Graphite pellicles, methods of formation and properties

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Abstract. The paper presents the results of experimental investigations aimed at the establishing the composition and the functional properties of the graphite pellicles formed on the metal surfaces by the action of plasma in the air media at normal pressure applying electrical discharges in impulse (EDI). It shows that they have the same behavior characteristics as fullerene, avoiding the stick effect between metal surfaces and between metal and liquid glass at temperatures of the order of 400-1200 °C.

1. Introduction
The formation of nano-scale graphite pellicles on the surfaces of pieces made of different metal alloys causes their diffusion in the surface layer accompanied by the formation of carbides with high hardness and, as a result, it increases wear resistance of this layer [1-5]. The formation of graphite films in all cases leads to the surface roughness decrease.

In accordance with the results obtained by the authors [4], the application of films on the surfaces of the work pieces in the kinematic pairs leads to the reduction of the coefficient of friction by at least 3 times.

The experimental tests on the stick effect of the threaded joints has shown that the stick effect caused by the mutual diffusion of the constituent materials of the joint parts is prevented by the presence of graphite films and even when the couple is maintained in the furnace at temperatures within (400-800)°C it has been showed that for the parts made of construction steel the stick effect in the joint is not present [4].

Film formation on the internal surfaces of pipes allows eliminating the stick effect for paraffin stoppers that are a problem for pipelines of oil transporting.

Experimental investigations and trials come to show that deposits are formed more efficiently when the workpiece is connected in the discharge circuit of the current impulse generator as anode, and the formed films can reach up to 7\textmu m thick, they increase the durability of the glass molding form components by at least 2 times, due to the qualities of solid lubricant and anti-refractory properties that they possess [2, 5].

From those mentioned above it follows that the development of an effective technology of graphite deposit formation on the surfaces of the parts from machine building industry would allow to successfully solve a number of problems such as: ensuring the surface refractoriness, obtaining wear resistant surfaces, reducing the coefficient of friction of parts surfaces functioning in the kinematic
2. Methodology of Experimental Investigations

Experimental investigations on graphite deposition formation on metal surfaces were performed in normal working environment - air. For this purpose electrical discharges in impulse have been applied that interact with electrodes’ surfaces in the regime of "cold" electrode spots maintenance to avoid melting, vaporization and removal of material from them. The bars of cylindrical cross-sectional area of (5-7) mm² made of technical graphite were used as tool-electrodes. To appropriate to maximum results of interests for production enterprises as workpieces were chosen: nuts and bolts with metric thread M16, plungers applied in molding packaging bottles, component parts of glass molding forms, pipe segments, etc. These pieces were connected in the discharge circuit of the current impulse generator as anode. Materials of which were executed were relative diverse and included group of steels (steel C45, C35), cast iron and bronze alloys. In order to form graphite depositions without melting and vaporization of the machined surface of the workpiece as a source of energy the current impulse generator was applied whose construction and principle of operation is described in [1]. It provides formation current impulses with duration ranging in limits of 10⁻⁶-10⁻⁷ s which corresponds to the life duration of the "cold" electrode spots. Generator offers formation of the current impulses with the following parameters: the energy released in the interstice $W_S=0\div4.8\text{J}$, the energy accumulated in the condenser battery $W_C=0\div12\text{J}$, the charging voltage applied to the condenser battery $U_C=(0\div250)\text{V}$, for its capacity contained within the $C=100\div600\mu\text{F}$ with the step of 100μF. It provides electrical discharge impulses within the interstice values $S=0.05\div2.5\text{mm}$; discharge frequency $f=0\div50\text{Hz}$. The morphology of the machined surface was studied by means of SEM technique and the chemical composition by means of EDX technique. The adherence of the formed film on the machined surface was achieved by shear tests on a dynamometer type FPZ HECKERT 100. To identify changes in adhesion properties as a result of applying graphite films, it was performed by measuring comparative detachment forces of assemblies made with a strong adhesive - polyurethane - between a set of samples and specimens treated with graphite and without treatment. A set of 3 specimens with graphite treatment and a set of three samples without treatment were supposed to adhesive; the specimens were treated at the end with the graphite film as disclosed in the paper [3]. After adhesive application the specimens overlap an area of 25x25 mm, and after drying of the adhesive they were subjected to the traction.

