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**INVESTIGATIONS ON THE ELIMINATION OF STICK EFFECT  
BETWEEN METALLIC AND NON-METALLIC SURFACES BY  
MEANS OF GRAPHITE FILMS**

**Scientific specialty-242.05 Technologies, Processes and Processing Equipment**

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## CONCEPTUAL LANDMARKS OF RESEARCH

At this moment, in order to **increase the durability of the pieces and also to increase the wear resistance of the surfaces, various thermal, thermochemical treatments are applied, as well as deposits of resistant layers both by conventional and nonconventional methods**, among which we might mention: traditional thermal and thermochemical processing, metallization processing, plastic deformation processing, gas flame processing, galvanizing processing, hardening by ionic nitriding, magneto-pulses, laser radiation, pulsed electric discharge machining (PEDM), in electrical contact mode and in under-excitation mode [1].

The surface treatments have the role of modifying the chemical composition of the metallic surface on a small depth, of 5-10  $\mu\text{m}$ . Thus, as a result of the surface treatments: **oxides, nitrides or salts of the metal to which the surface treatment is applied are obtained.**

The research uses the method of PEDM in **under-excitation mode**, with the use of **pyrolytic graphite tool electrodes.**

**The actuality of** the research topic and its degree of study are argued by the following desideratum: **the development of contemporary technology** is caused by the energy crisis and that of materials too. The actual conditions require the discovery of new methods to reduce energy and material consumption. The research topic is linked to the National Research - Development Program priority - ECONOMIC COMPETITIVENESS AND INNOVATIVE TECHNOLOGIES, Strategic direction Materials, Technologies and Innovative Products, **as well as programs in Romania - NUCLEUS – „Increasing competitiveness and promoting innovation in the field of capitalization of bioresources, chemistry and petrochemistry – INOVACHIMBIO” Objective 4 „Development of new technologies for obtaining nanocomposites and compounds with controlled properties”** , NUCLEUS – „Priorities for sustainable development chemistry – PRIORICHEM „ Objective 2 **„Ecological technologies and products for environmental protection in the chemical and petrochemical industry”**. The research results were approved and disseminated in the research projects.

**Description of the situation in the field of research and identification of research problems.** The scientific research developed in the thesis is dedicated to the elaboration of new processes for the formation of carbon films, in order to increase non-stick, anti-adhesion, anti-corrosion, wear resistance and also refractory growth, by means of PEDM in order to increase the

operating performance of pieces made of common materials, with the use in the construction of various machines and devices.

**The purpose of the paper:** *Development of graphite deposition formation technology in order to omit the stick and adhesion effects between metallic with other metallic and non-metallic surfaces.*

**The objectives of the paper:**

-identification of *technological conditions* for graphite film formation in case of application of electric impulse discharges (EDI);

**-elaboration of the physical model for obtaining graphite films** in optimal conditions;

**-determination of the chemical, structural and phase composition of the deposits** formed on the working surfaces of the pieces;

**-determination of the functional properties** (solubility, absorption, non-grip, and adhesion) of graphite films;

**-Elaboration of recommendations** for the *practical application of the elaborated technology*;

**Scientific research methodology.**

As an object of scientific investigations were pieces made of special steels and cast which are used in machinery construction when obtaining different subassemblies and parts. The tool electrodes used are in the form of cylindrical bars and are made of pyrolytic graphite. Carbonic formations were deposited on the test surfaces in the form of a thin film under the action of PEDM. Experimental installation for research into the process of carbonic film formation is an electric pulse generator RC type with parallel ionization of the gap.

The gravimetric method was used for quantitative research and Sartorius-type analytical balances were used, for qualitative research (morphology of processed surfaces as well as the shape of the electrodes) SEM electron microscopy and optical microscopy were used. In order to determine the chemical and phase composition of the formed carbon films SEM electron microscopy, TGA thermogravimetric method, XPS, EDX, RAMAN spectroscopic methods are applied. In order to determine the functional properties of carbon films, wear tests, non-stick tests, corrosion tests, solubility tests were applied. The results of experimental research were subjected to mathematical modelling by the instrumentality of programs Microsoft Excel, MathLab.

**The novelty and originality of the work:** *is the fact that a method of applying carbon thin film on a metal surface, through an innovative process, ie PEDM has been developed.*

The carbon film thus obtained has the capacity to reduce the adhesion between two metallic or non-metallic surfaces in contact. The technical modality of verifying this attribute of the carbonic film, is another scientific novelty and was made using a polyurethane adhesive and it is the scientific conception of the PhD student. A subsidiary scientific novelty represents the obtaining and identification through specific analyses of 3D carbon formations *such as fullerenes and carbon nanotubes* in the carbon film obtained by PEDM.

**Scientific problem solved:** Omission of the stick and adhesion effect of metallic surfaces with other metallic and/or non-metallic surfaces.

**Theoretical significance:** Based on the experimental research, a new hypothesis of the erosion phenomenon was advanced and substantiated, which comes to prove that this is a complicated one, being one of a physical, chemical and energy particles bombardment nature (cathodic dissipation). Based on these findings in the paper, **a physico-chemical and technological model of graphite erosion and the formation of carbon deposits with fullerenes and nanotubes under the action of PEDM in normal conditions was developed.**

**The applicative value of the thesis.** *Carbon films formed on the surfaces of the parts applied in the glass molding process increase functionality by three times, removing the adhesion effect and protecting them refractory* and those applied on screw-nut joints removes the stick effect even at a temperature of **800 °C**.

**The main scientific results before defending the thesis.** **To identify the optimal technological parameters** - number of electrical discharges applied to a processed surface area, gap value, discharge capacity of the condenser battery, the charging voltage of the condenser battery, qualitative and quantitative analyses of graphite film filed through PEDM, the physical model of the carbon film deposition through the PEDM procedure, pyrolytic graphite cathode electrode geometry.

**Implementation of scientific results** *based on the scientific results of the real tests at the enterprise IS „Glass factory” from Chisinau an implementing act was obtained. The scientific results are also applied in the elaboration of the curriculum regarding the master's course „Modern technologies and innovations in engineering”* from Alecu Russo Balti State University, Republic of Moldova.

**Approval of scientific results.** The scientific results were presented at national and international scientific conferences, scientific colloquies and symposia: INTERNATIONAL SCIENTIFIC CONFERENCE OF PHD STUDENTS “Contemporary trends in the development of science - visions of young researchers”, Advanced Manufacturing Technologies 2013; 7th International seminar Advanced Manufacturing Technologies Sozopol Bulgaria; International Scientific Conference Light and Photonics : Science and Technology; 4<sup>th</sup> Central and Eastern European Conference on Thermal Analysis and Calorimetry CEEC-TAC 4; ModTech International Conference, Modern Technologies In Industrial Engineering ModTech 2014 Gliwice Poland; International Conference on Manufacturing Science and Education MSE 2017; 16<sup>th</sup> International Balkan Workshop on Applied Physics; INTERNATIONAL CONFERENCE ON INNOVATIVE RESEARCH ICIR 2017; Advanced Manufacturing Technologies 7<sup>th</sup>International seminar Advanced Manufacturing Technologies. The publications obtained 4 distinctions at the scientific forums.

**Publications on the topic of the thesis.** The following publications were published as part of the thesis: **a monograph chapter, 2 articles with impact factor of 0.87 and 2.601, 4 papers in journals of category B, one – in journal of category A, 15 abstracts at scientific conferences, 2 single author patent applications, 2 single author papers.**

**The volume and structure of the thesis:** The paper consists of: introduction, four chapters, general conclusions and recommendations, bibliography of 168 titles, 1 appendix, *113 pages of basic text (up to bibliography), 163 figures (72 in the thesis and 91 in appendix) and 24 tables (8 in the thesis and 16 in the appendix).* The obtained results are presented in **24 scientific papers.**

**Keywords:** graphite electrode, pulsed electric discharges, under-excitation regime, graphite film, polyurethane adhesive, 3D carbon formations, fullerenes, nanotubes.

## **1. BIBLIOGRAPHY STUDY REGARDING TECHNICAL-SCIENTIFIC ACHIEVEMENTS IN THE FIELD OF THE RESEARCH PROBLEM**

The main purpose of the surface treatment applied to some materials is to improve its quality. As methods of surface treatment, specialized literature mentions a wide range of procedures that we will present below without being exhaustive.

**Vapor deposition (PVD) methods in a thin layer by physical methods were identified: vaporization, cathodic arc, Physical electron vapor deposition or EBPVD, Pulsed laser beam deposition (PLD), Chemical thin film deposition of chemical vapor thin layer (CVD), The results**

**of research on thin film deposition of carbon films** (*polymeric carbon films deposited with plasma, crystalline carbon films*) **were also analyzed.** *Graphite films are mainly used for applications in tribology torques* - reducing friction between the surfaces of parts in frictional contact. As a coating it represents a hard system of protection against wear performing an additional function of "*dry lubrication*". Another field of application is in electronics, where they are used *for conductive paths on circuit boards as well as resistive films*. Another area of their use includes *obtaining sample coatings* for SEM scanning electron microscopy, thus making the test surfaces non-conductive from an electrical point of view to allow them to be exposed in this form of a microscope.

## **2. MATERIALS AND METHODS OF CONDUCTING EXPERIMENTAL RESEARCH**

The doctoral thesis aims at the experimental research of the modification of the superficial adhesions *between metallic and non-metallic surfaces* by means of *carbon films* deposited by PEDM process.

