discharge plasma / *Micro geometria suprafeței electrodului-piesă (executat din grafit pirolitic) dupa interacțiunea cu plasma descarcarii electrice în impuls.*

SEM surface analyses of the tool-catode made of pyrolytic graphite demonstrate the formation of micro formations (Fig. 4), which in turn are assembled from discovered nanostructures (Fig. 5). These experimental findings require that a chain of phenomena specific to electrical erosion of graphite occurs.

An explanation of the phenomenon of generation of fullerenes and carbon nanotubes in the case of applying electrodes made of pyrolytic graphite according to the authors [20,21,24], such as the fetus, as from the beginning, melting and vaporization, as well as followed by carbon crystallization, are generated by pnctiform sources of heat and strong electric fields.They impose the formation of fullerenes at first, and as a result of their development, condition the formation of carbon nanotubes.

We could admit that at first fullerene-like space structures are generated, and then (of course, not in all cases), under the influence of temperature and strong electric fields and in the presence of beneficial iron ions, their development into single-walled nanotubes takes place.

It is important to mention that at the beginning, SEM analyzes attested to the presence of spherical carbon formations on the electrode surfaces (fig. 5.) and as a result raised new questions, so followed other types of analyzes.

First, the authors [20,21-27] admitted that carbon deposits of this type are characteristic of metal surfaces and especially those made of Steel-45. If we were to admit that the tool-catode is made of graphite (it is the source of the deposition material) and graphite would crystallize on the processed surface (similar to deposits formed by metals), then we would be wrong.

We consider that the deposition layers are graphite formations and knowing the constant of its crystal lattice, arising from the fact that the functioning of parts in kinematic couplers breaks the formations deposited after the crystallographic planes layer by layer, we could determine how long they are functional. The experimental research of the authors [34,38,42], proved that this is not so, and the service life is many times longer than in the case of pyrolytic graphite.

In real research, the thickness of the deposition was taken into account as a maximum and minimum value, knowing the constant of the crystal lattice of graphite, we would determine the maximum number of cycles that a carbonic deposition can withstand, its composition does not correspond to the usual wear of graphite [28-31], which is why Raman analyzes were performed.

Raman analyses have allowed elucidation of which carbonaceous structures are actually formed during vaporization of pyrolytic graphite in plasma, transfer of carbon atoms to the surface of the anode part (made of Steel-30) and accelerated crystallization (due to the high thermal conductivity of steel) in the presence of iron atoms.

Thus, if we compare the Raman bands of the carbon depositions on the samples' surfaces shown in Fig. 6, and Fig.7, then corresponding maxima "1281, 1596 and 1899" are attested on them, followed by "1280" and "1843", and these correspond to the characteristic of 3D structures (fullerenes and single-walled carbon nanotubes).

The functional properties of carbon deposits, their chemical composition and morphology indicate that they exhibit 3D structures and especially fullerenes and carbon nanotubes. The presence of iron on the target-anode, the purity of graphite in the tool-cathode, and high temperatures (10^4K), as well as rapid force cooling of the target anode, provides the necessary and sufficient conditions for the synthesis of 3D structures.

The presence of fullerenes and nanotubes can only be confirmed or disproved experimentally. Thus, the authors of the papers [32,33] subjected thermogravimetric analysis to crbon films in nitrogen medium at different temperatures. . They found an increase in sample mass under the influence of nitrogen at temperatures of 222.99 °C, 476.12 °C and 614.73 °C, which can only be explained by the fact that fullerenes include nitrogen atoms. Solubility tests with the application of a wide range of average, it has been established, that it ranges from 51 for chloro-naphthalene to 0,006 for tetrahydrofuran.

