REZULTATE ŞI CONCLUZII

În figură (a, b, c şi d) sînt prezentate, sub formă de diagramă câteva fragmente din spectrele de emisie al antimonidului de galiu dopat cu 0,38 şi 3,0 % at. de *Fe*. Din analiza diagramei figurei. uşor se observă că intensitatea liniilor analitice creşte odată cu mărirea concentraţiei atomilor dopanţi în eşantioane în limitele erorii măsurătorilor şi slab se schimbă de la o probă la alta selectate discret din materialul primar. Pe baza rezultatelor analizei spectrelor de emisie atomice conchidem că în procesul de sinteză şi creştere a monocristalelor atomii de *Fe* sunt solubili în antimonidul de galiu şi în procesul de sinteză a compusului şi de creştere a monocristalului prin metoda topirii zonale modificate se distribuie omogen în volumul monocristalului.

S-a stabilit lungimea de undă din spectrul de emisie a fierului ($\lambda = 302{,}064$ nm) intensitatea căreia liniar depinde de concentraţia fierului în *GaSb* în limitele concentraţiei 0,38≤*C*≤3,0 % at.

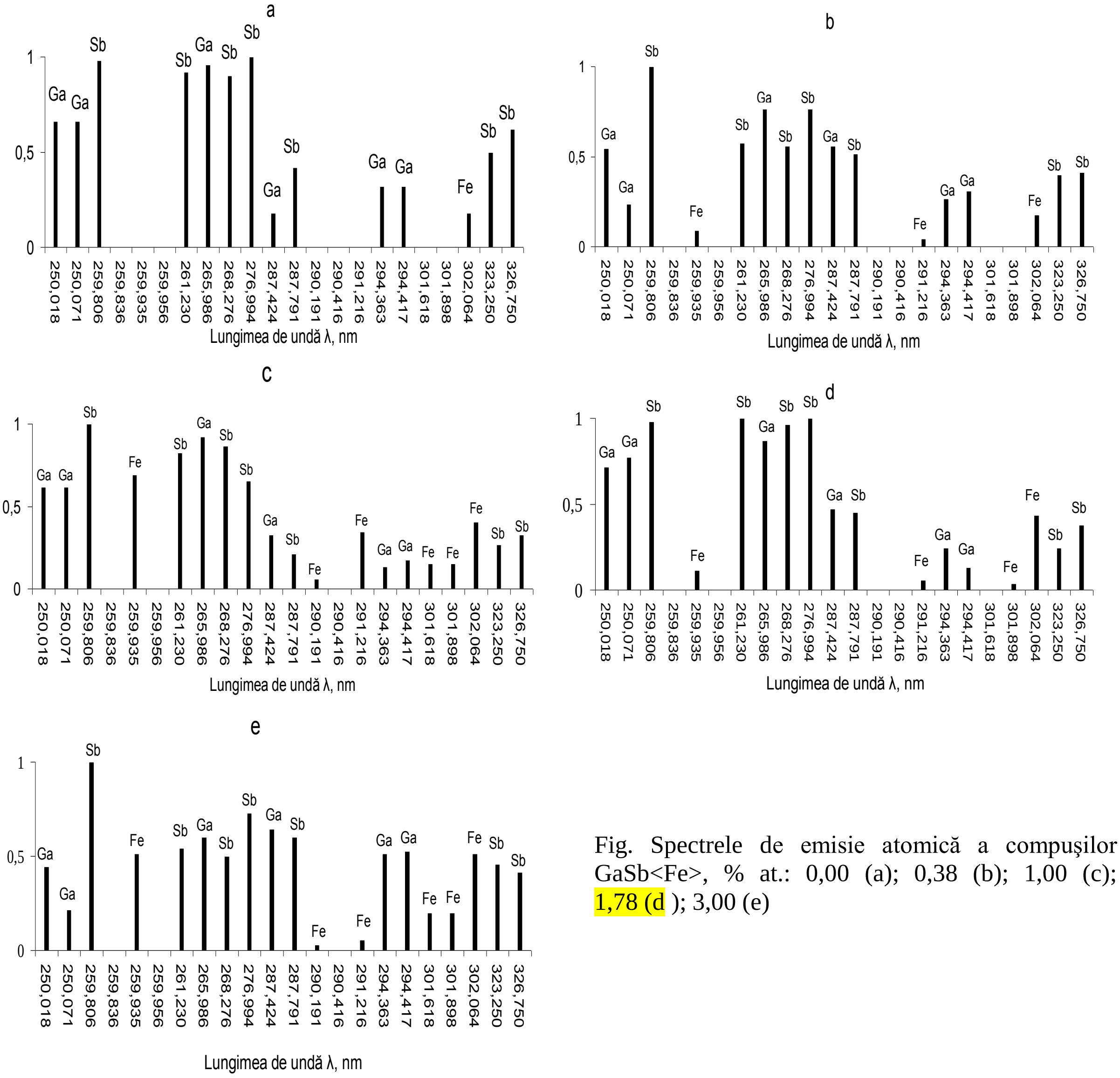

Fig. Spectrele de emisie atomică a compuşilor GaSb<Fe>, % at.: 0,00 (a); 0,38 (b); 1,00 (c); 1,78 (d); 3,00 (e)

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APPLYING GRAPHITE PELLICLES FORMED BY ELECTRICAL DISCHARGES IN IMPULSE TO IMPROVE THE EXPLOITATION PERFORMANCES OF METAL SURFACES

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There is a number of issues such as the effect of wax formation in the pipe plugs during the extraction and transportation of oil (petroleum) through pipelines. For this purpose, different technologies are used to avoid this effect (surface hardening, surface pellicle formation, ultrasound application, etc.). We have developed a technology of graphite pellicle formation by applying electrical discharges in impulse. For