In the research papers of this doctoral thesis, the method of PEDM [24-26], in under-excitation mode, with tool-electrodes made of pyrolytic graphite was used [6,7]. When using the graphite tool-electrode with anode polarity on the surface of the piece, heat treatments with diffusion of graphite in the surface layer take place, which leads to an increase of the microhardness by about 5 times compared to the base metal [3]. When using the cathode processing regime, the micro-hardness of the surface layer can be increased by about 10 times compared to the base one [3]. When using the combined tool-electrode [2], the microhardness increased by 2-3 times compared to the base material, but a micrometric graphite film is also obtained on the surface of the piece, whose thickness depending on the processing regimes [5].

### **Experimental installation for generating and applying pulsed electric discharges.**

The experimental research on the deposition of carbon film on metal surfaces using pyrolytic graphite cathode by PEDM process were carried out using the installation from the endowment of the Laboratory of Micro- and nanotechnologies of the Alecu Russo Balti State Univerity and Technical University of Moldova, Republic of Moldova.

*The pulse generator* for the application of the PDM consists of power pulse generator, initiate block (intended for initiating electrical discharges) and control unit, whose role is to synchronize the impulses of power and initiation. It was concluded that for the application of graphite films on the



surfaces of the conductive pieces, RC type generators with parallel initiation can be successfully used [29].

*Electrodes* are graphite rods with a diameter of  $\varnothing$  3-6 mm and a length of about  $l = 50$  mm [4].

*The specimen clamp device* is a vise-type device which has the possibility of moving horizontally "left-right" so that electric discharges can be made in different areas of the active surface of the specimen [4].

*The graphite electrode clamp* is a three-jaw rotary clamping mandrel that has the possibility of vertical adjustment - so that the graphite electrode can approach and move away from the metal surface of the specimen [4].

***Establishing the technological conditions for the procedure for applying graphite films by PEDM.***

The settlement of graphite films on metal surfaces was done by means of PEDM, on a target surface made of steel OL 37 on which the carbon film is applied. Thus, the following measurable and adjustable technological parameters have been established: capacitor battery charging voltage (adjustable in the range 0-500 V); discharge capacitor capacity (adjustable in the range 0... 600  $\mu$ F); tool-electrode - sample surface gap (adjustable in the range 0-10 mm); the number of electrical discharges made at an adjustable target surface point (0-n).

***Determining the number of electric discharges in a point necessary to apply the graphite film.*** A number of tests were performed starting with 2 discharges and ending with 16 discharges, keeping the voltage 250 V constant, the discharge capacitors capacity 600  $\mu$ F.

***Determining the capacity of the electric discharge capacitor required to apply a graphite film.*** Was performed by the method of successive tests. Thus, keeping constant the optimal number of discharges previously established, impulse electric discharges were applied on the target surface using capacitors with a capacity of 400, 500 and 600  $\mu$ F. Determination sets were performed for 1 mm and 1.5 mm gaps.

***Determining the optimal gap size.*** A series of tests were performed at distances of 1 mm and 1.5 mm using capacitor battery charging voltages of 200 and respectively 250 V and a capacity of 400-600  $\mu$ F;

***Determining the charging voltage of the capacitor battery when applying graphite films on the target metal surfaces by impulse electric discharges.*** A series of tests were performed at a gap of 1.5 and 1 mm, using discharge voltages of 200 and 250 V respectively and a capacity of 400-600  $\mu$ F.

Following this high number of performed tests, it was concluded that the optimal parameters are the following: the number of electric discharges performed in a single point - 10; the value of the gap - 1.5 mm; discharge capacitor capacity - 600  $\mu$ F; charging voltage - 250 V. The representative sample for the whole work will be coded **10 / 1.5 / 600/250**.

***Experimental polyurethane adhesive used to demonstrate the non-stick properties of graphite film.*** The adhesive is of the *doctoral student's own design* and is a polyurethane nanocomposite obtained by a polyaddition reaction between the following reactants: a polyol or a mixture of polyols, a reaction catalyst for the polyaddition reaction, and a polyisocyanate crosslinker. (-N = C = O).

***Verification of the functional capacity of graphite films deposited by the process of electrical discharges in a pulse for diminishing adhesion.*** In order to identify the changes in the adhesion properties as a result of the application of carbon films, *it was performed by comparative measurement of the shear forces* of assemblies made by the instrumentality of the strong adhesive - polyurethane - *in comparison between a set of samples treated with graphite and samples without treatment.*

***Performing experimental specimens.*** A set of 3 graphite treatment specimens from those shown in fig. 2.1 and a set of 3 untreated specimens shown in fig. 2.2 are cover with adhesive at the extremity shown in the figures 2.1 and 2.2.

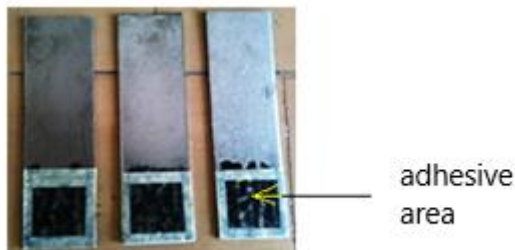


Fig. 2.1 specimens with surface treatment

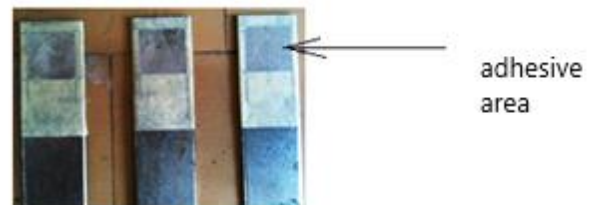


Fig. 2.2 specimens without surface treatment

***Shear test of assemblies made with nanocomposite polyurethane adhesive.***

Polyurethane adhesive bonded test specimens were subjected to shear tensile tests according to STAS 4587-90, on a HECKERT FPZ 100 dynamometer (Germany)

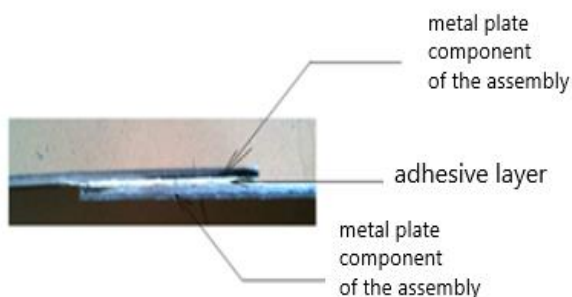


Fig. 2.3 Assembly glued side view

After adhesion, the specimens are superimposed on an area of 25x25 mm, and after crosslinking (hardening) the adhesive is subjected to traction. After evaporation of the solvent from the adhesive recipe – 10 min - two specimens are overlap so that the spaces obtained by cutting the adhesive tapes to overlaps perfectly. In this way the bonding surface of two specimens will be **4 cm<sup>2</sup>**

***Thermogravimetric analysis of graphite films.*** Graphite film deposited on the surface of metal specimens was subjected to thermogravimetric analyzes - TGA (thermogravimetry), to identify the reaction products - except for graphite film - appear as a result of treatment. Thermo-gravimetric analysis of graphite films was performed using a Du Pont Instruments 951 device, which ensures determination and measurement: the temperature range within the limits **20-800 °C**, temperature change dynamics **10 °C/min**, analysis environment **N<sub>2</sub>**, operating pressure – 760 mm Hg. As a result of the measurements, the thermogram is drawn. A similar procedure was used to analyze the carbon films deposited on several samples obtained within the technological parameters established as a result of the determinations.

***Method for determining the anticorrosive properties of graphite films.*** The electrochemical research method was chosen for the express determination of the corrosion of graphite films[29]. In an electrochemical cell, a set of samples was studied using a 5% solution of NaCl. Another set of samples was placed in a 30% solution of HNO<sub>3</sub>. The corrosion rate was determined by the relationship [29]:

$$K_m = \frac{\Delta m}{A \tau} \quad (2.1)$$

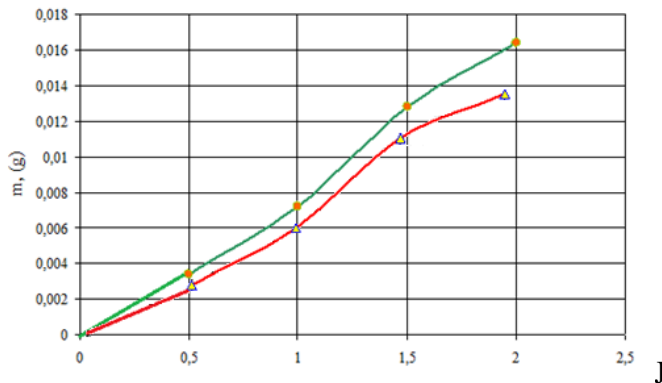
in which:  $\Delta m$  - the difference in metal mass of the sample before and after corrosion;  $\tau$  - duration; A- sample surface subjected to corrosion.

### 3. EXPERIMENTAL RESEARCH PROGRAM AND METHODOLOGY

***Analysis of the dependence between the shape of graphite electrodes and their wear.*** „Tool electrodes” with the active surface of the cylindrical bar with diameters of 1-6 mm and with the active surface sharp to the hemisphere, and tool-electrodes with the active surface of the cylindrical bar with diameters of 1-6 mm and with the active surface sharp to the cone, were subjected to research. The

wear of the graphite tool electrode *can be explained by the fact that this material is not a metal, and the connections between its constituents are of the Wander Wales type (weak links)*. At the same time it is necessary to mention that, *graphite also interacts with plasma from a chemical point of view, is active in oxidation, which additionally causes its erosion*.