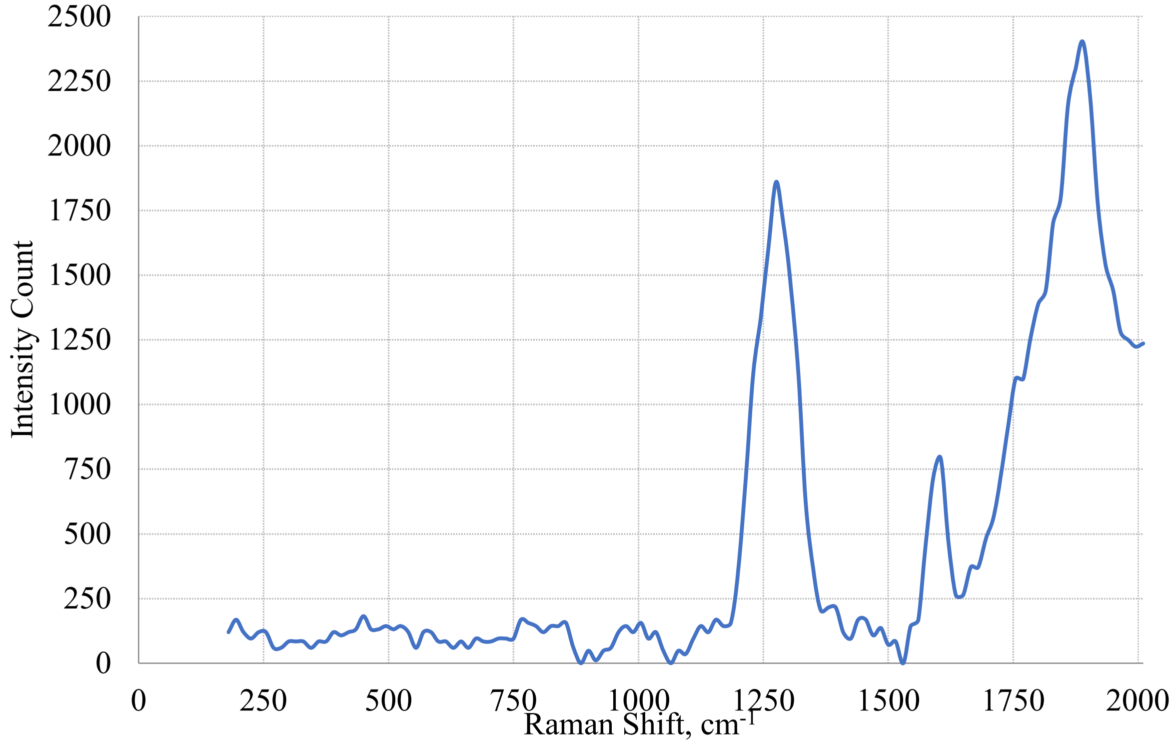


Fig. 6 - RAMAN spectrum of the carbon film (S=0,8mm,W=3,2 J, f=50Hz) .*Spectrul RAMAN al filmului de carbon (S=0,8mm, W=3,2 J, f=50Hz)*

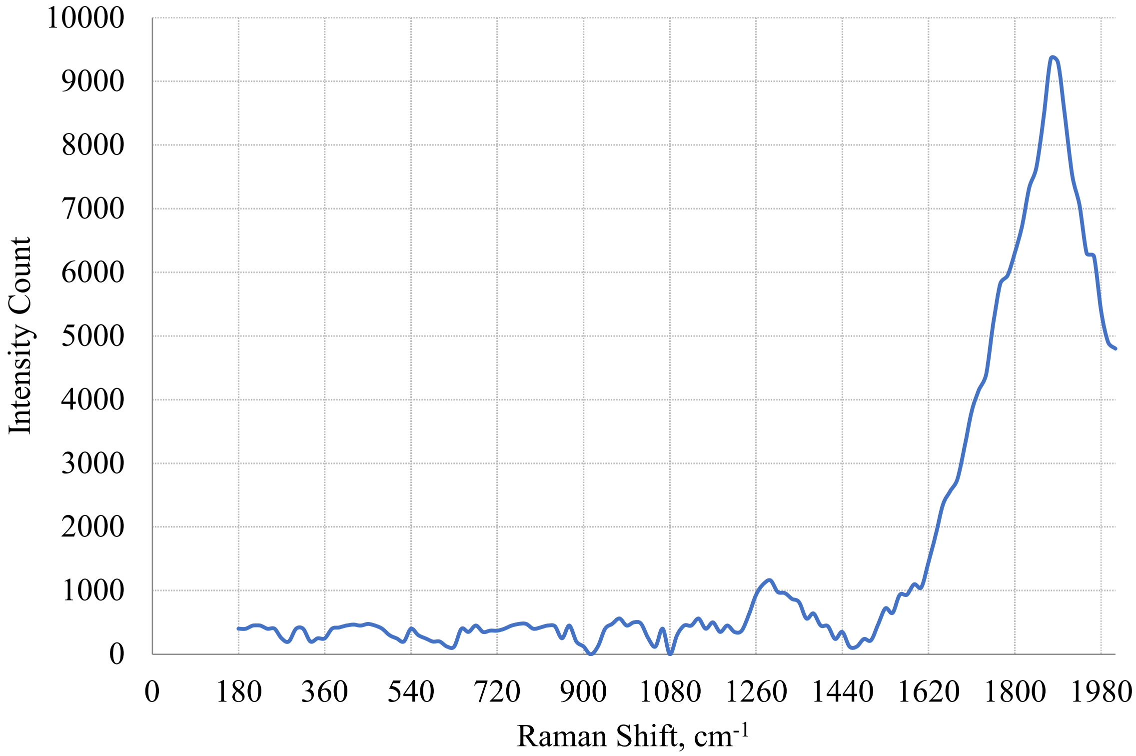


Fig. 7 - RAMAN spectrum of the carbon film (S=2mm, W=5,23 J, f=50Hz) / . *Spectrul RAMAN al filmului de carbon (S=2mm, W=5,23 J, f=50Hz)*

