Research on Lessening of Bonding Effects Between the Metallic and Non-Metallic Surfaces Through the Graphite Films Deposited with Pulsed Electrical Discharges Process

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Abstract. The paper presents the results of experimental research on the physics of natural graphite film formation, the establishment of chemical composition and functional properties of the graphite films, formed on metal surfaces, as a result of the action of plasma in the air environment, at a normal pressure, under the electrical discharge in impulse conditions (EDI). The researchings were performed in the frame of doctoral thesis “Research on lessening of the bonding effects between the metallic and nonmetallic surfaces through the graphite films” and aimed to identify the phenomena that occur at the interface metal/ film of graphite, and to identify also the technological applications that it may have the surface treatment for submitting the films of graphite on metallic surfaces achieved through an innovative process of electrical pulsed discharges. After the research works from the PhD theme above mentioned, a number of interesting properties of graphite pellicle have been identified ie reducing of metal surface polarity. This led to drastic decreases for the values of adhesion when bonding of metal surfaces was performed using a structural polyurethane adhesive designed by ICECHIM. Following the thermo-gravimetric analysis, performed of the graphite film obtained by process of electrical pulsed discharges, have been also discovered other interesting properties for this, ie reversible mass additions at specific values of the working temperature. Chemical and scanning electron microscopy analysis have revealed that on the metallic surface subjected to electrical pulsed discharges process, outside the graphite film, it is also obtained a series of spatial formation composed of carbon atoms fullerenes type which are responsible for the phenomenon of addition of mass.

1. Introduction
The formation of graphite films at micrometric and nanometric scale on the surfaces of alloys-made parts causes their diffusion in the surface layer accompanied by the formation of high hardness carbides, and, as a result, the wear resistance of this layer increases [1-5].

The process of formation of graphite films, in all cases, leads to a decrease in surface roughness of the processed surface. According to the results obtained by the authors [4, 6-9], the application of films on the surfaces of the components that work in cinematic couples, leads to a decrease of the friction coefficient of at least 3 times. Experimental research and industrial tests are aimed at demonstrating that the deposits are formed more efficiently if the processed piece is included in the discharge contour of the current pulse generator used as anode. The formed films can reach up to 7
micrometers in thickness, increasing, at least twice, the operating durability of the casting molds components, due to their solid lubricant and anti-refractory properties [5, 10, 11].

2. Technology of graphite film forming
Experimental tests of forming graphite deposits on metal surfaces were performed in normal working environment – air. To achieve this technology a special installation was applied and it was further thoroughly described as a construction and as an operating system in the paper [6]. To achieve this, electrical discharges in impulse were applied, which interacted with the electrodes surfaces in electrode patches maintenance regime “cold” in order to avoid melting, vaporization and removal of material from them. Bars, made of technical graphite, were used as electrode tools, having a cylindrical form and the cross-sectional area of 5-7 mm². This ensures the formation of current impulses with duration ranging between $10^{-6}$-$10^{-7}$ s, which corresponds to life duration of “cold” electrode spots. Generator offers the formation of current impulses with the following parameters: gap released energy $W_s=0 \cdot 4.8J$, accumulated energy on the capacitor $W_c=0 \cdot 12J$, at the voltage applied to the charging capacitor $U_c=0 \cdot 250V$, for its capacity comprised within $C=100$-$600 \ \mu F$ with $100 \ \mu F$ pace. This ensures the priming of electrical discharges in impulse at the gap values of $S=0.01$-$2.5 \ mm$, with the discharge frequency $f=0$-$50Hz$.

The morphology of the treated surfaces was studied by means of SEM method, and the EDX and XPS phase methods were used to study the its chemical composition.

The adherence of the formed film to the treated surface was made by attempts of shearing on a HECKERT FPZ 100 dynamometer type. To identify the emerged changes in adhesion properties, as a result of applying graphite films, a comparative measurement was performed, related to the detachment forces of the assemblies, made with the help of a strong adhesive - polyurethane - between a set of samples treated with graphite and non-treated samples. A set of 3 graphite-treated samples and a set of 3 non-treated samples are glued; the treated samples with graphite film at the end, as it was shown in the paper [3]. After bonding, the samples are overlapped on top of an area of 25x25 mm, and afterwards, when the adhesive hardens, they are subjected to traction.