In fig. 3.1 shows the wear depending on the energy for tool - electrodes made of conductive materials (graphite). As can be seen from these dependencies, **the wear of the tool electrodes increases in all cases with the increase of the energy accumulated on the capacitor bank**. In addition, it has been observed that in this case the wear of the "tool electrodes" is slightly more pronounced when their working body is sharpened in the shape of a hemisphere without being a significant difference.



**Fig. 3.1. Dependence of tool electrode wear made of graphite depending on the energy stored on the capacitor bank: comparative tool-electrode - cone-shaped and tool-electrode – hemispherical**

**Graphite film analysis by X-ray spectroscopy.** For XPS analysis of the surface in the case of the samples subjected to analysis in the present study, the measurements were performed using PHI 500 Versa Probe equipment (manufactured by PHI-ULVAC Inc. USA) which uses a hemispherical analyzer of kinetic energy of photoelectrons (resolution 0.50 eV).

**Chemical and spectral analysis of graphite film deposited by DEI on steel substrate.** The experimental researches with the formation of graphite films on the metal surface of a plunger of the pouring form of the bottle made of cast iron, they demonstrated: the analysis of the morphology of the surface subjected to processing had confirmed that the surface formations do not exceed micrometric quantities. In addition, to the initial components of the processed material, there is a considerable amount of carbon (about 80%) in atomic content which **leads to the conclusion that it is possible to form the carbides and graphite phases separately**. It has also been found that the vast majority of the carbon transferred to the surface of the piece is attested at **depths of the order of micrometers**. In the demonstration of those above mentioned are the results obtained when testing

plungers under real operating conditions, by which it was established that the plungers of the molds for bottle shaping, on whose active surface carbon films were deposited, they operated at 57,600 cycles without changes in their shape and size.

***SEM electron microscopy analysis of graphite film deposited by the process of pulsed electric discharges (EDI) on the target steel surface.*** Graphite film from another series of samples obtained under the same conditions was subjected to electron microscopy analysis by SEM process. The most interesting and relevant images were obtained from the coded 10/1,5/600/250 and 10/1,5/600/200 samples - which also showed the most important percentages of water absorption and mass additions

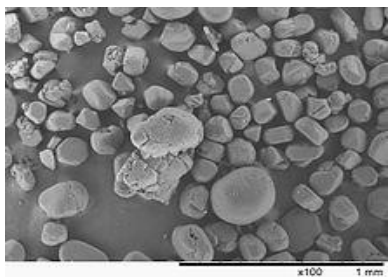


Fig. 3.2. Fullerene type space formations (electron microscope images) [10,11]

The images were taken with the **Type Quanta FEI Phillips** electron microscope. From the images presented in fig 3.3 it is observed that the graphite film is deposited homogeneously without major defects of superficial structure cracks or parts with lack of continuity. However, in the case of the 10 / 1.5 / 600/250 sample, a series of cracks are found of graphite film deposited on metal surface - probably due to higher capacitor battery charging voltage. (250 V vs. 200 V). At the same time, a series of interesting spherical formations were observed, more often in the case of the 10 / 1.5 / 600/250 sample.

Consulting the specialized literature, images with space formations made up of fullerene-type carbon atoms were identified [14, 15]. These are shown in fig. 3.2 and they are similar in shape and the dimensions are comparable to those of the globular formations identified in the graphite film images, which *suggest that these globular formations appearing* on the metal surface are of the **fullerene type** (fig.3.3).

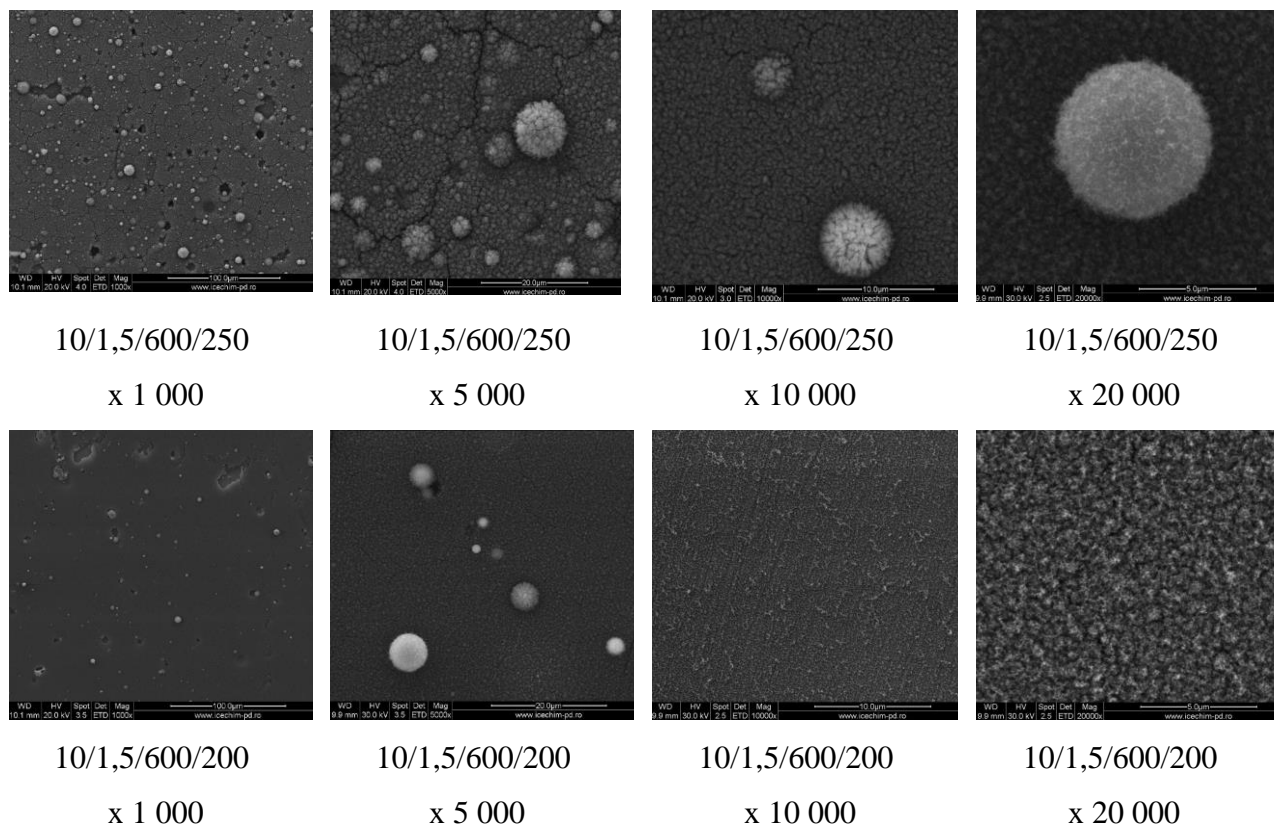


Fig. 3.3. SEM morphology of the samples 10/1,5/600/250 și 10/1,5/600/200 comparative images

Their different spatial dimensions, **corroborated with the appearance of the graph** of the thermogram of the graphite sample, collected from the carbon film deposited by DEI, which have **mass addition peaks** at different temperatures and with different intensities, they also lead to the conclusion that they are *fullerene formations* with **different numbers of carbon atoms** and that these spatial formations are *of different sizes* – the specialized literature notes C 20 (the smallest spatial formation) - C 100 [16, 17].

***Physical model of graphite film formation obtained by applying electric impulse discharges (EDI).*** The efficiency of the formation of graphite deposits on the processed surface is determined by the fact that at the moment of the impulse electric discharges, the temperature in the plasma jet reaches values of up to  $10^4$  K, which is more than enough for **the vaporization of graphite and its polar transfer** on the surface of the piece to be processed. It should be noted that the electroerosion of graphite is a special one in relation to metallic and semiconductor materials. The concept of the physical model [12, 13] starts from the analysis of the previously obtained experimental results, which established that the more pronounced erosion of graphite occurs when the electrode is connected to the discharge circuit of the **current pulse generator as a cathode**.

The process of electro erosion is actually an **electrochemical one**, which takes place at high temperatures, then we can assume that recombinatory and dissociative processes take place on the surface of the "anode-electrode" and the "electrode-cathode" and in the plasma channel. Summarizing the above and taking into account the processes that take place in the gap, the following physical context of the formation of graphite deposits under the action of the plasma of PEDM is proposed. (a) see fig. 3.4 - *electric shock is triggered, according to the **Townsend mechanism** and the conductivity channel occurs*; (b) *a whole series of dissociations of atmospheric components into separate atoms, oxygen ions, hydrogen and nitrogen take places, and of course there are present electrons from the previous phase in the plasma*; (c) *they interact with each other also and with the surfaces of the electrodes, producing surface activation and causing their erosion*.

In both step (c) and step (d), a series of **intense reactions of oxidation of the graphite electrode surface** occur, **as well as the dissociation** of the product into **oxygen and carbon**, with further transfer to the processed surface, both under the action of the electric field in the gap and under the action of the component atoms of the plasma.

