EFFECTS OF ABNORMAL DISSOLVING OF OXYGEN IN METALS UNDER THE INFLUENCE OF ELECTRICAL DISCHARGES IN IMPULSE PLASMA

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Abstract: The results of experimental investigations and their analysis concerning the formation of oxide pellicles by applying electrical discharges in impulse are presented in this article. It is demonstrated that the oxidation processes take place not only on the processes piece surface, but on that of the electrode-tool as well, a fact that produce its passive state. To respect the technological regime of processing the electrode-tool surface is subjected to the process of clearing or continuous renovation.

Key words: oxide, pellicle, electrical discharge, microoxidation, amorphous state, corrosion.

1. INTRODUCTION

The formation of oxide pellicles on the active surfaces of pieces has been widely applied, its aims being the increase of their resistance to corrosion and the modification of electric conductibility properties for pieces in electronics and micro-electronics. Arc micro oxidation in electrolyte (Cernenco et al., 1991; Gavrilov, 2007, Ilii, S.M. et al, 2010), oxygenic jet plasma bombing (Kiseliov, 2005), etc are applied in the formation of oxides on the surfaces of pieces made of different materials. The method of forming oxide pellicles by applying electrical discharges in impulse is less known today. Several papers (Topala et al., 1989; Topala, 1993; Topala & Ojegov, 2008; Topala et al., 2009) attest the possibility of forming oxide and hydro-oxide pellicles in an amorphous state on metal surfaces.

The physical, chemical and mechanic properties of the piece surface layer may play a very important role in the succession of corrosion phenomena.

The authors (Nemoshkalenko et al., 1990) have demonstrated that the effective thickness of the oxide layers formed by applying electric discharges in impulse may be determined with the help of the relation:

$$h \cong \frac{KE}{AS},$$ (1)

In which $E = \int_0^\tau U(t)I(t)dt$ is the energy emitted in the interstice at a requested discharge; U, I are respectively the voltage in the interstice and the tension of the discharging current; τ is the duration of the power impulse; A is the activity area; S is the size of the interstice; K is the coefficient of proportionality that depends on the thermo-physical properties of the processed material.

Thus, an oxide pellicle of a certain thickness, stable and adherent to the surface of the metal it is made of, compact, continuous and devoid of pores or cracks may hinder to a certain extend the development of the corrosion process. The condition of pellicle protection may be expressed by the value of the expansion coefficient (Gutt & Gutt, 1992) that points to the correlation between the volume of the oxide and that of the metal:

$$\frac{V_{oxide}}{V_{metal}} > 1$$ (2)

2. THE METHODOLOGY OF EXPERIMENTAL INVESTIGATIONS

In order to realize the experimental investigations the authors have used the generator impulses of a current induced from a voltage block at a high tension of 12kV and the current being of 0,3A, a laboratory installation which provides the sample positioning, fixation and rotation in the process of processing with a rotation frequency adjustable within the limits between (0…150)rot/min. The tool electrode that was used was made of stainless steel in the form of a cylindrical bar rounded at the working edge as a hemisphere. The cathode piece is a cylindrical bar whit a 13mm diameter.

The anode tool electrode was made in the form of a cylindrical bar with ∅6mm and its active edge is rounded at the hemisphere. The piece was fixed in the tool machine while the tool electrode was placed in its tool holder, thus the piece was connected to the generator of current as a cathode while the tool electrode as an anode, their axes forming an angle of 90° (fig.1). When processing plane surfaces both the

piece and the tool electrode were made under the form of a cylinder with a 10 mm diameter; they were placed in the device of the tool machine with their active surfaces being parallel while the electrical discharges scanned the processed surface via the migration of the plasma canal on these surfaces for one cycle of processing (fig.2).

The following materials were used for the pairs of electrodes (tool-piece):
1) the alloy of aluminum D16 by GOST 4784-97 (in CIS) (its analogue is AlCuMg1 by ISO);
2) steel 45 by GOST 1050-88 (in CIS and China) (its analogues are: 1045 by AISI and AS (in USA and Australia), C45 by EN (in European Union), S45C by JIS (in Japan), OLC45 by STAS (in Romania), SM45C by KS (in South Korea));
3) the alloy of titanium VT8 by GOST 19807-91 (in CIS) (its ISO analogue is Ti-6Al-4Mo-0.5Zr-0.2Si).