this purpose, a rotating tool-electrode made of graphite, included in the circuit of a current pulse generator, is applied, and the work piece serves as a counter-electrode. Continuous or strip-like pellicles are formed by establishing the required parameters of electrical discharge, the interstice size and the frequency of discharge impulse through a relative movement between the tool-electrode and piece. The formation of graphite pellicles on the piece surfaces does not lead to changes in their geometry but gives them new properties. The process of graphite pellicle formation is accompanied by hardening the surfaces made of construction steel by 3 to 8 times at the depth of 3...10 µm. As a result of this type of machining, carbon partially diffuses into the work piece surface with carbide formation. The continuity of processed surface reaches 90...100 % shares and the amount of carbon on the surface exceeds 90 % of carbon. Wear tests of glass mold poansons have demonstrated that they resist over 57 000 cycles without any change of geometry and dimensions. The paraffin casting inside the machined tubes with graphite pellicle formation have shown that it does not adhere to the pipe surface. The graphite pellicle formation on the frontal surfaces of the nuts demonstrates that it omits the effect of their sticking to the mating surfaces. Graphite pellicle formation is possible on flat and rotating surfaces, that is why it may be applied to cover the interior pipe surface in order to avoid the effect of wax formation in the pipes during oil extraction and transportation; in anti-stick pellicle formation in mechanical joints; to increase the wear resistance of form pieces for glass molding.

Keywords: graphite pellicles, electrical discharges in impulse, anti-stick, hardening, carbon