The process is completed with the synthesis of a **carbon-containing film in various forms of crystallization**, as well as phases consisting of the components of the plasma gas (e).

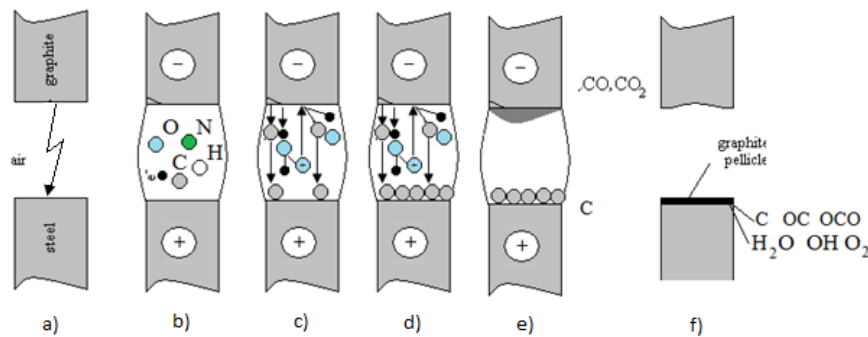


Fig. 3.4. The supposed physical model of graphite film formation obtained by PEDM [18]

Due to the fact that the oxygen in the plasma channel interacts more intensely with the surface of the "electrode-cathode", oxidation reactions occur with the release of carbon monoxide CO, accompanied by additional release of heat Q at the cathode surface and possible formation of carbon dioxide CO<sub>2</sub> according with the reactions: [29]



As a result of these phenomena that occur at the surface of the cathode, the energy released from it increases with that caused by intensive oxidation, and the summary energy on it can be expressed with the relation [29]:

$$W_c = U_c \int i(t)dt + W_Q, \quad (3.3)$$

in which:  $U_c$  - voltage drop across the cathode;  $i$  - the momentary value of the discharge current.

Due to the fact that the energy released at the surface of the anode is higher than that in the gap, the gas molecule dissociates into carbon and oxygen ions. The oxygen ones - return to the plasma channel and perform the superficial oxidation of the cathode again, and the carbon ones combine at the surface of the anode, forming the carbon film. Next, the graphite film formed on the surface of the piece, under the action of the heat released at the interface with the plasma channel, it is subjected to diffusion processes in the surface layer of the piece, forming the hardened layer. It is not excluded, however, in the last phase of the carbon film deposition process, erosion of a quantity of graphite on this surface.

### **Technological aspects at the carbon deposition formation on the surfaces of pieces made of iron alloys**

The analysis of the results obtained previously shows that no special surface preparation is required.

In order to form graphite depositions, in the absence of melting and vaporization of the processed work piece surface, the current pulse generator is applied as an energy source, which ensures the formation of current pulses with a duration of  $10^{-4} \div 10^{-6}$  s and the energy released in the gap  $W_S = 0 \div 4.8$  J, the energy accumulated on the condenser battery  $W_C = 0 \div 12$  J, at the voltage applied when charging the condenser battery  $U_C = 0 \div 250$  V, for its capacity within the limits of  $C = 100 \div 600$   $\mu$ F with the step of 100  $\mu$ F. The generator also ensures the formation of high voltage pulses ( $U = 12 \div 24$  kV), which ensures the priming of the pulsed electric discharges at values of the gap of  $S = 0.05 \div 2.5$  mm with the adjustable frequency of discharges of electric pulses within the limits  $f = 0 \div 50$  Hz. The following scientific-technological elements and surface processing regimes have been established:

1. The choice of tool-electrode material – pyrolytic graphite, as one of high purity and predictable by chemical composition;
2. The connection of the tool-electrode in the discharge circuit of the current pulse generator **as a cathode**, resulting from the specifics of graphite erosion and its transfer on the processed surface;



3. No special surface preparation is required (only cleaning, removal of oils or oxides because this function is taken over by the carbon from the formed graphite film);
4. Determining the size of the gap in the range from 0.1 to 1.5 mm;
5. Determination of solitary discharge energy from the relation:

$$Q = \frac{4W_s}{\pi d_c^2 S} \approx Q_{melt}, \quad (3.4)$$

6. Determination of the diameter of the processing area on the workpiece surface by the relation:

$$d = \sqrt{\frac{4W}{QS}} \quad (3.5)$$

7. Appointment of pulsed electrical discharge frequency:

$$P = \frac{km l^2 f}{4} \quad (3.6)$$

8. The processing productivity will be established by the relation:

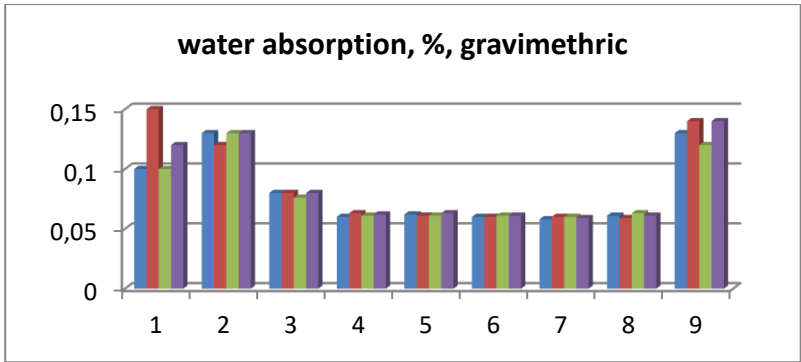
$$P = 60k\pi d^2 f / 4 \text{ (mm}^2/\text{min)} \quad (3.7)$$

where: k is the coefficient of overlap of the areas of interaction of the plasma channel with the surface processed at a solitary discharge.

#### **4. EXPERIMENTAL RESEARCH - FUNCTIONAL PROPERTIES OF CARBON FILM**

A number of functional properties of carbon films **deposited on the active surfaces of different types of pieces, in the construction of machines and other appliances** are presented below.

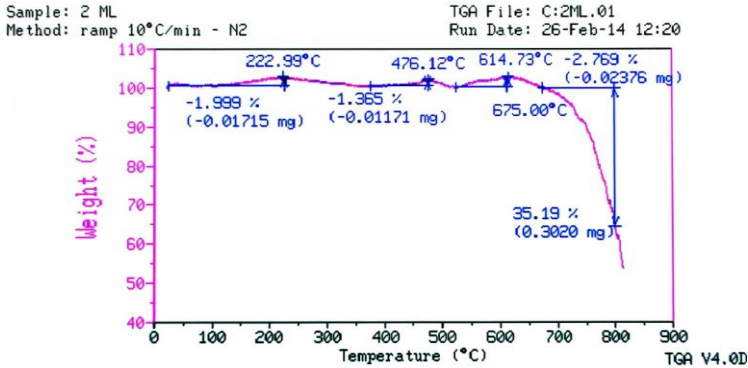
*Thermogram of graphite film deposited by pulsed electric discharges.* Graphite film deposited on the surface of metal specimens was subjected to thermogravimetric analysis – TGA, (thermogravimetria), to identify which reaction products - other than graphite film - appear following treatment [27]. In order to analyze the chemical composition, graphite film resulting from the application of EDI treatment, thermogravimetric determinations were performed in parallel, for a graphite control sample collected from the deposition electrode, and a sample of the material harvested from the surface of a specimen subjected to EDI treatment. The samples subjected to thermogravimetric analysis were small portions of graphite dust collected from the surface of the metal plates (anodes). Before collecting graphite dust samples, the metal samples were conditioned for 48 hours in a perfectly dry controlled atmosphere, to remove moisture [8, 9]. These observations are contained in fig. 4.1.



**Fig. 4.1. Percentage of water absorption from graphite samples deposited by the process of applying pulsed electric discharges EDI 1.10/1.5/600/250; 2.10/1/600/250; 3.10/1.5/500/250; 4.10/1/500/250; 5.10/1.5/400/250; 6.10/1/400/250; 7.10/1.5/400/200; 8.10/1.5/500/200; 9.10/1.5/600/200**

Conditioning of the samples in order to submit these thermo-gravimetric analyzes, led to the following observations: graphite films adsorb 0.058% water - **sample 4**, 10 / 1.5 / 400/200 , and 0.15% of **the sample 1** 10 / 1.5 / 600/250. Percentages are expressed gravimetrically; graphite films deposited under energetic conditions 600  $\mu$ F and 250 V show the highest percentages of water absorption - **0.14-0.16%**, in relation to the other samples **0.058 - 0.06%** gravimetric percentages; films with the highest water absorption percentage 10 / 1.5 / 600/250 and 10 / 1.5 / 600/200, they overlap with those obtained in optimal parameters, determined in Chapter 2; the high voltage, 200 - 250 V and the high capacity of the discharge capacitor - 600  $\mu$ F - determine a series of features of the graphite film. Working parameters of the TGA analysis procedure for graphite collected from metal plates were identical to those of the control sample presented in Chapter 2.

The TGA curves are shown in fig. 4.2. These show a number of anomalies (mass additions). This phenomenon is even less explicable given that the thermogravimetric analysis was performed in the N2 atmosphere.



**Fig. 4.2 Thermogravimetric diagram of the sample, collected from the metal specimen**

The thermogram of the TGA analysis of the harvested graphite sample presents a series of very interesting aspects, which indicates that the graphite film, deposited by pulsed electric discharges EDI, it has a completely different structure from that of pure graphite, or that in addition to graphite,

other chemical compounds of carbon are also obtained - as stated a priori by Mr. dr.hab., prof.unv. Topala Pavel. [29].