3. Physical model of graphite film formation by applying electrical discharges in impulse
The formation efficiency of the graphite deposits on the processed surface is also determined by the fact that, while subduing the plasma to electric discharges in impulse according to [6], the temperature in the plasma jet reaches values up to $10^4$ K, which is more than sufficient for graphite vaporization and its polar transfer to the piece surface.

The physical model, offered below, refers to the transfer of electrode tool material made of graphite from the processed piece surface, through impulse electrical discharges under a sub-excitation regime. It is worth mentioning that the electro-erosion of the graphite is a special one, with regard to metallic and semiconductor materials.

The concept of physical model is based on the analysis of experimental results, previously obtained by the authors [11, 12], where, it was established that, a more evident erosion of the graphite occurs when connecting the electrode to the discharge circuit of electric impulse generator, functioning as cathode. While concerning the general case of processing electrically conductive materials in work [12] it was established that the amount of material collected from the surface of the electrode subdued to electric discharges in impulse can be determined by the following relationship:

$$m = k \rho U_e \int_0^r i(t) dt$$

(1)

where: $k$ – is the proportionality coefficient; $\rho$ – is the density of the electrode material; $U_e$ – is the voltage drop at the electrode surface; $i$ – is the actual value of the electric discharge in impulse; $r$ – is the duration of the electric discharge in impulse. With the increasing of the voltage drop at the
electrode-cathode surface, the amount of electric power, released from its surface, increases as well. It is equal to:

\[ W_e = U_e \int i(t) dt \]  

(2)

Considering that the process of electro-erosion is, actually, an electrochemical one, arising at high temperatures, we can assume that recombining and dissociative processes occur at the anode-electrode surface, at the electrode-cathode surface and that of the plasma channel.

Summarizing the above mentioned facts in work [8, 13] and considering the distributed processes, we suggest the following physical model of the formation of graphite deposits under the action of the plasma subdued to electric discharges in impulse: in the initial phase (a) (see figure 1) the priming of electrical discharge occurs according to Townsend mechanism and to the formation of conductive channel; in phase (b) there take place a whole range of dissociation of atmospheric components in separate atoms, ions of oxygen, hydrogen and nitrogen, and, definitely, the electrons from the previous phase are present in the plasma; in phase (c) they interact one with each other and with electrode surfaces, producing surface activation and causing their erosion; both in phase (c) and in phase (d) there are many series of intensive oxidation reactions of the surface of the graphite electrode, as well as there is a dissociation of the product in oxygen and carbon, with a further transfer on the treated surface, both under the action of the electric field gap and under the action of the plasma component atoms (e); the process ends with film synthesis, which contains carbon of various crystallization forms and phases formed from component elements of plasmagene gas.

![Figure 1. Physical model of forming the graphite film on the piece surface under the influence of electric discharges in impulse.](image)

Proceeding from concrete conditions (air working environment, at the atmospheric pressure), we might assume the followings:

Due to the fact that the oxygen, in the plasma channel, interacts more intensively with the cathode-electrode surface, the oxidation reactions take place, accompanied by the release of carbon oxide CO, complemented by additional discharge of heat Q on the cathode surface and accompanied probably by the formation of carbon dioxide CO₂. As a confirmation of the processes of graphite oxidation at the cathode surface can serve the obtained results by work authors [14] in the process of formation of oxides film on metal parts surfaces, with the application of electric discharges in impulse.

4. SEM electron microscopy analysis of the graphite films

A set of silicon samples were submitted on an electron microscopy analysis and a set of images have been obtained with magnification in the range (1000x – 20 000 x) for a large number of samples.