Există un şir de probleme cum ar fi efectul de formare a dopurilor de parafină în conducte în procesul extragerii şi transportării petrolului prin conducte. În acest scop se aplică diferite tehnologii de omitere a acestui efect (durificarea suprafeţelor, formarea peliculelor, aplicarea ultarsunetelor, etc). Noi am realizat o tehnologie de formare a peliculelor de grafit cu descărcări electrice în impuls. În acest scop se aplică un electrod-sculă rotitor executat din grafit care este înclus în circuitul unui generator de impulsuri de curent, iar în calitate de contra-electrod serveşte piesa de prelucrat. Stabilind parametrii necesari a descărcărilor electrice, mărimea interstiţiului şi frecvenţa impulsurilor de descărcare printr-o mişcare relativă înre elecrodul-sculă şi piesă se formează pelicule continui sau sub formă de fâşii. Formarea peliculelor de grafit pe suprafeţele pieselor nu conduce la modificarea geometriei acestora ci le conferă noi proprietăţi. Procesul de formare a peliculelor de grafit este însoţit de durificarea suprafeţelor executate din oţeluri de construcţie de la 3 la 8 ori la adîncimi de 3...10 µm . În rezultatul acestui tip de pelucrare carbonul parţial difuzează în suprafaţa pelucrată cu formarea carburilor. Continuitatea suprafeţelor prelucrate atinge cote de 90...100 %, iar cantitatea de carbon pe suprafaţă depăşeşte conţinutul de 90 % carbon. Încercările de rezistenţă la uzură a puansoanelor formelor de turnare a sticlei au demonstrat că acestea rezistă la peste 57000 de cicluri de turnare în lipsa modificării geometriei şi dimensiunilor. Turnarea parafinei în ţevi prelucrate în interior cu formarea peliculelor de grafit au demonstrat că ea nu aderă la suprafaţa ţevilor. Formarea peliculelor de grafit pe suprafeţele frontale a piuliţelor demonsrează că ele omit efectul de priză a acestora cu suprafeţele de îmbinare. Formarea peliculelor de grafit este realizabilă pe suprafeţe plane şi suprafeţe de rotaţie din care motiv poate fi aplicată la acoperirea suprafeţelor interioare a ţevilor în scopul omiterii efectului de formare a dopurilor de parafină în conducte atît la extragerea cît şi la transportarea lui; la formarea peliculelor antipriză în îmbinările mecanice; la sporirea rezistenţei de uzură a pieselor formelor pentru turnarea pieselor din sticlă.

Cuvinte-cheie: pelicule de grafit, descărcări electrice în impuls, antipriză, durificarea, carbon

INTRODUCTION

Modern technology continuously tends to save materials and energy consumed in realizing products and in the functioning of pieces, apparatus and tools in the building of which they had been used. An increase of metal surface durability permits the realization of these desiderata. For example, the industry of glass manufacturing faces a whole series of problems as far as transverse plates of glass molding are concerned. The increase of their durability would be possible if the active part is covered with a graphite pellicle via electric discharges in impulse that would allow to change the superficial stratum properties, namely the micro hardness and durability increase and would serve as an ointment to decrease the power of abrasion between the glass mass and the transverse plate. There are also problems in the oil industry where paraffin stoppers appear in the oil transport pipes that adhere to their surface and plug them.

It is known [1, 2] that pieces and machine aggregates wear out during the working process and this leads to the modification of geometric dimensions, form and superficial strata properties; in some cases fissures, curves, torsions, distortions or tears appear. To increase durability nowadays both traditional and non traditional methods of surface processing may be used. One of these is the method of electric discharges in impulse. To process the surface according to this method different electricity conducting materials may be used as anode tool electrodes, such as copper, nickel, metal alloys, metal carbides, graphite, etc. which influence the chemical composition and the physical – mechanical properties of the piece subjected to investigation (changing its hardness, resistance to fissures and roughness).

It was demonstrated that the use of tool-electrodes made of graphite may influence the decrease of roughness and the micro hardness increase in the superficial stratum subjected to processing; it increases the durability of pieces applied in machine and apparatus building [3-6]. In all the papers published by other authors the tool electrode made of graphite is connected as an anode to the current source. We suggest it should be used as a cathode (a situation in which it wears away more strongly), anode and a combination (cathode-anode). Thus, as it was demonstrated in many papers [3-8], we will be able to increase the chemical composition and the physical-mechanic properties of the processed surfaces more efficiently.

MATERIALS AND METHODS OF RESEARCH

The experimental research has been done under conditions of air at atmospheric pressure in a regime of under-excitation in which the piece or the tool-electrode had the possibility to change its polarity during one cycle of processing or in alternative cycles. Under the influence of induction impulse a conductivity channel was formed through which the power impulse energy was emitted accompanied by the formation of the plasma channel which provokes essential modifications at the piece surface.