1. In the temperature range 200 - 300 ° C (at 222.99 ° C) a mass addition occurs in a percentage of 1.999%. This shows that the graphite sample **instead of losing mass** due to the decomposition or loss of volatiles, **gains mass** - which indicates an absorption of matter into the structure of the graphite film;

2. The phenomenon is reversible - **around 300 ° C** the mass gain is canceled;

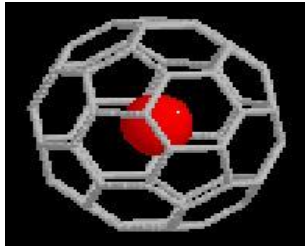
3. In the temperature range **450 – 550 °C (476.12 °C)** a new mass addition occurs in a significant percentage of 1.365%. This shows that **the graphite sample instead of losing mass due to decomposition or loss of volatiles gains mass** - which denotes an absorption of matter into the structure of the graphite film. The extremely high temperature cancels the presumption of an error of the device, the phenomenon of mass addition being concrete and real;

4. The phenomenon is reversible – around **550 °C** the mass gain is canceled;

5. In the temperature range **600 – 750 °C (614.73 °C)** a new mass addition occurs in a significant percentage of 2,769 %. This shows that **the graphite sample instead of losing mass due to decomposition or loss of volatiles gains mass** - which denotes an absorption of matter into the structure of the graphite film. The extremely high temperature cancels the presumption of an error of the device, the phenomenon of mass addition being concrete and real;

6. Reversible mass additions produced in intervals **200-300 °C, 450-550 °C, 600-700 °C** have values high enough that they are not considered to be device errors (max. 0,1 %). The absorption phenomenon followed by desorption (reversibility) is very similar to the absorption / desorption phenomenon that occurs in the case of zeolites. The similar phenomenon that occurs in the case of graphite film, leads to the conclusion that spatial structures made of carbon atoms are obtained this time as well, called fullerenes. Because the environment in which the thermogravimetric analysis is performed is nitrogen, the chemical process of oxidation, which could possibly have contributed to a mass addition - is excluded. The only scientific explanation is the presence of space structures that are able to store small molecules (N<sub>2</sub>) that they later release. The occurrence of the absorption / desorption phenomenon at different temperatures and also different percentages indicates that the possible spatial structures of carbon atoms have different dimensions;

7. In the interval 20-750 °C graphite film does not undergo any changes caused by thermal degradation.



**Fig. 4.3. Graphical representation of the property of 3D structures made up of carbon atoms and the phenomenon of adsorption of small molecules [10, 11].**

*Determination of the non-stick properties of graphite films by means of polyurethane structural adhesive.* Graphite film deposited by pulsed electric discharges has a thickness of 7-8  $\mu\text{m}$  and also reacts physico-chemically (theoretical model) with the metal surface, which leads to its special adhesion [18-20].

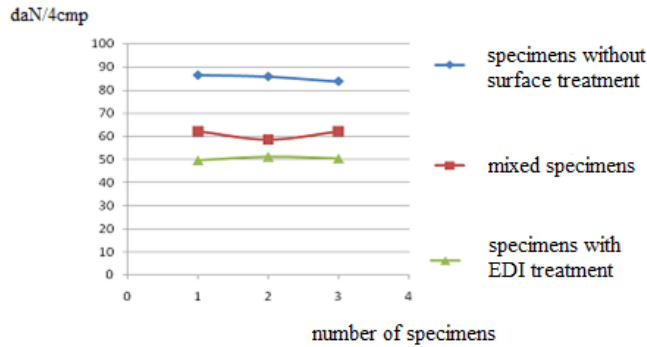
A first method of verifying the theory of the creation of a non-stick film on a metal surface as a result of a graphite treatment carried out by DEI, consisted of making test pieces to check the shear forces made up of two metal plates glued with a structural adhesive. The assemblies were subjected to a shear test [21-23]. As a result of the tests, the following values were obtained for the glued assemblies and they are shown in Table 4.1.

Table 4.1. Shear stress values for different ways of gluing specimens

<b>Both untreated specimens, daN/4cm<sup>2</sup></b>			<b>Mixed treated samples, daN/4cm<sup>2</sup></b>			<b>Both graphite-treated specimens, daN/4cm<sup>2</sup></b>		
86.40	85.80	83.70	62.10	58.60	62.00	49.60	51.20	50.40

As a result of the traction of the parts assembled by gluing, we can observe that the untreated test pieces have higher shear stress values than the other ones and constitutes approx 85daN/4cm<sup>2</sup>. Mixed - treated specimens have an average value of 60 daN/4cm<sup>2</sup>, which tells us that the graphite film deposited on one of the specimens reduces the adhesion between the adhesive and the metal surface. The last variant, in which both surfaces are covered with graphite film, the shear stress decreases approximately to 50 daN/4cm<sup>2</sup>, which is a 40% decrease in adhesion to untreated test specimens. (fig. 4.4). The decrease in adhesion forces is due to the interposition of the graphite film between the adhesive surfaces. In this context, the shearing of the specimens takes place in two ways. In the first variant breaking occurs inside the adhesive mass, which is characteristic of specimens which have not been treated by pulsed electric discharges EDI with graphite tool electrodes. In the second variant, already characteristic of EDI-treated specimens, the rupture occurs at the separating surface between the graphite film and the polyurethane adhesive. As a confirmation of these desideratums, comes the research of the morphology of the surfaces of the specimens treated and untreated with EDI - after shearing. In the case of specimens not subjected to the surface treatment of

electro-deposition, all splits of the assemblies were produced **by breaking in the mass of the adhesive. This indicates a strong adhesion of the adhesive to the metallic supports.** In this case, the greatest breaking forces were found, over 80 daN/4cm<sup>2</sup> [28].



**Fig. 4.4. Comparative graph of shear force values for the three categories of samples [28]**

In the case of specimens treated with graphite by EDI, the splitting of the structure as a result of the application of tangential forces to the adhesive mass is done at the adhesive support interface. Thus the whole mass of adhesive or a large part of it will remain on one of the supports. It is stated in this case that the internal strength of the adhesive is higher than the adhesion to the metal substrate, the structure is not destroyed by its disassembly into the component elements, ie the adhesive does not function as a structural adhesive. The numerical value of the shear forces determined in this case, is decreased by 40 % - approximately 50 daN/4cm<sup>2</sup>, compared to the situation of untreated surface specimens. All these attempts allow us to state that, graphite films deposited on metal surfaces by electric impulse discharges possess anti-socket properties, which confirms the assumptions in previous papers [22].

Table 4.2 shows the experimental data of the sample tests (samples - steel plates with graphite deposition treatment by the process of electric impulse discharges). For the samples presented in table 4.2, the following methodology was followed:

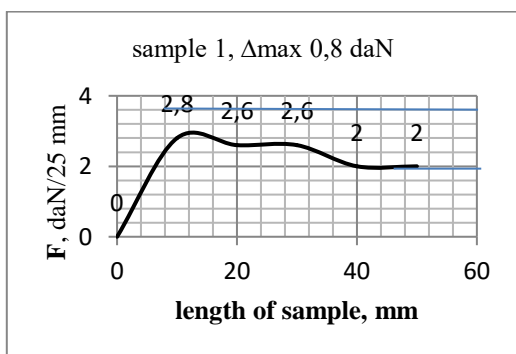
1. A set of 7 sets of samples of 4 metal plates each coded I-VII and a set of 4 untreated samples coded M were studied.;
2. These samples are in the form of metal plates 80 mm long, 25 mm wide. The samples were subjected to the treatment of deposition of a graphite film by the process of pulsed electric discharges EDI. The area subjected to the graphite film deposition treatment is located at one end of the metal plate and has a surface area of 25x25 mm<sup>2</sup>;

The forces of detachment are expressed in daN/25 mm adhesive tape width.

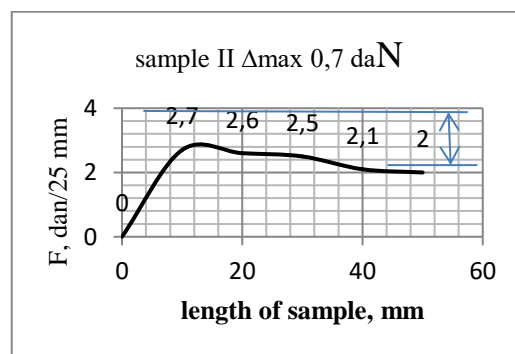
Table 4.2. Initial characteristics, linear adhesive strength and shear strength values

sample Indicative	Initial characteristics for the samples		linear adhesive strength (25mm lățime probă**)		shear strength (daN/625 mm <sup>2</sup> )
	No. of crossings				
I	No. of crossings	2	N***	2,8; 2,6; 2,6	51,8
	Voltage U, V	100			
	Electrode gap S, mm	1,5	T****	2,0; 2,0	
	Capacitor capacity C, μF	600			
II	No. of crossings	2	N***	2,7; 2,6; 2,5	49,7
	Voltage U, V	200			
	Electrode gap S, mm	1,5	T****	2,1; 2,0	
	Capacitor capacity C, μF	600			
III	No. of crossings	1	N***	2,7; 2,6; 2,5	67,2
	Voltage U, V	200			
	Electrode gap S, mm	1,5	T****	2,2; 2,3	
	Capacitor capacity C, μF	600			
IV	No. of crossings	4	N***	2,8; 2,6; 2,6	38,7
	Voltage U, V	200			
	Electrode gap S, mm	1,5	T****	1,6; 1,5	
	Capacitor capacity C, μF	600			
V	No. of crossings	4	N***	2,7; 2,6; 2,5	35,9
	Voltage U, V	200			
	Electrode gap S, mm	1,5	T****	1,2; 1,2	
	Capacitor capacity C, μF	600			
VI	No. of crossings	2	N***	2,7; 2,6; 2,5	48,8
	Voltage U, V	150			
	Electrode gap S, mm	1,5	T***	2,1; 2,1	
	Capacitor capacity C, μF	600			
VII	No. of crossings	3	N***	2,7; 2,6; 2,5	41,2
	Voltage U, V	200			
	Electrode gap S, mm	1,5	T****	1,3; 1,2	
	Capacitor capacity C, μF	600			
M*	No. of crossings	-		2,8; 2,6; 2,6; 2,7; 2,6; 2,5	68,7
	Voltage U, V	-			
	Electrode gap S, mm	-			
	Capacitor capacity C, μF	-			