From these images is clearly evidenced, that besides graphite film, was also obtained a series of globular formations with spherical shape. These spherical formations appear randomly on the sample surface and they due to the electrical discharges in pulse – EDI treatment. It is very clear that these
formations it can not have another composition than carbon. The resulting shape and the dimensions of these formations, from the images taken by electron microscopy, they are comparable to those of fullerenes, molecules spatial type with C\textsubscript{60} – C\textsubscript{80} [15]. These images bring a new argument in favor of a priori assertions regarding the occurrence of these chemical species - fullerene type - to application of the procedure of electrical discharges pulsed EDI.

5. Thermal Gravimetric Analysis (TGA) of graphite film
TGA tests on graphite films were conducted on a Du Pont Instruments 951 device. In order to avoid errors – due to the oxidative process that takes place at high temperature and results in a weight increase – TGA tests on graphite films were carried out in nitrogen atmosphere. Graphite powder was collected from three conditioned samples and, further, introduced in the platform unit. Afterwards, it is placed on the platform and the sample is inserted into the heating chamber.

The following parameters were set for the reference sample and for the graphite deposit material on the surface of the work piece: 20-800°C temperature range; 10°C/min heating rate; medium N\textsubscript{2} analysis at a working pressure of 760 mm Hg.

5.1. TGA tests on reference samples
First of all, TGA tests were done on a pure graphite sample, which was thought to be the reference sample.

![Figure 3. TGA curve corresponding to pure graphite reference sample.](image-url)
About 5 mg of powdered graphite reference sample was inserted into the device platform. TGA adsorption curve of reference sample is given in figure 3.

The following features are observed from figure 5 up to 100°C – the curve shape does not reveal any unusual thermal behaviour for graphite; within the temperature range of 100-280°C a weight loss of 7.485% (0.4683 mg) occurs as a result of volatiles and water evaporation; between 280-600°C no weight loss occurs which shows a high thermal stability of graphite; some non-significant decomposition (of about 18% of baseline) occurs within the temperature range of 650-800°C, caused by decomposition of tars and heavy hydrocarbons that are found in most varieties of graphite and, finally, considerable amount of graphite is found in the residue – more than 75%, at the end of determination 800°C. These aspects are characteristic for graphite behavior, a compound well-known for its particularly high chemical and thermal stability.

5.2. TGA tests on experimental sample deposition

A similar procedure was used to analyse the graphite films, deposited on the experimental samples. Since the available amount was extremely low, the graphite powder was collected from 3 of the 4 samples of each alternative. The collection process was done by the mechanical graphite scraping, without contacting the sample. The registration of the tested sample weight change versus the temperature is presented in figure 4.

![TGA curve graph](image)

**Figure 4.** TGA curve corresponding to 10/1,5/600/250 sample.

TGA curve of 10/1,5/600/250 sample (figure 6) shows a completely different allure from that characteristic of pure graphite. The graph shows a number of very interesting aspects suggesting that the graphite film, deposited by electrical discharge in impulse, has a completely different structure from that of pure graphite or that, besides graphite, other chemical compounds of carbon are formed. From figure 5, one may notice that within 200-300°C temperature range (at 222.99°C) a significant weight increase (of 1.999%) occurs, showing that the graphite sample gains weight, instead of losing it due to decomposition or loss in volatiles – showing a material adsorption in graphite film structure (as the adsorbed material cannot be anything but nitrogen from the atmosphere in which the tests are run). The phenomenon is reversible – at about 300°C the weight does not increase anymore, which may be the result of substance volatilization at this evaporation temperature.

Within the temperature range of 450-550°C (476.12°C) a new significant increase in weight (of 1.365%) may be observed, suggesting that, as a sample of graphite increases its weight instead of losing weight due to decomposition or loss in volatiles, a material adsorption occurs in the graphite film structure. Predominantly, a high temperature denies the assumption of a device error; the phenomenon of weight increases, being concrete and real. The phenomenon becomes reversible again at about 550°C and a weight increase does not occur anymore.
Within the temperature range of 600-750°C (614.73°C), a new weight increase occurs in a significant percentage of 2.769%, showing that the graphite sample weight increases instead of decreasing due to volatile decomposition or loss of weight gain – showing a material adsorption within the graphite film structure. Particularly, high temperature denies the assumption of a device error, the phenomenon of weight increase being concrete and real.