Construction steel 3, 45 and different types of cast iron were used to make pieces or samples subjected to processing. The tool-electrode is a bar with a 2-3 mm diameter and is made of pirolytic graphite. The graphite tool-electrode was used as cathode, anode or in a combined regime. Based on the data given in specialized literature and taking into account our own experimental results [3-6], we may state that it wears out more strongly when it functions as a cathode than when it is an anode. It means that there is a greater quantity of carbon which due to the applied energy impulse diffuses in the surface stratum provoking structural and chemical composition modifications in it. When it is connected as an anode it may influence the modification of the surface stratum micro hardness, the roughness decrease and the oxidation of the processed surface. When the combined regime of processing is applied, a more advantageous modification of the processed piece hardness and durability takes place due to the physico-chemical processes that occur in the interstice and in the surface stratum of the piece [4, 6].

Unipolar and bipolar impulse energy sources were used to perform the experiments. The unipolar impulse supply source ensures the following parameters: emitted energy in the interstice - W_S=0…4,8 J, discharge frequency – f=0…50 Hz, impulse duration – τ=0…250 μs. The generator of bipolar impulses ensures the following technological parameters: energy emitted in the interstice – W_S= 0…4,8 J, discharge frequency – f=0-50 Hz, the impulse discharge duration varied between 9 and 94 μs, the intervals between impulses constituted 6…15 μs. During the experiments the interstice size was adjusted to the micrometric scale and varied between 0…2,5 mm.

Due to the technological parameters ensured by the installation, the processing could be realized in the regime of maintaining EDI on both „warm" electrode spots (when the processed surface melted) and on „cool" electrode spots (when the processed surface did not melt, though at nanometric depths the melting does take place).

EXPERIMENTAL RESULTS AND THEIR ANALYSIS

Below we offer a physical pattern of the graphite tool-electrode material transfer to the processed surface piece via electric discharges in impulse in a regime of under-excitation.

The concept of the physical pattern comes from the analysis of other authors' experimental results [7, 8] which stated that a more obvious graphite wearing away occurs when the electrode is connected to the discharge circuit of electric power impulse generator as a cathode. It was stated in paper [8] that the quantity of material drawn from the electrode surface during the process of electric discharges in impulse may be determined according to:

$$m = k\rho U_e \int_0^{\tau} i(t)dt \qquad (1)$$

in which k is the proportionality coefficient; ρ is the density of the electrode material, U_e is the voltage decrease at the electrode surface; i is the power momentary value of electric discharges in impulse; τ is the duration of the electric discharge in impulse.

According to papers [7, 8] the ratio for the same conditions of thermal or thermo - chemical treatment will be the following:

$$\frac{m_a}{m_c} = \frac{U_a}{U_c} \qquad (2)$$

in which m_a and m_c are respectively the anode and cathode worn away mass, U_a and

U_c - the power decrease at the anode and cathode surface. If we take into account the fact that the graphite electrode wearing away is higher when it is connected as a cathode we have to conclude that the power decrease at the surface is higher too:

$$U_c \rangle U_a \qquad (3)$$

The higher the voltage decreases at the cathode-electrode surface the bigger the quantity of emitted energy at its surface which is equal to:

$$W_c = U_c \int i(t)dt \qquad (4)$$

In conformity with the theory of electroerosion the material from the anode surface is drawn under the form of positive ions while electrons are mainly emitted from the cathode surface. These statements are not valid for electrodes made of graphite used as cathodes. As the process of electroerosion is an electrochemical one and occurs at high temperatures we may suppose that recombining and dissociative processes take place at the anode-electrode and cathode-electrode surfaces and in the plasma channel.