The deposits of carbon structures by PDEM method possess a wide spectrum of functional properties, such as: elimination of the grip effect of metal surfaces, reduction of adhesion for metal surfaces [32] by 3-4 times, reduction of wear speed by dry friction [25-27]from 1.5-2 to 7-10, increase of wear resistance (refractory properties) of components of parts of glass casting forms [32,34] by about 10 times, conditioning to increase corrosion resistance [25] in chemically aggressive environments of 1.5

3.4. Oxide pellicle formation

As mentioned by the authors of the papers [23,27, 34] the transfer of charged electric particles (electrons and ions) the development of plasma channels in the interstitium [34], the interaction of electrode surfaces with plasma occurs with the direct assistance of electrode spots. They are of two types: "cold" and "warm". The first ones are born on impurities and irregularities and move at speeds of 100m / s, the second ones are born on the first ones melt the surface of the electrodes and migrate on the surface at a speed of 30 m / s.

Previously, a series of researches were carried out [25, 31. 34], which established that in order to have heat or chemical-thermal treatment effects it is necessary to ensure the interaction of PEDM with electrode surfaces only through "cold" electrode spots.it is necessary to satisfy the condition, as volume density of heat in the interstitium be less than melting heat of the execution material of the electrode-part. According to the authors [34,36], this condition can be expressed mathematically with the relationship:

$$Q = \frac{4W}{\pi d_c^2 \cdot S} < Q_{melt}, \qquad (5)$$

The parameters in relation (5) are the same as in relation (1), and Q_{mel}- is hot melting of the workpiece execution material.

Detailed experimental research conducted by the authors of the paper [35], who investigated the processing of surfaces in the regime of maintaining impulse electrical discharges on "cold" electrode spots, demonstrated that it is possible to thermochemically treat surfaces with its enrichment with elements from the working environment and electrodes. After surface processing of steel-3 parts, Mössbauer spectral analyses were performed.

The results of spectral analyses are shown in fig.6. From the diffractograms, we can see that they show an overlap of doublets of iron oxides and hydroxides and confirm the presence of the γ-Fe phase in the case of the size of the gap S = 0.5 mm and the energy of the electric discharge released in the interstitium W = 4,5J The processing of samples was carried out in the -air environment at atmospheric pressure and temperature 24$°C$.

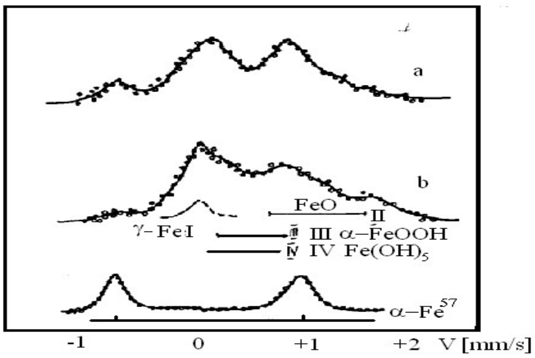


Fig. 8 -. Mössbauer spectra of Steel 3 samples processed by PEDM: / *Spectrul Mössbauer pentru suprafețele pieselor executate din Otel-3 si prelucrate cu PDEI:* W=4.5 J; S=2 (a); S=0.5 mm (b)

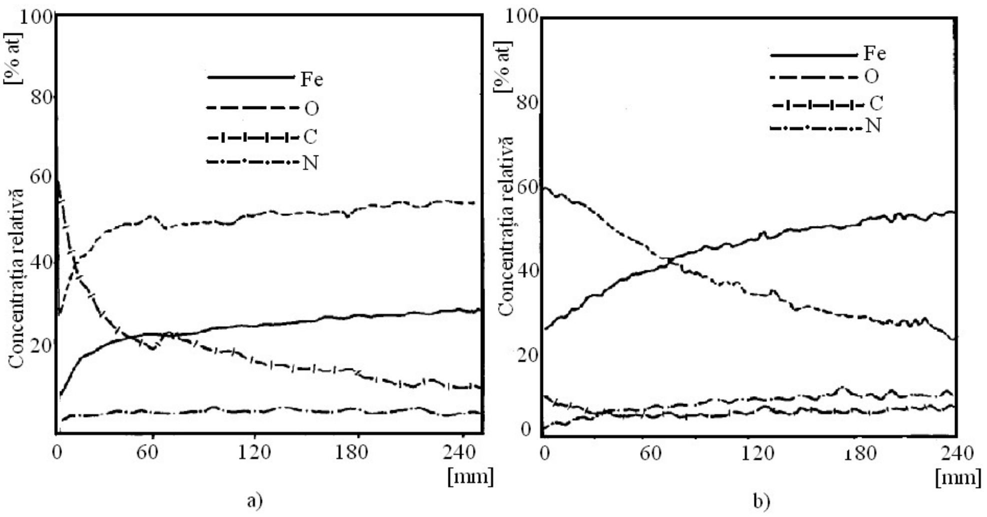


Fig. 9 - The concentration of elements in the processed layer depending on its depth for the sample made of Steel-3 for: / *Dependența concentrației elementelor în funcție de adâncimea stratului prelucrat pentru probe executate din Oțel-3 și prelucrare cu PDEI:* (a), S=0.5 mm W_s= 4,5J and (b); S=2mm and W_s= 4,5J;