Reversible weight increase occurs within temperature ranges of 200-300°C, 450-550°C, 600-700°C having enough increased values, that cannot be assigned to device errors (permissible error being of max. 0.1%). The phenomenon of adsorption/desorption (reversibility) is very similar to the one occurring in zeolites, which presents spatial molecular structures made of atoms of Si, O, Al, able to close smaller molecules within them and to release them later. A similar phenomenon occurs also in graphite film, showing that besides graphite, spatial structures are also synthesized, in this example consisting of carbon atoms, which are known as fullerenes. These structures are made up of spatial molecules of 40-70 carbon atoms and have 20-40 nm in size. Because TGA tests were carried out under N₂ atmosphere, the chemical oxidation process, that could eventually bring mass intake, is excluded. The only scientific explanation consists of the presence of spatial structures able to store small molecules (N₂) and release them later. The emergence of the adsorption/desorption phenomenon at different temperatures and different percentages also shows that the potential spatial structures of carbon atoms have different sizes.

It is noteworthy that within the 20-750°C temperature range graphite film does not suffer any changes arising from thermal degradation.

In literature it is mentioned that spatial structures, containing fullerenes-type carbon atoms, could be found in carbon particles, resulting from incomplete combustion of hydrocarbons and, generally, in everything that involves violent combustion – combustion in internal combustion engines. It is also stated that spatial structures of these molecules, consisting of carbon atoms, can embed – without reacting to them – small molecules (H₂, N₂, monatomic inert gas molecules, HOH) inside their spatial structure (figure 5).

These scientific literature [28-30] explanations provide a plausible elucidation on weight increase phenomena, which were observed in TGA tests on graphite coating sample and nearly double the proportion in which the sample absorbs water – compared to other samples under investigation.

6. Chemical analysis of the graphite films
Globular formations present on the surface of graphite film, obtained by the procedure of electrical discharges in pulsed EDI, have led to the preliminary conclusion that besides graphite film itself mostly, of which is composed the deposited film on the metallic surface of the target, was also obtained a number of other carbon chemical species [16,17] Starting from the idea that these globular
formations are compounds of carbon, with spatial molecules fullerenes and / or nanotubes type, with relatively high number of carbon atoms, (60 – 80), the samples presented in figure 2, previously subjected to a non-destructive SEM microscopy analysis, have been subjected subsequently to chemical analysis. The chemical analysis of samples, consisted of their treatment with many organic solvents [18] for 48 hours, under continuous stirring. The best results were obtained in case of using α-chloronaphthalene, in which the carbon spatial formations have the highest solubility [19-21]. The most representative graphite film sample, after the action of α-chloronaphthalene for 48 hours, it was subject to a new electron microscopy SEM analyse. Following this further analysis in electron microscopy SEM it has been found that a large part of globular formations have been removed. In figure 6 they are shown the initial SEM image (left) and the final image (right) after the action of α-chloronaphthalene for 48 hours.

![Figure 6](image1.jpg)

**Figure 6.** Sample before and after the action of α-chloronaphthalene for 48 hours.

| Initial Mass of graphite film sample, g | 6  | 12 | 18 | 24 | 30 | 36 | 42 | 48 |
|----------------------------------------|----|----|----|----|----|----|----|----|
| hours                                  |    |    |    |    |    |    |    |    |
| 5.7998                                 | 5.7997 | 5.7997 | 5.7997 | 5.7996 | 5.7996 | 5.7995 | 5.7995 | 5.7995 |

**Table 1.** Mass variation of a graphite film sample as a result of the action of α-chloronaphthalene for 48 hours.

![Figure 7](image2.jpg)

**Figure 7.** The loss of mass for the sample of graphite film coded 2_001 as the result of the action of α-chloronaphthalene.

The result of the action of α-chloronaphthalene, is that the most significant sample of graphite film coded 2_001 suffers a significant loss of mass – 0.4 mg - perceptible for measuring instruments.
5.7998g to 5.7994g). This fact indicates that some component of graphite film it is removed by solubilisation.