Concluding from the real conditions (working medium – air at atmospheric pressure) we could make the following assumption: due to the fact that the oxygen in the plasma channel interacts more intensively with the surface of the cathode – electrode, oxidation reactions take place accompanied by carbon oxide CO emission and possibly the formation of carbon dioxide CO_2 according to the reactions(Fig. 1, b):

$$\begin{aligned} C + O &\rightarrow CO \\ C + 2O &\rightarrow CO_2 \qquad (5) \end{aligned}$$

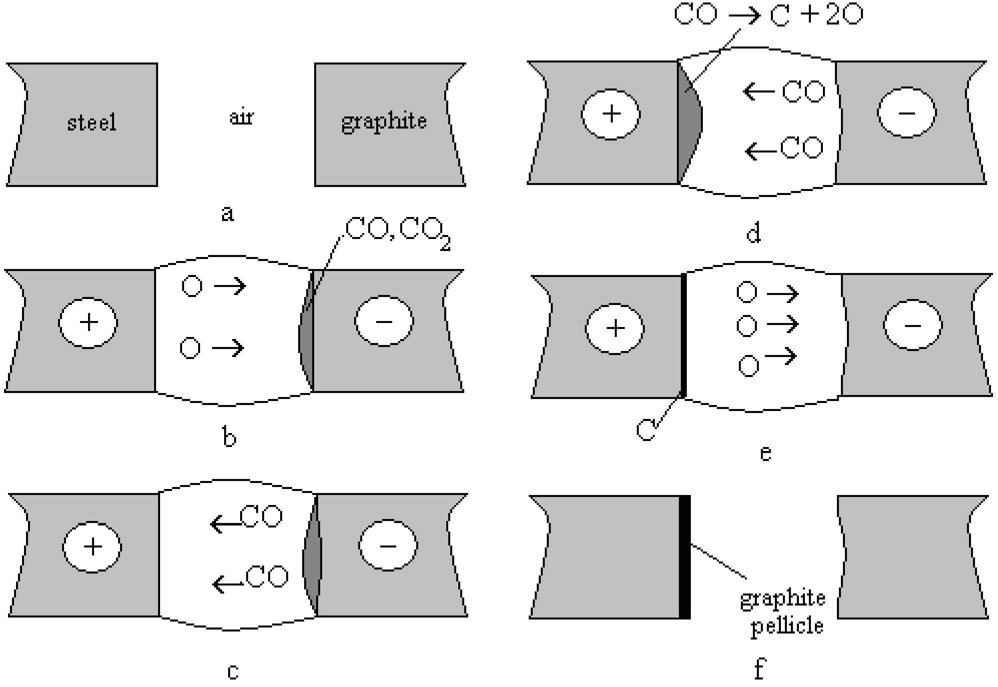

Fig. 1. Physical model of forming the graphite pellicle on the piece surface under the influence of electric discharges in impulse: a) initial state of electrodes; b) formation of oxide dioxide carbon; c) electrifying the gas molecule; e) formation of the graphite pellicle and of oxygen; f) the final state of electrodes.

The results obtained by the authors of the paper [9] concerning the processes of forming oxide pellicles on the metal piece surfaces by applying electric discharges in impulse may serve as confirmation of graphite oxidation processes at the cathode surface. The carbon oxide in the plasma of electric discharges in impulse electrifies negatively by picking up an electron and it is pushed towards the anode piece (Fig. 1, c).

Due to the fact that the emitted energy at the anode surface is greater than that in the interstice the gas molecule dissociates into carbon and oxygen ions (Fig. 1, d).The oxygen ones return to the plasma channel and again execute the superficial oxidation of the cathode, while the carbon ones recombine at the anode surface forming the graphite pellicle (Fig. 1, e). Then the graphite pellicle formed on the piece surface (Fig. 1, f) is influenced by the heat emitted at the interface with the plasma channel and is subjected to processes of diffusion in the piece surface accompanied by the formation of the hardened stratum. However the erosion of a certain amount of graphite from this surface is not excluded in the last phase.

When the polarity is changed the tool-electrode wears away less and under the influence of the plasma channel energy the diffusion of the graphite pellicle in the piece and the micro hardening at the surface take place, thus intensifying the functional properties of the processed pieces.