The plasmogenic gas contains oxygen, nitrogen, hydrogen in significant quantities and other elements in insignificant quantities and the piece contains mostly iron and carbon. The distribution of these elements in the workpiece surface is shown in fig.7a. From this it can be seen, that carbon agglomerates at the surface of the sample and its oncentry decreases rapidly with the depth of the surface layer. If we refer to the concentration of oxygen, then it constitutes about 30% at the surface and with the increase in the depth of the surface layer of the piece at depths of 60nm exceeds the concentration of 50%.

According to the authors [35}, such a high concentration of oxygen can be obtained by forming not only oxide solutions, but hydroxides solutions in the surface layer of the sample. At the same time, the presence and concentration of nitrogen, at depths of the surface layer up to 300 nanometers, its concentration does not exceed the quota of 5-6%.

In the case of solitary electrical discharges at interstuium sizes of 2 mm and the amount of energy released in it of 5J, oxygen and iron are present in the surface layer in considerable quantities, and in much smaller quantities, carbon and nitrogen (fig. 7, b). It was established that at the end of the sample the oxygen concentration reaches precisely 60% and decreases much in the depth of the surface layer of the sample. This can be explained by the fact that hydroxides are formed at the surface and metastable oxides are formed at depth. According to roentgenograms, FeO is missing in the sample surface - the only iron oxide that is paramagnetic at room temperature.

Based on the experimental results obtained by the authors of the paper [35], they accepted that stable oxides of Fe_2O_3 and Fe_3O type are present in the formed layers. The analysis of the results obtained by the authors of the papers [35,36] allows as possible and real the synthesis of iron hydroxides in amorphous state. As seen from Fig.6, Mössbauer spectra have a very complex character, which is why the strict and indisputable identification of iron hydroxides in amorphous state is extremely difficult.

Examination of diffractograms and technological regimes for processing surfaces with impulse electrical discharges in their maintenance regime on "cold" electrodic spots allowed to establish that determinative for the formation of strits with important content of oxides and hydrooxides are, the size of the interstitium, the energy released in it and the number of electric impulse discharges attacking a sector of the surface of the part

The mathematical relationship, which exemplifies the reality between the depth of diffusion of elements in the surface layer of the piece as a function of the energy of the electrical discharge in momentum and magnitude of the gap was experimentally deduced by the authors of the papers [34,35] can be described with the relation:

$$h = kW_s / AS \tag{6}$$

In relation (6): k - own coefficient of the workpiece execution material; Ws – the part of the energy of an impulse electrical discharge that has been released into the gap; A – the area of the target surface and S – the size of the gap.

Research previously conducted by the authors [36-40] allowed to detect in the processed surfaces of compounds: a) OH- component; b) – O^{2-} component and c) O-C and O-C=O - components .

The detailed chemical analysis of the concentration ratio of components in the formed layer is: C(a):C(b):C(c)=0.89:1.00:0.50. This fact comes to attest that in fact, as expected, the surface layer contains mostly oxides, hydroxides and, of course, the base metal of the part. Research of the composition of the surface layer with great rigor allowed to establish the presence in quantities of approximately 0.15% of the oxygen component type $O\text{-}H_2$