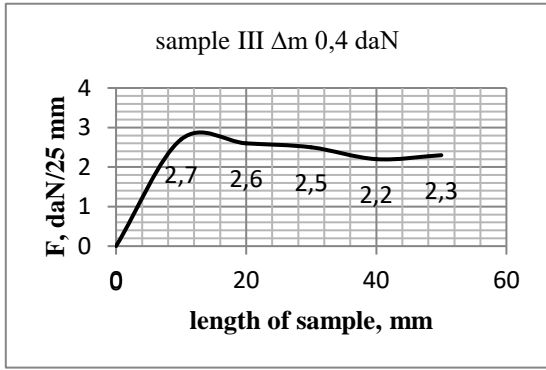
\* control sample without treatment; \*\* reading from 10 to 10 mm; \*\*\* portion without treatment; \*\*\*\* portion with EDI treatment.



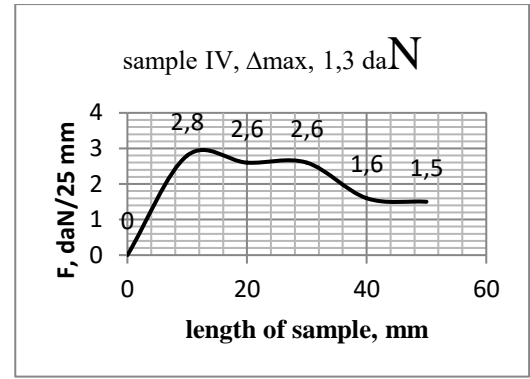
a)



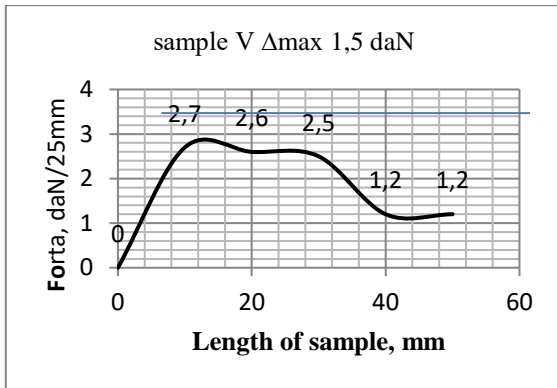
b)



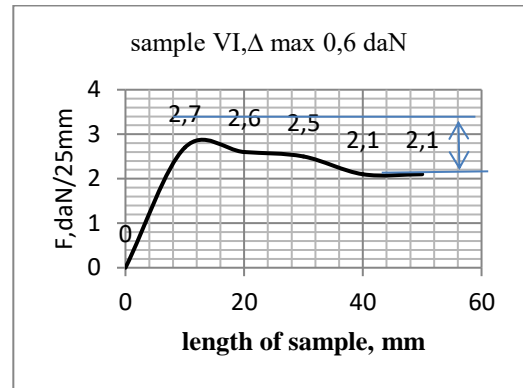
c)



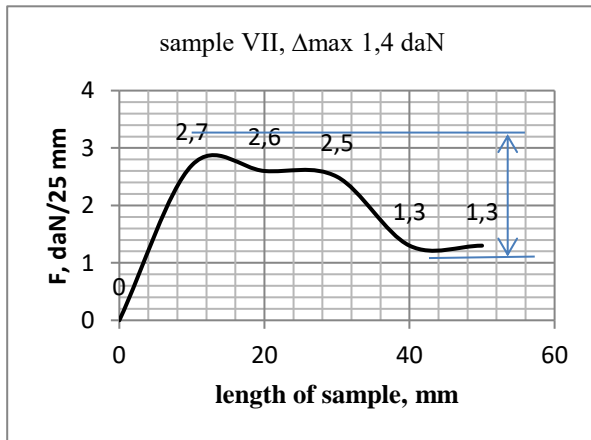
d)



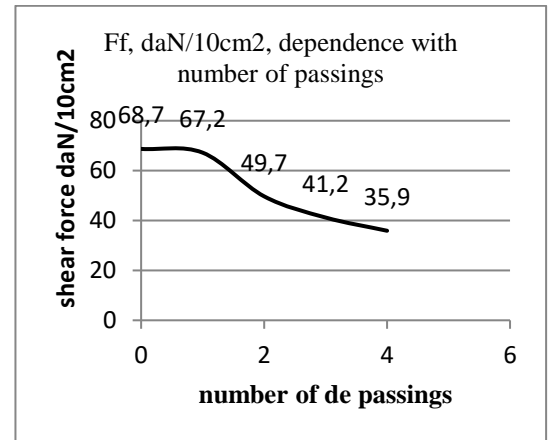
e)



f)



g)



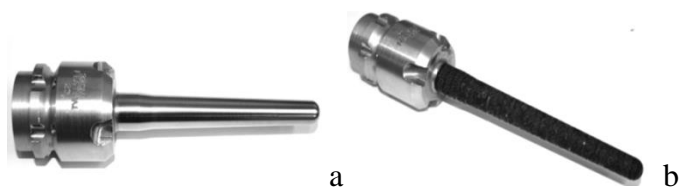
h)

Fig. 4.5. Graphic form (a-h) of the results of the study of the samples analyzed in the table 4.2

**Wear resistance of graphite films** [29]. Applying graphite films on surfaces the constituent parts of the molds for glass pouring, allowed to establish their very efficient functionality. The treatment allows a durability for parts of the molds, of at least 2 times larger than factory-fitted parts [28]. This can be explained by the fact that graphite is a solid lubricant and prevents the glass adhering to the surface of the mold, and, respectively its abrasion wear, as well as by the fact that, graphite film

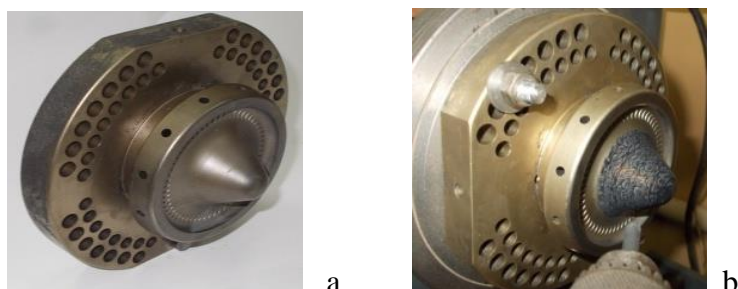
has anti-refractory properties and serves as a thermal insulator between the surface of the metal mold and the liquid glass.

*A series of exploitation tests were performed at SE „Glass Factory” from Chisinau for the constituent parts of the glass molds.*



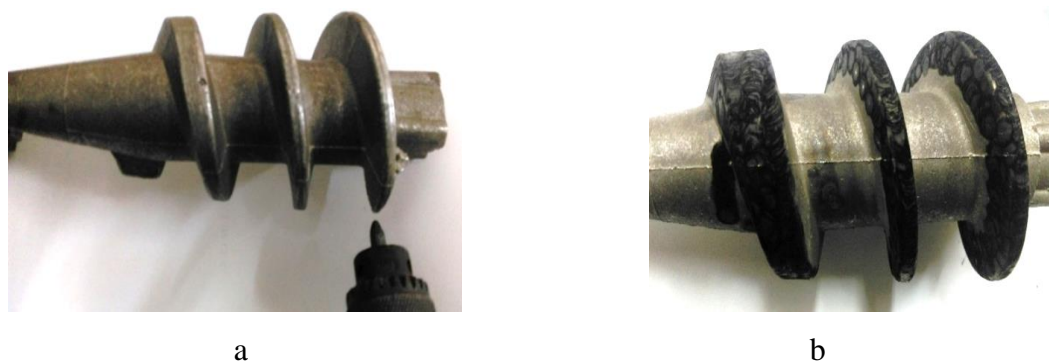
**Fig. 4.6. Overview of the punch surface.: a) initially; b) after processing [29]**

The ones exposed above is also confirmed by the results obtained by the authors of the paper [29] who tested the dives in real operating conditions. As a result, it was established that the plungers of the molds on the active surface of which graphite films were formed, they operated at 57,600 cycles in the absence of changes in their shape and size. In this sense, in order to compare the wear of the plungers of the forms of glass casting, experimental researches in technological cycle were performed [18-19]. Two plungers were tested, one covered with graphite by electric impulse discharges and the other unprocessed , fig. 4.6 a, b as well as the second finishing palette fig. 4.7. a,b



**Fig. 4.7. Overview of finishing pallets:  
a) in normal conditions; b)  
after coating with graphite film  
[29]**

During the project, screws were processed used for processing briquettes at the Criuleni plant (fig. 4.8. a, b). ). As a result, there has been an increase in productivity about 30–50 %.