To measure the wear resistance of graphite films deposited on glass molding plungers the universal microscope of UIM-21 type was used permitting measurement with an error of 1μm as described in [2]. The component parts of glass molding forms (numbered in accordance with the their assembling drawing) were subjected to wear in glassy mass for 44625 cycles (85 hours) for the sample no.19 and for 39900 cycles (75 hours) for the 23 sample. The speed of cycles constitutes $v=8.75$ cycles/min, the temperature of the glass drop is 1129 °C, the glass of BT-1 type for bottles’ molding was used, its chemical composition corresponds to the standard GOST R 52022-2004 SM.

In order to determine the anti-stick properties 6 pairs of bolt joints were selected, of which three pairs of pieces were with deposited on bolt’s surface graphite films and another three were kept intact. They were engaged through the action of the same torsion moment. Thus, three pairs were formed for investigations; there were two couples with and without the presence of graphite film in each of them. The studied pairs were placed in the NaCl solution with a concentration of 3% for 24 hours after which they were insert into oven at temperature of 800 °C where were maintained for 10 hours, then the measure of the unscrewing moment of the investigated joints was made in accordance with [4].

3. Results of experimental investigations and their interpretation

The morphology analysis of the surface machined by applying EDI with graphite tool-electrodes showed that physic-chemical changes on the surface does not exceed micrometer sizes. Apart from the initial components of the processed material a considerable amount of carbon (about 80%) in atomic
content is attested. The microstructure analysis of the transverse micro section demonstrates that the majority of carbon transferred into the workpiece surface is observed at micrometer depths, which allows concluding that it is possible formation phases of carbides and those of graphite at the interface “metal piece-deposition formed by applying EDI”.

![Figure 1. SEM morphology of the graphite film deposited on steel C45 support.](image1)

If you look at those shown in figure 1, we can see that the film is composed of clusters of nano-scale formations. Between these clusters and formations that constitute them the holes (pores) are attested, fact that can explain a set of properties they possess.

As a result of graphite film formation on the piece surface the plunger diameter increases on average by about 14μm beside the initial diameter, i.e. as a result we form the graphite depositions with the respective dimension on the surface of the workpiece as continuous film (figure 2).

![Figure 2. The chemical composition of the formed film determined by the EDX technique.](image2)

Thus, the application of films on the surfaces of the constituent parts of glass molding forms allowed to determine very effective their functionality. It was guaranteed to parts the durability at least 2 times higher compared with the parts coming from factory [2, 5]. This can be explained by the fact that graphite presents a solid state ointment and prevent adherence of the glass to the surface of the workpiece, and respectively its wear by the adherence, and by the fact that the graphite film has the anti-refractory properties and serves as thermal isolator between metal parts and liquid glass surface. The mentioned above is confirmed by the results obtained by the authors of the paper [5], where the
plungers were tested under real exploitation conditions, as a result it was established that the plungers of molding forms with formed graphite films on their active surface were worked at 57600 cycles without modifying their initial shape and size. In this regard, the experimental investigations in technological cycle were performed to compare the wear of glass molding forms plungers [2]. The two plungers, the one coated with graphite by EDI and the other unprocessed, were subjected to the test (figure 3).

![Figure 3](image3.png)

**Figure 3.** Overview of finishing pallets: a) with unprocessed surface, b) with graphite film.

![Figure 4](image4.png)

**Figure 4.** Dependence of the difference of piece diameter on its active length for:
1 – sample no.19 after functioning in technological cycle; 2 – sample no.23 after functioning in technological cycle; 3 – sample no.23 after applying EDI

If we examine the unprocessed by EDI sample (figure 3a) before and after its functioning at technological cycle (figure 4, curve 1), then we can see that in some investigated points its diameter decreases by about 11μm. The sample (figure 3) is studied from three points of view: at the initial stage, then after applying EDI and finally after being subjected to wear. The plunger's diameter increases in the allowable limits due to the graphite depositions on the surface after the piece was processed by DEI. The research of the piece after functioning under the above prescribed regimes showed the decrease in piece diameter by tens of micrometers, as shown in figure 4.
To confirm or to refuse the adherence on the piece surface of different materials the couples consisted of pieces with graphite films by pasting them surface to surface through the adhesive were tested according to the methodology described in [3, 13].