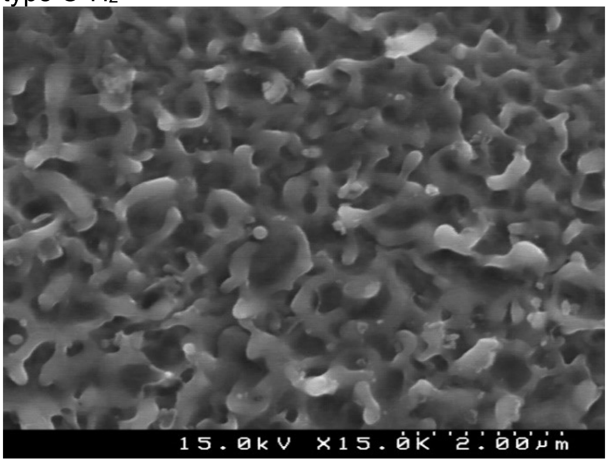
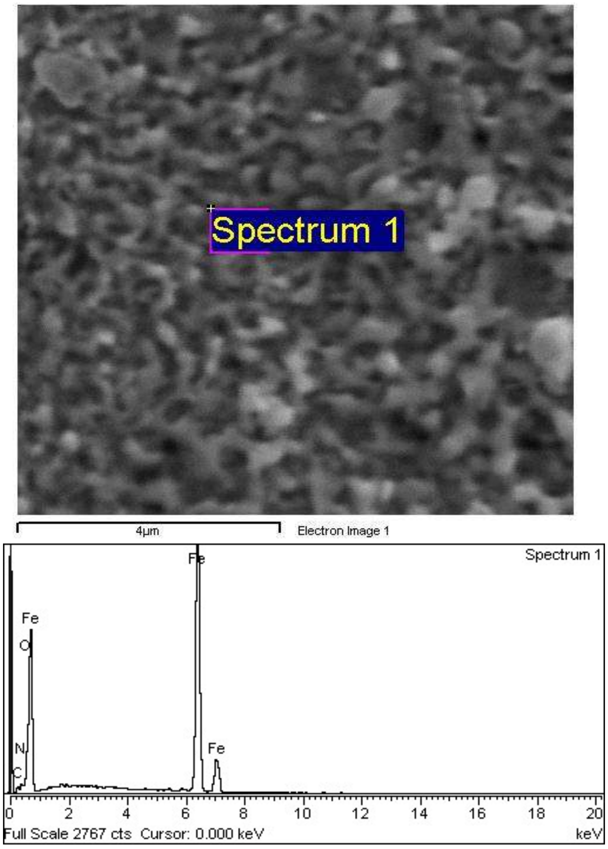


Fig. 10 - View obtained by electron microscopy of the morphology of the processed surface of the sample made of Steel-45 / *Vedere a morfologie suprafeței piesei obținute prin metoda microscopiei electronice , piesa prelucrată fiind executată din Oțel-45*

Analyzing the morphology of the processed surface with impulse electrical discharges, shown in fig.8, we can find that the roughness on the processed surface (the one containing the large amount of oxides and hydrooxides) has roughness (Ra≈0.1÷0.2 μm) and the initial mechanically polished surface has roughness (Ra≈0.63 μm), ie there is a considerable improvement in its quality. This is explained by the fact that "cold" electrode stains migrate, attack roughness, melt and vaporize them.

The results [41,42] of the SEM and EDX analyzes of the samples processed at the optimal regime established are presented in fig. 9-12. For the first time it was observed abnormal dissolving of oxygen up to 60% in steel surface.

Thus, it was found that the dissolution of oxygen during the processing of construction steel samples reaches 60% at., from titanium alloys - 30-35% at., those made from aluminum alloys - up to 20% at., and those from copper alloys - 50 % at. The superficial layer of the surface of the sample



Element	Weight%	Atomic%
C	1.89	4.32
N	7.82	12.43
O	29.77	58.74
Fe	60.52	24.51

Fig. 11 - Morphology (SEM) and composition (EDX) of surfaces of samples executed by Steel 45 and processed by PEDM.
Morfologia (SEM) şi compoziţia (EDX) a suprafeţelor pieselor executate din Oţel-45 şi prelucrate cu aplicarea PDEI