The obtained experimental results are a good confirmation of this. The experimental research on the formation of graphite pellicles on the transverse plate surface of the glass molding form made of cast iron points out the following: the analysis of the processed surface morphology has shown that the formations on the surface do not exceed micrometric sizes. A considerable amount of carbon (about 80 %) is found in the atomic content besides initial components of the processed material [10].

It cannot freely exist as it forms connections in the metal structure forming carbides (maybe diamond phases too) or in separate structures under the form of graphite.

If we analyze what is represented in Fig. 2 we may state that the greater part of carbon transferred to the piece surface is found at micrometric depths which gives us the possibility to conclude that it is possible to form separate carbon and graphite phases.

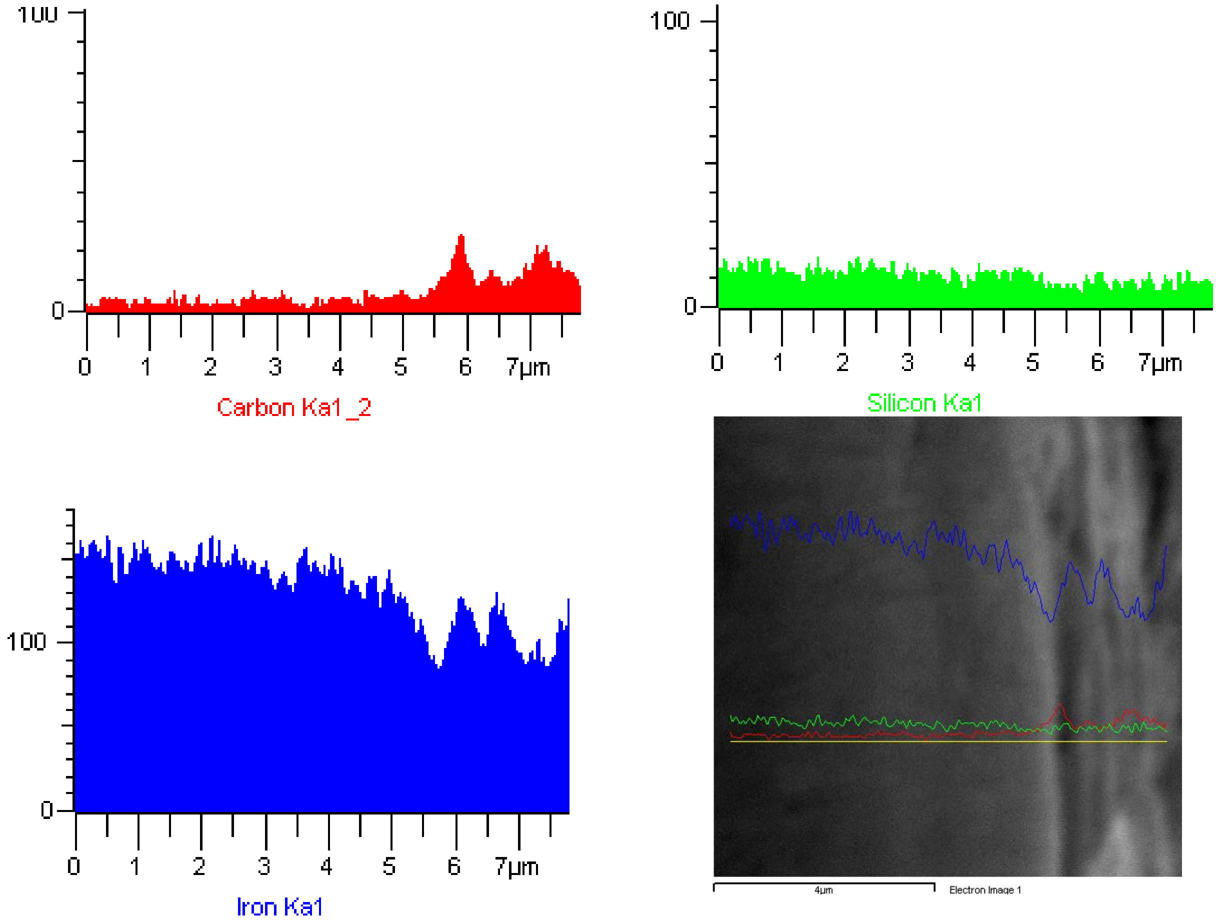

Fig. 2. Carbon distribution in the processed surface.