**Fig. 4.8. General view of screw for briquetting machines: a) initial; b) after processing [29]**



If we examine the sample (fig. 4.6 a) unprocessed by PEDM before operation in the technological cycle and after operation then we notice that its diameter in some points decreases by up to about 11  $\mu\text{m}$ . The sample (fig. 4.6 b) is studied from three points of view, at the initial stage, then after the application of graphite films and finally after it has been subjected to wear. After the part has been subjected to PEDM processing, the diameter of the plunger increases, within the allowable limits, due to the graphite deposits on its surface. When inspecting the part after operation in the above prescribed regimes, there is no decrease in the diameter of the part due to the fact that the deposited graphite film acted as a protective film that prevented friction and thus the wear of the plunger [29].

### **GENERAL CONCLUSIONS AND RECOMMENDATIONS**

As a result of the bibliographic study, of the experimental researches on the thesis, the following general conclusions can be drawn:

- the erosion of the graphite and its transfer on the processed surface under the action of electrical discharges of PEDM is more efficient when the graphite tool-electrode is connected to the discharge circuit of the impulse generator as cathode [30];
- the process of graphite erosion under the action of pulsed electric discharges under normal conditions is an electrophysical and electrochemical complex one that occurs at high temperatures [28];
- the carbon depositions on the surfaces of the parts made of Steel OL-37 and Steel OL-45 also lead to the formation inside them of 3D structures such as fullerenes and nanotubes, due to the fact that iron serves as a catalyst [33];
- due to the presence of fullerenes and carbon nanotubes in the formed film, they absorb nitrogen at temperatures 222.49  $^{\circ}\text{C}$ , 476.12  $^{\circ}\text{C}$ , 614.73  $^{\circ}\text{C}$  [34], and the solubility in different solvents ranges from 0.006 g/l in tetrahydrofuran to 51 g/l in alpha-chlorine naphthalene [35];
- graphite depositions formed by applying PEDM possess a number of beneficial properties such as: reduction of metal surface adhesion by 1.4 times, reducing the coefficient of friction between metal surfaces up to 0.1 [31, 32], increase the durability of the glass molding components by 2.5-4 times, increase the corrosion resistance of steel parts in aggressive environments by 1.5 times [36];
- SEM, EDX and Raman chemical analyzes attest 3D space formations, and their functional properties confirm what would be correct to say that non-metallic structures are formed under the action of plasma ( $4 \cdot 10^4 \text{ K}$ ) [37];

– formation of carbon depositions on silicon surfaces emphasize the fact that these 3D structures are also formed, having a more discreet but less adherent character [38].

### **TECHNOLOGICAL RECOMMENDATIONS**

1. The carbon depositions obtained under the research conditions of the thesis (charging voltage, capacity of the capacitor battery, gap) can be applied to remove adhesion effects in the case of glass molding and the stick effect for the screw-nut joints which operates at a temperature up to 800° C;
2. Carbon depositions can be obtained in order to increase the piece surface corrosion resistance in aggressive environments;
3. The use of carbon depositions in practice requires additional research, to supplement them on increasing the absorption coefficient of light radiation;
4. It is proposed to continue research for other metallic or semiconductor materials as samples;
5. To appreciate the productivity of 3D formations (fullerenes and nanotubes);
6. To develop processes for washing them, as well as preserving them for commercial production.

### **PROPOSALS FOR THE PERSPECTIVE**

Research in a field cannot be completed by a single doctoral thesis. This is only a partial contribution to scientific development for which reason it is proposed the following for the future:

- Deepening the study of the effects that pulsed electric discharges have on the quality of carbon films;
- Implementation of the obtained results in the apparatus manufacturing, research and production technology, micro- and nano-electronics;
- Development of equipment and construction of devices for applying carbon films by means of PEDM processes for use at pilot or industrial level.

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6. **Marin L**, Topala P Stiocev P Besliu V Ojgov A, Pinzaru N, Guzman D Platon A *Influenta parametrilor tehnologici – tensiune, cantitate de electricitate – la generarea formatiunilor spatial alcatuite din atomi de carbon la aplicarea descarcarilor electrice in impuls*, Meridian Ingineresc nr, 1, 2017, Editura tehnica UTM, pag ISSN 1683-853X 30-35, Categoria B
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10. **Marin Laurentiu**, Marin Catalina Daniela, Vasilievici Gabriel, Topala Pavel, Besliu Vitalie, *Analiza la interfata a micropeliculelor de grafit depuse prin descarcari electrice in impuls* CONFERINTA STIINTIFICA INTERNATIONALA A DOCTORANZILOR” – Tendinte Contemporane ale Dezvoltarii Stiintei: Viziuni ale Tinerilor Cercetatori, 10 martie 2014, ISBN 978-9975-4257-2-8, pag 18 ;
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## ADNOTARE

**MARIN Laurențiu, „Cercetări privind omiterea efectelor de priză dintre suprafețele metalice și nemetalice prin intermediul peliculelor de grafit”, teza de doctor în științe inginerești, Chișinău, 2022**

**Lucrarea este compusă din:** Introducere, patru capitole, concluzii și recomandări, bibliografie din 169 titluri, o anexă, 126 pagini text de baza, 168 figuri și 24 tabele. Rezultatele obținute sunt publicate în 24 lucrări șt.

**Cuvintele cheie:** electrod de grafit, descărcări electrice în impuls, regim de subexcitare, pelicula de grafit, adeziv poliuretanic, formațiuni spațiale de carbon, fulereni, nanotuburi.

**Domeniul de studii:** științe inginerești și tehnologii.

**Scopul lucrării:** elaborarea tehnologiei de formare a depunerilor de grafit aplicate prin DEI în vederea omiterii efectului de priză și aderență a suprafețelor metalice cu alte suprafețe metalice sau nemetalice.

**Obiectivele lucrării:** - identificarea *condițiilor tehnologice* de formare a peliculelor de grafit pe suprafețe metalice în cazul aplicării *descărcărilor electrice în impuls (DEI)*; - elaborarea modelului fizic de formare a depunerilor de grafit în condiții optime; determinarea compoziției chimice, structurale și de fază a depunerilor formate pe suprafețele lucrătoare a pieselor; - determinarea proprietăților funcționale (*solubilitate, absorbție, anti-aderență, anti-adeziune, anti-coroziune*) a *peliculelor* de grafit depuse; - elaborarea recomandățiilor de aplicare în practică a *peliculelor de grafit*.

**Noutatea și originalitatea științifică a lucrării:** Noutatea științifică principală rezultată chiar din titlul tezei *o constituie faptul* că s-a elaborat o tehnologie de aplicare a unor pelicule aderente de grafit *pe o suprafață metalică* printr-un procedeu inovativ și anume *DEI*. Pelicula de grafit astfel obținută are capacitatea de diminuare a aderenței între două suprafețe metalice sau nemetalice care vin în contact. Modalitatea de verificare tehnică a acestui atribut al peliculei de grafit reprezintă o altă noutate științifică și a fost realizată prin utilizarea unui adeziv poliuretanic structural, concepție științifică a doctorandului. O noutate științifică subsidiară a tezei o reprezintă obținerea și identificarea prin analize specifice a formațiunilor de tip fulerene și de nanotuburi de carbon în pelicula de grafit depusă prin procedeul DEI.

**Rezultatele obținute care contribuie la soluționarea unei probleme științifice importante:** În urma tratamentului DEI pe suprafețele metalice s-au depus pelicule de grafit ale căror proprietăți s-au studiat în teză.

**Problema științifică importantă soluționată:** a constat în diminuarea semnificativă a efectului de priză și aderență a suprafețelor metalice cu alte suprafețe metalice sau nemetalice la temperaturi normale sau sporite, prin formarea depunerilor carbonice cu aplicarea DEI, aceste conținând structuri de tipul fulerenilor și nanotuburilor monoparietale. În acest context s-a determinat modul de conexiune a componentelor în circuitul de descărcare: piesă (anod) și electrodul-sculă (catod), dat fiind faptul că în acesta schemă tehnologică, se asigura atât eficiența eroziunii sculei cât și transferul de material pe suprafața prelucrată și formarea depunerii.

**Semnificația teoretică:** În baza cercetărilor teoretice și experimentale a fost înaintată și fundamentată o nouă ipoteză a fenomenului eroziunii, care vine să demonstreze, că acesta este unul complicat, fiind de natura fizică, chimică și de bombardament cu particule energetice (disipare catodică) iar în baza acestor constatări, în lucrare este elaborat un model fizico-chimic și tehnologic al eroziunii grafitului și formării depunerilor carbonice cu fulereni și nanotuburi sub acțiunea descărcărilor electrice în impuls în condiții normale.