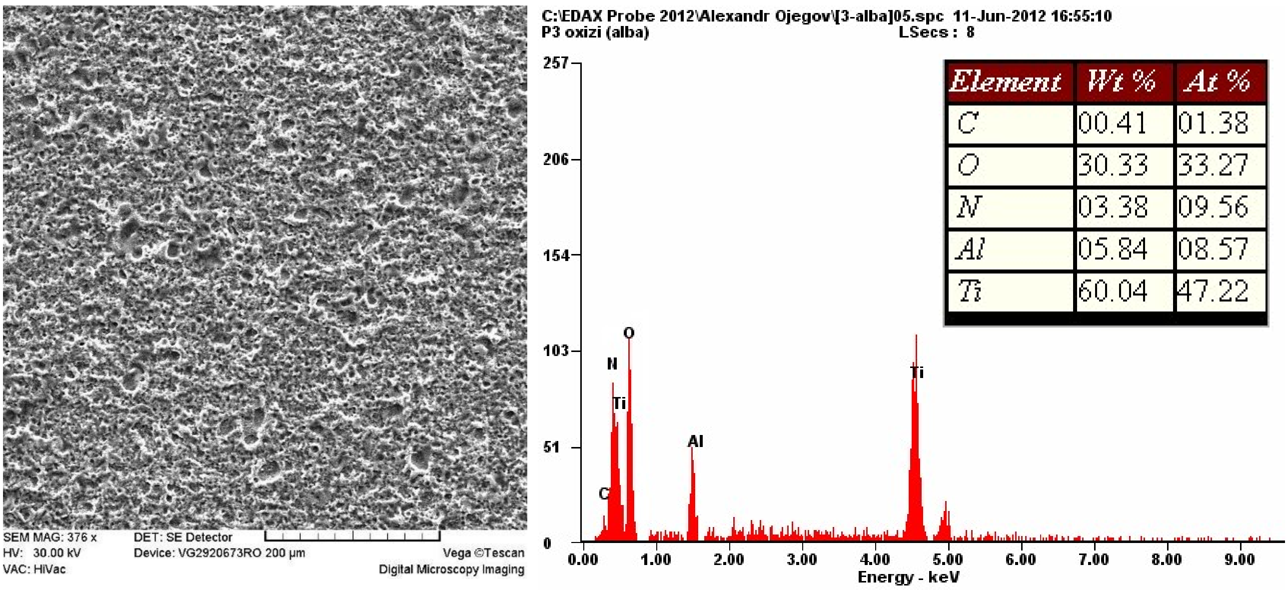
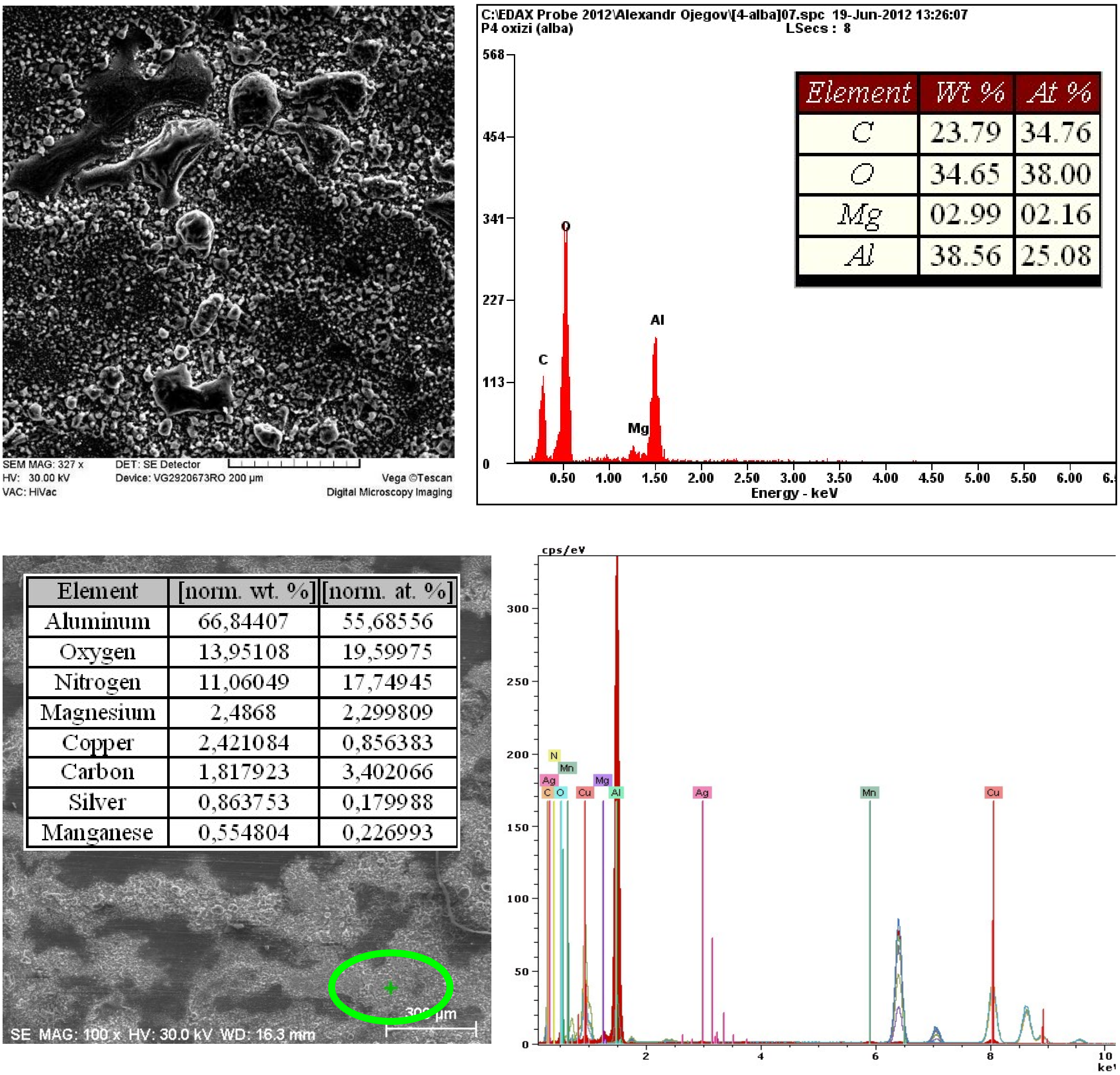