7. Functional properties of graphite films
Carbon and its allotropic forms in which it crystallizes, shows a particular interest for researchers both as material and in particular as functional properties for technical applications in contemporary technologies. Following are presented a number of functional properties of graphite films deposited on active surfaces of the various types of pieces of machinery and equipment industry.

7.1. Anti socket
In order to broaden the applicability of the practical domain related to the scientific elaborations and, particularly, to graphite films deposited on metal surfaces, with the help of EDI method, a number of attempts, on the timing of screw driving - unscrewing of threaded joints (bolt-nut), were made by the authors [22, 23]. Measurements were made concerning the value of screwing moment in bolt couplers - screw nut with the formation of deposits on its front surface and the second solution - on the surface of the thread bolt (see table 2).

If we compare the results shown in table 2, we can see that the moment of screwing is increasing, being variable and dependent on the number of tracers (surface processing with EDI). It would seem that the deposit formation is not beneficial and leads to an increase of the screwing moment value.

This unimportant increase of the screwing moment is also caused by increasing the size of the pieces that form the couple. In contrast to the reverse - the unscrewing was not registered, together with the outlet effect for parts of couplings with graphite film on the active surface (also in case of keeping them at high temperatures, ad in case of placing mounted joints in solutions presenting active chemical environments).

Table 2. Values of the unscrewing moment of screw nuts, covered with a graphite film, M_{des}, Nm.

| Number of passes | Screwing force, kN |
|------------------|--------------------|
| 2                | 1                  |
| 3                | 2                  |
| 4                | 3                  |
| 5                | 4                  |
| 6                | 5                  |
| 8                | 6                  |
| 10               | 7                  |

7.2. Antiblocking properties of graphite films
Graphite films deposited by pulsed electrical discharges with 7-8 μm thickness, react physico-chemical as theoretical model, with metallic surface which leads to a high adhesion of graphite film [51-53].

A first method of verifying the theory on the creation of an anti-adhesive film on the metal surface as a result of treatment with graphite, achieved by electrical discharges, it consisted in achieving of a set of specimens made of two metal plates bonded by an structural adhesive to verify the shear forces.

According to the valid standardization, structural adhesives are the adhesives used to create structures- assemblies of components- which can not be removed only with the destruction of the structure. It follows that adherence achieved with this type of adhesive is stronger than the resistance of the glued components. Structural adhesives are used to achieve structures that no longer can be sold in parts. Therefore, a permanent structure is produced.

In these conditions the adhesives that made the structure should have excellent bonding characteristics and excellent resistance. Assemblies made with structural adhesive obtained were
subjected to shear stress test. As the result, the values presented in table 3 were obtained for the shear test.

Table 3. Shear stress values for different ways of gluing the specimens.

|                      | both specimens untreated daN/cm² | Mixed treated specimens daN/cm² | both specimens treated with graphite daN/cm² |
|----------------------|---------------------------------|---------------------------------|---------------------------------------------|
|                      | 86.4                            | 85.80                           | 83.7                                       |
|                      | 62.1                            | 58.6                            | 58.1                                       |
|                      | 62.0                            | 51.2                            | 50.4                                       |

From the shear stress test results table it can be observed that the untreated specimens have the higher values about 85 daN/cm². Mixed treated specimens are averages of shear stress values about 60 daN/cm², which proves that the graphite film, deposited on one of specimens, reduces the adherence between the adhesive and the metal surface.

The last version where both specimens are treated with graphite tension the shear stress values diminishes up to the approximate value about 50 daN/cm², which represents a decrease of approximately 40% compared to untreated specimens [26, 27] (version 1) (figure 8).

![Figure 8. The dependence of the shearing stress on the way of conditioning the test pieces.](image)

In this context, it is also observed that the shear occurs in two ways as it is shown in figure 9. In the first version breakage occurs in the adhesive mass figure 9 b) which is characteristic of specimens that were not subjected to the treatment of electrical discharges with graphite tool-electrode.