As a result of traction of assembled by pasting pieces we have observed that untreated specimens have higher values of shear stress than treated one, that constitutes about 85daN/cm$^2$, mixed-treated specimens have on average value of shear stress of 60daN/cm$^2$, which tells us that graphite film deposited on one of the specimen reduces the adhesion between the adhesive and the metal surface. The last variant is when both surfaces are coated with the graphite film; shear stress is reduced down to about 50daN/cm$^2$ that represents a 40% decrease in adhesion beside the untreated specimens. Also, it is noted that untreated specimens’ shear takes place within the adhesive, as compared to those treated where shearing takes place in the separation surface of the adhesive with the graphite film. This effect can be explained by the fact that the formed film is porous and, respectively, the adhesive penetrates into its pores.

We may assume that one of the reasons of absorption of component adhesive substances is that the formations of the graphite film present fullerenes and they have the ability to absorb some components from the environment.

The results on solubility of graphite films formed by DEI method on metal surfaces in the interaction with different solvents are presented in [11, 12]. It is also led to the conclusion that the other susceptible chemical species are dissolved after treatment with a suitable solvent. Assuming initially due to electronic microscopy analyzes presented in figure 1, we can state that after the treatment of the metallic surface with graphite films by EDI other chemical formations are also obtained - probably some spatial carbon structures of fullerenes type.

In papers [6-10] it was stated that fullerenes are black, opaque solids, of low hardness and low conductive of heat and electricity. The behavior of samples treated with a specific to fullerenes solvent provides a first indication for assuming, according to which after treatment by EDI with formation of graphite films the same spatial formations composed of atoms of C are also obtained.

In order to broaden the field of application in practice of scientific elaborations and especially of graphite films deposited on metal surfaces by DEI method, a number of attempts on the determination values of screwing-unscrewing moment of threaded joints (bolt-nut) were made by the authors [4]. They were performed measurements on the amount screwing moment in couples “bolt-nut” with the formation of depositions on the frontal surface of the nut and the in the other case on the threaded surface of the bolt (see table 1).

| Table 1. The values of the unscrewing moment of the nut coated with graphite $M_{un}$, N·m. |
| --- |
| **Number of passes** | Screwing force, kN | 0.5 | 1 | 1.5 | 2 |
| 2 | 2 | 6 | 9.9 | 13 |
| 3 | 2.2 | 5.8 | 9.5 | 12.5 |
| 4 | 2.5 | 4.5 | 8.2 | 10.15 |
| 5 | 3 | 6.1 | 10.2 | 14 |
| 6 | 2.9 | 8 | 12 | 16 |
| 8 | 3.5 | 6.2 | 11 | 14.1 |
| 10 | 3.5 | 5.9 | 11 | 13.2 |

If we compare the results shown in table 1, it can be seen that the screwing moment increases being dependent variable and on the number of passes (number of surface processing by DEI). It would seem that the formed depositions are not beneficial and lead to the increase of the value of screwing moment. Insignificant increase of the screwing moment is also caused by the enlargement of parts forming the couple.
However, at the reverse operation – unscrewing – the stick effect was not attested for parts of joints with graphite films on the active surface maintaining them in ordinary conditions (also in the case when maintaining them at high temperatures or if fitted joints was placed in chemically active environments)

4. Conclusions
As a result of the application of graphite films on metal surfaces by the electrical discharges in impulse method we can say that they have anti-adhesive properties, possess ointment properties, and decrease kinematic couplings corrosion in certain aggressive environments and increase wear resistance of pieces that work at high temperatures by about 10 times; Behavior of graphite films could be caused by the formation of structures such fullerene synthesis; Graphite pellicles can be successfully used to eliminate paraffin stoppers formation in pipes at oil and petroleum transportation due to their high anti-adherence properties

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