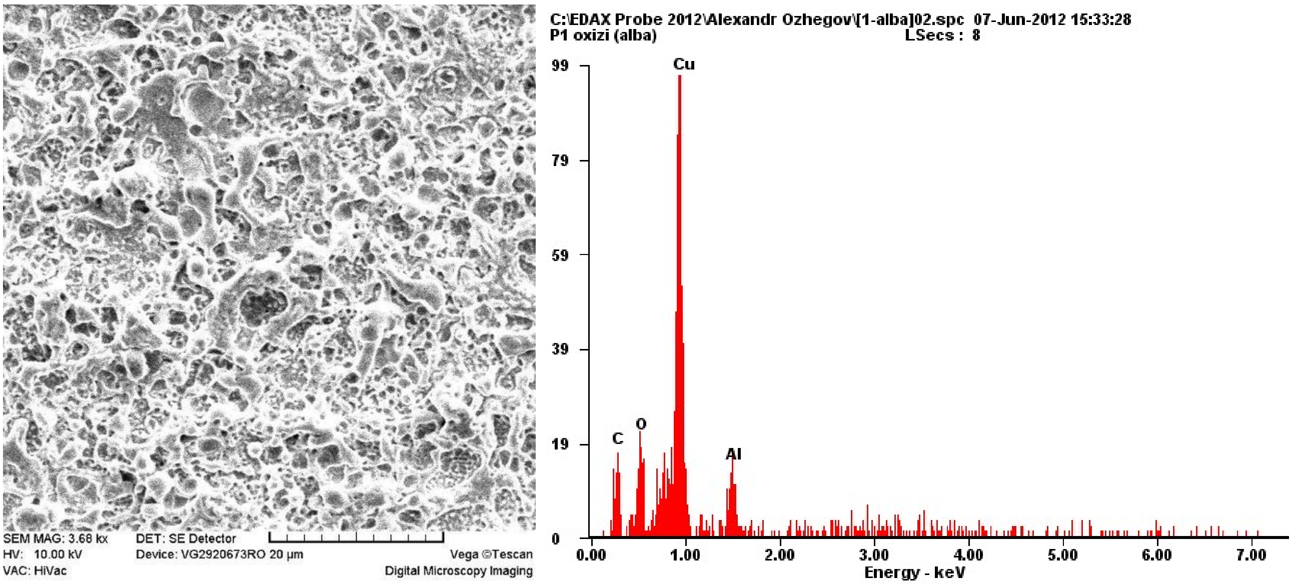
Fig. 12 - Morphology (SEM) and composition (EDX) of surfaces of samples executed by titanium alloy BT8 and processed by PEDM
Morfologia (SEM) şi compoziţia (EDX) a suprafeţelor pieselor executate din aliaje ale titanului BT8 şi prelucrate cu aplicarea PDEI



Element	Wt %	At %
C	23.79	34.76
O	34.65	38.00
Mg	02.99	02.16
Al	38.56	25.08

Element	[norm. wt. %]	[norm. at. %]
Aluminum	66,84407	55,68556
Oxygen	13,95108	19,59975
Nitrogen	11,06049	17,74945
Magnesium	2,4868	2,299809
Copper	2,421084	0,856383
Carbon	1,817923	3,402066
Silver	0,863753	0,179988
Manganese	0,554804	0,226993

Fig. 13 - Morphology (SEM) and composition (EDX) of sample surfaces executed by aluminum alloy D16 and processed by PEDM
Morfologia (SEM) si compozitia (EDX) suprafetelor pieselor executate din aliaje ale aluminiului D16 si prelucrate cu aplicarea PDEI