In the second version breakage occurs at interface graphite pellicle and adhesive surface which is characteristic of specimens that were subjected to the treatment of electrical discharges with graphite electrode too.

As a confirmation of this goal comes the surface morphology research for EDI treated and untreated specimens after the shear.

In the case of the specimens which do not have been subjected to electrodeposition treatment, all assemblies cleavage occurred in the adhesive mass, which is demonstrated by the pictures shown in figure 10. This shows strong adhesion to metal substrates of the adhesive.

It can be seen from figure 10 that breaking assembly occurred in adhesive mass. This is noticed by the presence of adhesive on whole active surface of the specimen (dark coloured zone).
In this case the higher shear forces have been observed (over 80 daN/cm$^2$). In the case of the specimens treated with graphite by electrical discharges pulse treatment EDI breaking structure if they applied a tangential force occurs at the adhesive support interface (figure 11). So the whole mass of the adhesive or much of it will remain on one of the supports. It says in this case that the inner resistance of the adhesive is greater than adherence to the metal support, the structure is not destroyed as a result of unbundling in parts, and i.e. the adhesive cannot works as structural adhesive. Determined share forces in this case are only to half (50 daN/cm$^2$) compared with the superficial untreated specimens.

**Figure 9.** Main scheme shear rupture assemblies: a - initial state; b - final state for untreated specimens; c-final state for EDI treated specimens; 1- metallic sheets, 2-structural adhesive.

**Figure 10.** Component of the assembly without surface treatment after shearing: a-general view; b, c - microscope image, ×80.

**Figure 11.** Component of the assembly with EDI surface treatment after shearing: A - general view; b, c - microscope image, ×80.
It can be seen from figure 11, that the existence of large stretching dark area, means that breaking assembly occurred at adhesive graphite film interface.

In figure 11, a may also be better observed, an area where film deposition of graphite treatment was not performed properly with a continuity 100% - area with a lighter colour - where there was a breakage in the adhesive mass, and in other areas where electro-deposition treatment of graphite was performed properly with a continuity 100% assembly rupture occurred at the graphite adhesive interface - area with a dark colour.

These images taken under the microscope demonstrate these statements. In figure 11, c is observed really well the area where the adhesive remains – area with a lighter colour - in contrast with the dark area, where the cleavage occurred at the interface adhesive - graphite film from the metallic surface.

All these observations allow asserting that the graphite films deposited by pulsed electrical discharges - EDI- determine non-adherence properties, which confirm the assumptions made in previous papers [28].

8. Conclusions
From the above mentioned are drawn the following conclusions:

The erosion of the graphite and its transfer on the metal surfaces with deposition film formation by the action of electrical discharges in impulse is more effective when the tool electrode made of pyrolytic graphite is connected in the discharge circuit of the current impulse generator as cathode. The erosion process in ordinary conditions (air at atmospheric pressure and room temperature) is one complex, of electro-physical and electro-chemical nature that devolves at high temperatures.

The presence of the sample made of steel containing an important amount of the iron stimulates the formation on its surface of 3D type formations (fullerenes or nanotubes). These goals are confirmed by the behaviour of depositions at thermo-gravimetric actions (stating mass increase under the influence of nitrogen at the temperature of 222.99°C, 476,12°C and 614.73°C) and by solubility tests in different environments: it varies from 51 for chloronaphthalene down to 0,006 for tetrahydrofuran).

The graphite films formed by applying electrical discharges in impulse possess a set of beneficial functional properties, such as: decrease the surface adherence by 1.4 times, decrease the wear coefficient from -0.1 down to 4, increase the wear resistance of piece components of glass molding forms, condition the increase of corrosion resistance in chemically aggressive media by 1.5 times.

Functional properties of the graphite depositions, their chemical composition and morphology indicate the fact that they presents 3D structures and in particular carbon nanotubes. The presence of iron in the sample, graphite purity of the tool-electrode, as well as energetic parameters of electrical discharges in impulse provide sufficient and necessary conditions for carbon nanotubes synthesis.

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