The above said is supported by the results obtained when testing the transverse plates from the glass molding forms under real conditions of exploitation. The thickness of the graphite pellicles formed on the transverse plate processed surfaces are within the limits of nano- and micrometric scale. It was stated that the transverse plates of the glass casting forms on the surface of which graphite pellicles were formed functioned in 57600 cycles with no modification of their geometric form and dimensions.

Taking this into account experimental research has been done in a technological cycle to compare the wearing away of transverse plates of glass molding forms. We tested transverse plates covered with graphite pellicles using the method of EDI and pieces without deposits. After depositing the graphite pellicle the transverse plate diameter increased approximately by 14 µm compared to the initial diameter, that is, graphite deposits were formed with a thickness of about 7µm on the surface under the form of a pellicle. After measuring the fissure of the iron cast transverse plate covered with graphite after functioning in the technological cycle (for 75 hours) it was possible to notice that its dimensions along its active length did not reach the initial quota, while the uncovered transverse plate was greatly worn away at about 10 µm on some portions, on others there was an increase of the initial dimension because of the adhered glass mass. Comparing the obtained results concerning the dimensional wearing away of transverse plates with and without graphite deposits we may state that the ones that have graphite deposits possess another reserve to function before reaching the initial dimensions and, of course, a considerable reserve before reaching the value of the admissible technological fissure. This proves that the graphite stratum deposited on the functional surface simultaneously performs more functions: anti-wearing away protection, exclusion of glass mass adherence to its surface, it is a solid ointment and it intensifies the piece refractibility.

The practical applications, executed on steels confirming the fact that when the tool-electrode is used in any of the three suggested regimes of processing (described in details in papers [4, 6]) the white stratum of a certain hardness is formed, confirm the model of surface stratum formation when graphite is deposited. The experimental research shows that when the tool-electrode is used as cathode [5] a white stratum is formed under the graphite pellicle and its micro-hardness is higher than that of the basic material by about 1,5…2 times. When the tool-electrode functions in the regime of anode [8, 11] an intensification of the micro hardness is noticed by about 2-5 times; it is also noticed that the surface gets oxidized when the graphite pellicle is missing.

The surface hardening is probably caused by the chemical-thermal effects that are produced in the processed surface (micro-hardening and enrichment with elements that originate from the working medium: nitrogen, oxygen and hydrogen). The above mentioned confirms what was expressed in the initial hypothesis about wearing away and graphite transfer. When the combined regime of processing is used, we may notice that the maximum micro-hardness is obtained in two passings, for the emitted energy in the interstice of *W*=0,42 J and it makes $101{,}8\times10^8$ Pa which is about 10 times higher than the micro-hardness value of the material used to make the piece Fig.3(2), after which the maximum micro-hardness of the white stratum decreases. For the energy emitted in the interstice of *W*=0,58 J Fig. 3(3) the maximum value of micro-hardness is also obtained for two passings that make $47{,}88\times10^8$ Pa, being approximately 4 times higher than that of the piece material, then also following a decrease of maximum micro-hardness at a greater number of passings. For energy emitted in an interstice of about *W*=0,26J the curve of maximum micro-hardness of $22{,}6\times10^8$ Pa has an exponential form Fig. 3(1) because the maximum micro-hardness is obtained at a single passing. The thickness of the white stratum does not exceed 10…11 μm for maximum values of micro-hardness. In some cases, we can notice that the white stratum micro-hardness decreases while its thickness increases. This effect may be explained both by the processes of returning the material to the surface of the piece that is treated thermo-chemically via electric discharges in impulse and by the surface stratum self destruction under the influence of remanent voltages in it.