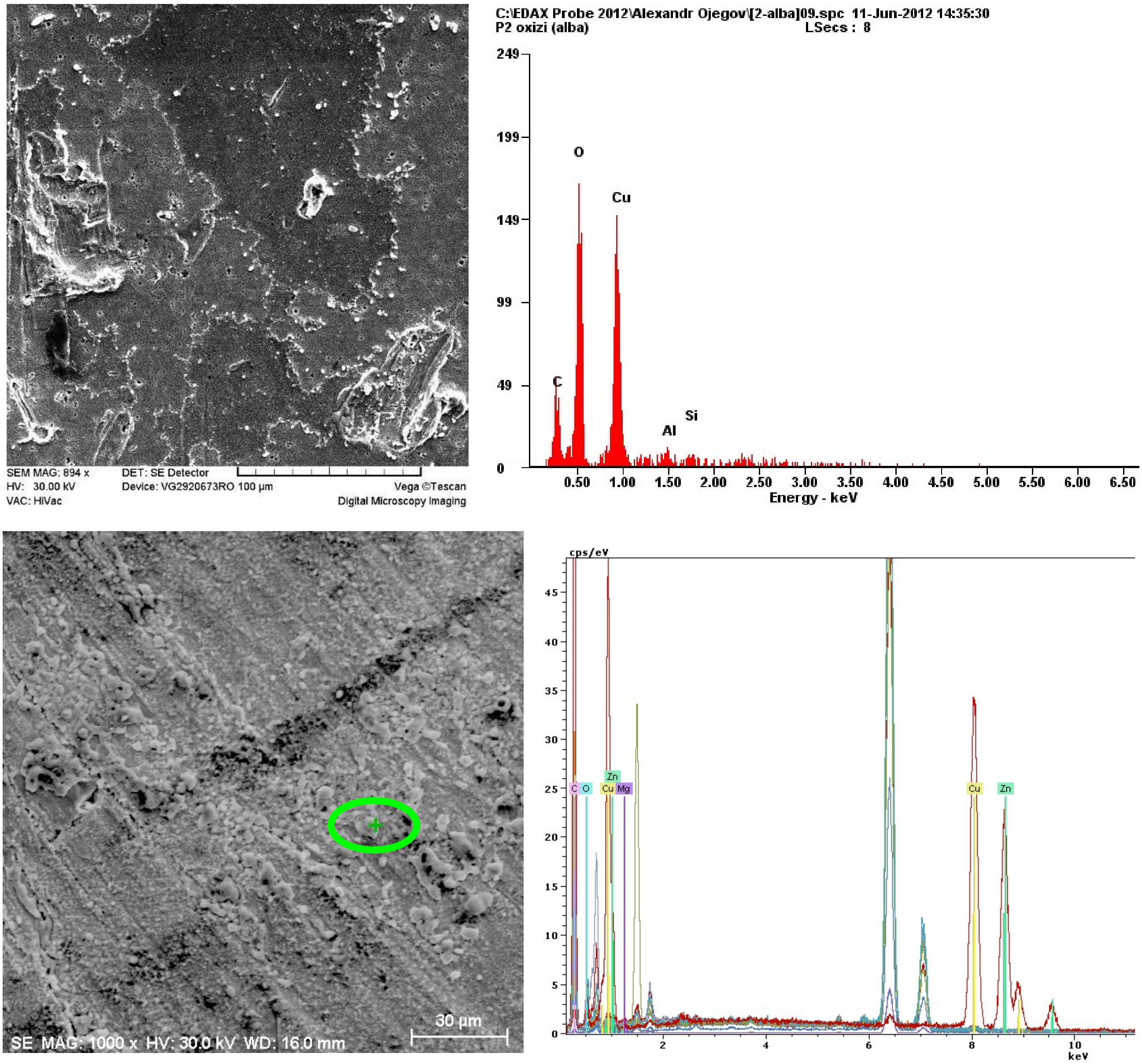


Fig. 14 - Morphology (SEM) and composition (EDX) of surfaces of samples executed by copper alloy and processed by PEDM : 1 – pure copper of brand M0; 2 – bronze based on aluminum brand BrA5; 3 – brass brand L63 / . *Morfologia (SEM) si compozitia (EDX) suprafetelor pieselor executate din aliaje ale cuprului si prelucrate cu aplicarea PDEI*
1 –cupru de puritate tehnica de marca M0; 2 – bronz In baza de aluminiu de marca BrA5; 3 – bronz de marca L63

processed from steel and titanium alloys besides oxygen also includes nitrogen. The different dissolution of oxygen in metals is explained by their different avidity towards oxygen and the electro-physical and chemical properties of the constituent elements.

Corrosion resistance [43] tests of oxide and hydro-oxide films applied to the surfaces of parts made of iron alloys have shown that the corrosion potential increases by more than one volt, and the corrosion resistance can increase by up to 100 times in the aggressive media.

4.Conclusions

From the analysis presented above, we can conclude that:

Knowledge of the phenomenology of plasma in various environments, the legitimate behavior and of course its application in material processing technologies could provide solutions to the crises that humanity is currently facing;

The interaction of pulsed electron discharge plasma through "cold" and "warm" electrode spots with the surfaces of samples made of various metallic materials, causes thermal, chemical-thermal, morphological, structural changes and their chemical and phase composition;

"Warm" electrode stains cause melting of surfaces and extraction from them of conical roughness of the Tylor cone type, the dimensions of which are depending on the processing regime and properties of the processed material;

The deposition of carbon films (containing fullerenes and nano tubes) on the surfaces of parts ensures a decrease in surface adhesion by 3-4 times, a decrease in the wear coefficient between two parts from kinematic couples poop 5 times;

Strong temperature and electric fields generated by electrodic stains cause abnormal dissolution of oxygen in iron (up to 60%). The strong temperature and electric fields generated by electrode spots cause abnormal dissolution of oxygen in iron (up to 60%). As a result of abnormal dissolution of oxygen in iron, for parts made of steel, it is attested to increase the active surface resistance by 10^7 and corrosion resistance in active media by 2 to 100 times.

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