**Valoarea aplicativă a tezei:** Lucrările științifice ce s-au derulat în cadrul tezei de doctorat, sunt importante deoarece s-au stabilit parametri tehnologici ai procedului de aplicare a peliculelor de grafit prin DEI pe suprafețe metalice. De asemenea, în urma lucrărilor de cercetare *s-a identificat o metodă nouă de obținere a formațiunilor spațiale* tip fulerene și nanotuburi de carbon. Proprietățile antiaderente ale peliculei de grafit au valoare tehnologică deosebită în procesele tehnologice care presupun alunecarea unei suprafețe pe alta în scopul diminuării frecărilor reciproce, în scop antiblocaj la structurile „șurub/piuliță”, la diminuarea aderenței între materialul fluid – sticla - și pereții matriței la curgerea printr-o matriță a unui material topit. *Peliculele carbonice*, formate pe suprafețele pieselor aplicate în procesele de turnare a sticlei, *sporesc funcționalitatea* lor de cca 3 ori, înlăturând efectul de aderență și protejându-le pe acestea antirefractar, iar cele aplicate pe suprafețele îmbinărilor „șurub-piuliță” înlătură efectul de priză chiar și pentru temperaturi de 800 °C.

**Implementarea rezultatelor științifice:** *în baza rezultatelor științifice a încercărilor reale la întreprinderea ÎS „Fabrica de sticlă” din Chișinău a fost obținut un act de implimentare.* Rezultatele științifice sunt aplicate și la elaborarea curriculumului privind cursului de Master: „Tehnologii moderne și inovații în inginerie” din cadrul Universității de Stat „Alec Russo” din Bălți.

## АННОТАЦИЯ

### МАРИН Лауренциу, «Исследования по исключению эффекта схватывания между металлическими и неметаллическими поверхностями с помощью графитных пленок», Кишинев, 2022

**Работа состоит** из введения, четырех глав, общих выводов и рекомендаций, библиографии из 169 названий, 1 приложения, 126 страниц (до библиографии), 168 рисунков, 24 таблицы. Полученные результаты опубликованы в 24 научных работах.

**Ключевые слова:** графитный электрод, импульсный электрический разряд, режим недонапряжения, графитная пленка, полиуретановый клей, пространственные углеродные структуры, фуллерен.

**Область исследований** - технические науки и технологии.

**Цель работы:** Разработка технологии формирования графитных покрытий, применяемой для исключения эффекта схватывания и адгезии металлических поверхностей с другими металлическими или неметаллическими поверхностями.

**Задачи работы:**

- выявление технологических условий формирования графитных пленок на металлических поверхностях в случае применения электрических импульсных разрядов (ЭИР);
- разработка физической модели получения графитных покрытий при оптимальных условиях;
- определение химического, структурного и фазового состава покрытий, образующихся на поверхностях деталей;
- разработка рекомендаций по практическому применению разработанной технологии.

**Научная новизна:** было показано, что графит более эффективно эродировать и осаждается на поверхности, если электрод-инструмент подключен к разрядной цепи генератора в качестве катода. Эрозия графита вызвана электрофизическими и электрохимическими эффектами, происходящими при высоких температурах. Покрытия, образованные на металлических поверхностях, отличаются от исходного материала тем, что они образуют трехмерные структуры типа фуллеренов и одностенных углеродных нанотрубок.

**Решаемая научная проблема:** устранение эффекта схватывания металлических и неметаллических поверхностей с другими металлическими и неметаллическими поверхностями.

**Теоретическая значимость:** В работе представлена физическая модель эрозии графита и образования углеродных покрытий в форме фуллеренов и нанотрубок под действием ЭИР в нормальных условиях.

**Результаты, способствующие решению научной проблемы.** После обработки ЭИР на металлические поверхности наносились графитовые пленки, свойства которых изучались в ходе выполнения диссертации. Наблюдалось значительное снижение эффекта схватывания и адгезии металлических поверхностей с другими металлическими или неметаллическими поверхностями при нормальных или высоких температурах за счет образования с применением ЭИР углеродных покрытий, содержащих такие структуры, как фуллерены и нанотрубки. В связи с этим был определен режим подключения компонентов в разрядную цепь импульсного генератора (детали – анод и электрода-инструмента – катод), учитывая тот факт, что в данной технологической схеме обеспечиваются как эффективность эрозии инструмента, так и перенос материала на обрабатываемую поверхность с образованием покрытий.

**Прикладная ценность работы:** в работе приведено практическое применение для увеличения срока службы стеклолитейного штуцера и шнека для производства гранул. Углеродные пленки, образованные на поверхности деталей, используемых в стеклолитейном производстве позволили повысить их функциональность примерно в 3 раза, устранив эффект адгезии и придав им жаропрочные свойства, а пленки, применяемые на поверхности соединений «винт-гайка», устраняют эффект схватывания даже при температуре в 800 °С.

После внедрения научных результатов, основанных на промышленных испытаниях в ГП «Кишиневский стекольный завод», **был получен акт внедрения технологии.**

Научные результаты работы также применяются и в преподавании курса мастерата «Современные технологии и инновации в инженерии» Бэлцкогo Государственного Университета им. Алеку Руссо.



## ANNOTATION

### MARIN Laurentiu, "The elimination of stick effect between metallic and non-metallic surfaces using graphite pellicles", PhD thesis in engineering sciences, Chisinau, 2022

**The work consists of** an introduction, four chapters, general conclusions and recommendations, a bibliography of 169 titles, 1 appendices, 126 pages, 168 figures, 24 tables. The results are published in 24 scientific papers.

**Keywords:** graphite electrode, pulsed electric discharge machining, sub-exciting regime, graphite pellicle, polyurethane glue, 3D carbon structures, fullerene nanotubes.

**Field of studies** engineering sciences and technologies.

**The purpose of the work:** Development of technology for the formation of graphite coatings used to eliminate the stick and adhesion effect of metal surfaces with other metal or non-metal surfaces.

**Objectives of work:** - *identification of technological conditions for the formation of graphite pellicles on metal surfaces by applying pulsed electric discharge machining*; - development of physical model for obtaining graphite coatings under optimal conditions; - determination of the chemical, structural and phase composition of coatings formed on the piece surfaces; - determination of functional properties (*solubility, absorption, anti-stick, anti-adhesive, anti-corrosion properties*) of applied pellicles; - development of recommendations for the practical application of graphite pellicles.

**Scientific novelty:** The main scientific novelty resulting from the title of the thesis reflecting the fact that a technology has been developed for the application of graphite films on a metal surface using an *innovative process by pulsed electric discharge machining (PEDM)*. The graphite film thus obtained has the ability to reduce the adhesion between two metallic or non-metallic surfaces in contact. The way of technical verification of this attribute of graphite film is another scientific novelty and was made using a structural polyurethane adhesive - a scientific concept of PhD student. A scientific novelty subsidiary to the thesis is the identification by specific analysis of 3D formations composed of carbon atoms such as fullerenes or carbon nanotubes in graphite film obtained by PEDM.

**Results that contribute to solving a scientific problem:** Following the PEDM treatment, graphite films were deposited on the metallic surfaces, the properties of which were studied during the elaboration of thesis.

**The important scientific problem:** It consisted of a significant decrease the effect of stick and adhesion between metallic surfaces and other metallic and/or non-metallic surfaces at normal or high temperatures, by the formation of carbon films obtained through PEDM. They contain structures such as fullerenes and single-walled carbon nanotubes. In this context, the connection mode of components in the discharge circuit of the impulse generator was determined, because in this technological scheme both the efficiency of tool erosion and the transfer of material on the machined surface are ensured and also obtaining the carbon film.

**Theoretical significance:** Based on theoretical and experimental research, a new hypothesis was advanced and substantiated of the erosion phenomenon which comes to prove that this is a complicated one being of physical, chemical nature accomplished by bombardment with energy particles and based on these findings in the paper physico-chemical and technological model of graphite erosion and the formation of carbon deposits with fullerenes and nanotubes under the action of PEDM under normal conditions is developed.

**Applied value of the work:** the scientific works that took place within the doctoral thesis are important because the technological parameters of the process of applying graphite pellicles on metallic and non-metallic surfaces through the PEDM process were established. *Also, following the research works, a new method of obtaining fullerene and carbon nanotubes type 3D formations was identified.* The non-stick properties of graphite film have a special technological value in technological processes that involve sliding one surface over another in order to reduce mutual friction, for anti-lock purposes in screw-nut joints, to decrease the adhesion between the fluid material and the surface of the mold at the flow through a mold of a fluid material. Carbon pellicles formed on the surface of parts used in glass-molding processes allowed to increase their functionality by about 3 times, eliminating the effect of adhesion and giving them refractory properties, and the pellicles applied on the surface of the screw-nut joints eliminate the stick-effect even at a temperature of 800 °C.

**The implementation of scientific results:** After the implementation of scientific results based on industrial tests in the State Enterprise "Chisinau Glass Factory", an act of technology implementation was obtained. The scientific results are also used in the teaching of the master's course "Modern Technologies and Innovations in Engineering" at the Alecu Russo Balti State University.

**MARIN LAURENȚIU**

**CERCETARI PRIVIND OMITEREA EFECTELOR DE PRIZĂ  
DINTRE SUPRAFETELE METALICE ȘI NEMETALICE PRIN  
INTERMEDIUL PELICULELOR DE GRAFIT**

**242.05 TEHNOLOGII, PROCEDEE ȘI UTILAJE DE PRELUCRARE**

**Rezumatul tezei de doctor în științe inginerești**

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