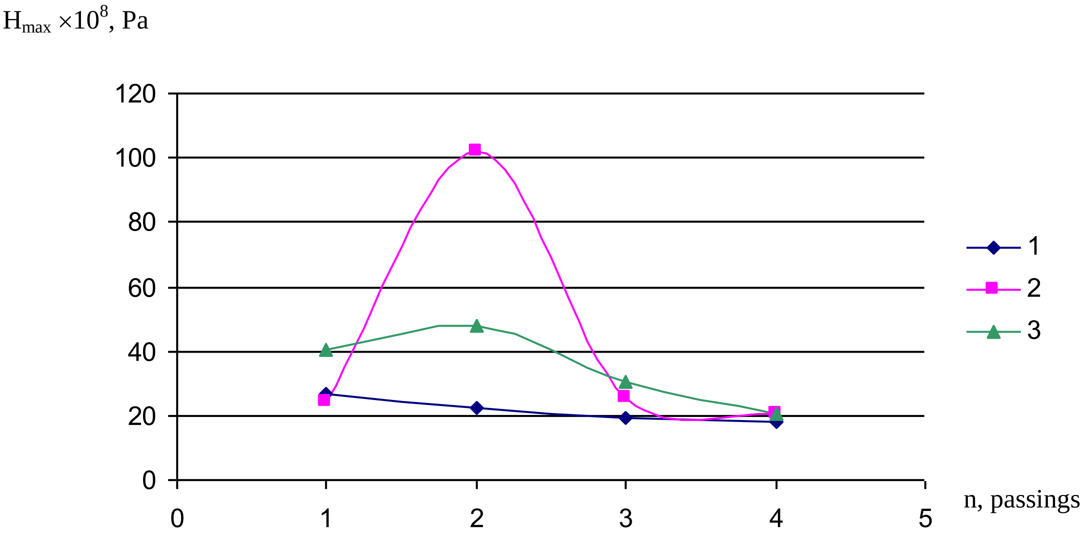

Fig. 3. Dependency of micro hardness maximum value on the number of passings for pieces made of steel 45 after the interaction of electric discharges in impulse through ”cold” electrode spots for: C=8 μF; f=8 Hz; S=0,5 mm: 1)-W=0,26 J; 2)-W=0,42 J; 3)-W=0,58 J; the combined processing regime

Thus, in the case of combined processes, depending on the chosen technological regimes of processing, the increase if micro-hardening may be about 10 times higher than that of the material used for the pattern.

Latest experimental research attests the fact that the use of the graphite tool-electrode for the surface processing via EDI improves the mechanical properties at the macroscopic level, such as the mechanic resistance at tearing. The testing of patterns processed with uni and bipolar impulses in the presence or absence of the graphite pellicle showed that the maximum tearing force for the steel St 3 covered with graphite constitutes 81000 N and for the one that is uncovered - 80500 N, that is, as a result of processing with graphite the maximum tearing force increases with 500 N, which is not found when using electrodes made of metal carbides, a case when the maximum mechanic tearing force decreases after the deposit from the respective material is formed. That is why the carbide pellicles could be convenient for use in the formation of poli-component strata.

CONCLUSIONS

From what was shown in the present paper we may conclude the following principled moments:

- Graphite erosion is strongly conditioned by the energy emitted supplementary in the interstice under the influence of oxidation reactions;
- The graphite pellicle formation flows more intensive when the tool-electrode is connected in the circuit of discharge as cathode;
- The formation of metal carbides with an increased resistance to wearing away is possible under the graphite pellicle deposited on the piece surface;
- The deposited graphite pellicle simultaneously performs more functions: anti-wearing away protection, exclusion of glass mass adherence to its surface, it is a solid ointment and it intensifies the piece refractibility;
- The micro-hardness of processed piece surface stratum increases by about 10 times in comparison with the micro-hardness of the material used for execution at depths of maximum 10-11μm;
- The maximum force at mechanic tearing (at stretching) increases with 500 N compared to those not processed via EDI.

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