The measurement of the dimensions of the processed stripes is done in a continuous regime of processing in which the solitary zones of interaction of the plasma canal with the sample surfaces overlapped one another, the overlapping coefficient being k = 0,5 while the frequency of piece rotation is established depending on the frequency of electrical discharges in impulse, taking into account the value of k.
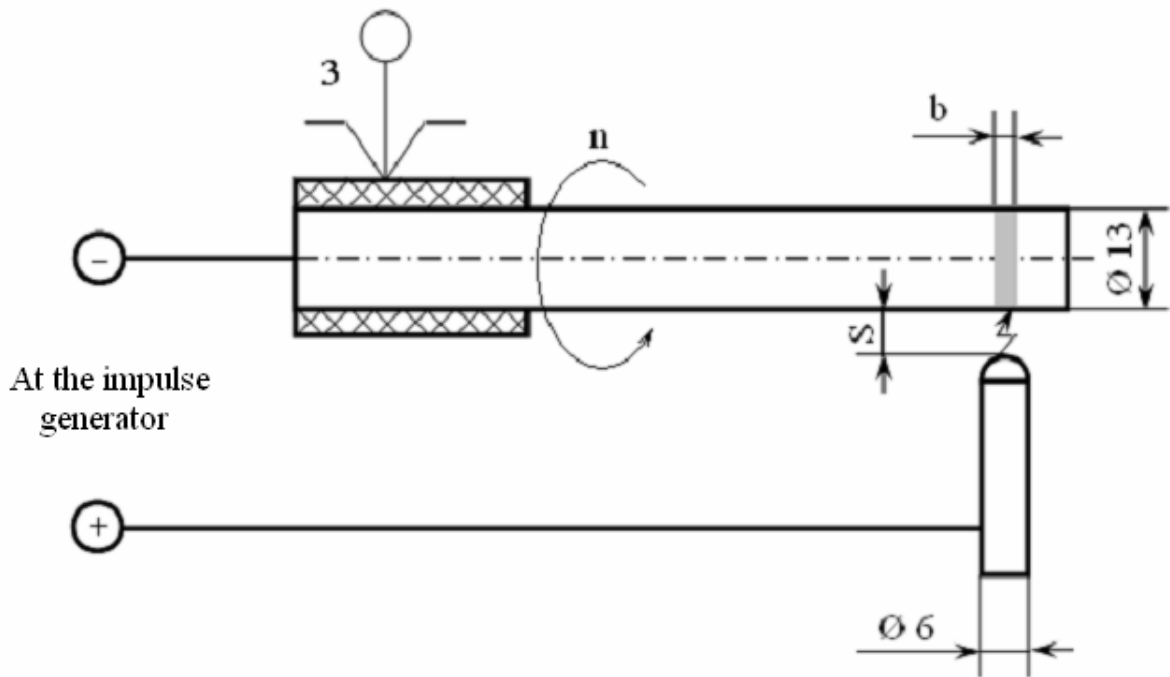

Fig. 1. The scheme of processing for experimental investigations
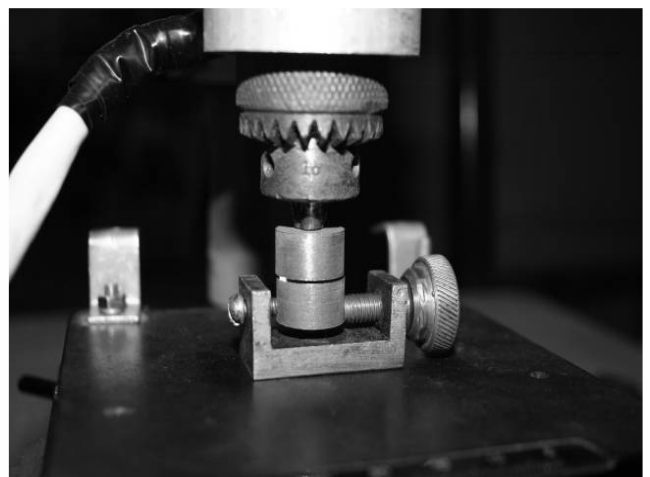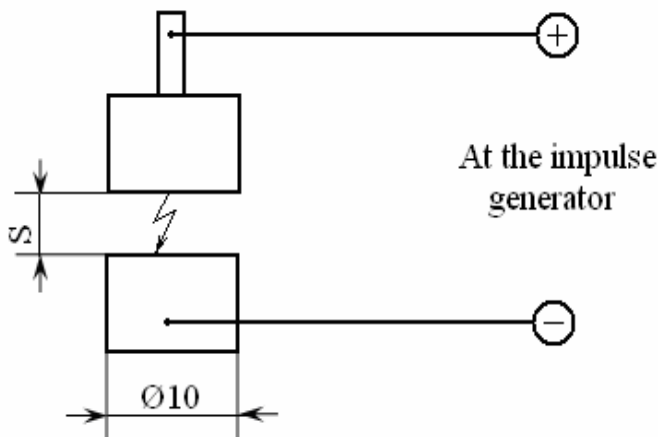

Fig. 2. Fixation of samples at processing plane surfaces

The width of the measured parts is presented for different materials and technological regimes of processing in fig. 3-5 respectively: D16, steel 45 and VT8. The measurements of the dimensions of stripes on processed surfaces are done on the microscope XJM600T.

The analysis of the morphology and chemical composition of the processed samples was done with the help of the electronic microscope of the type TESCAN.
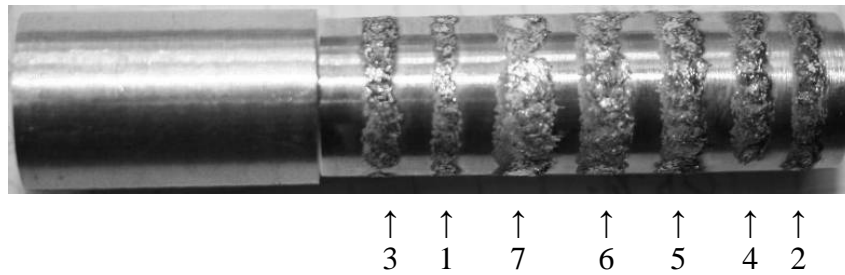
Fig. 3. General view of the sample made of the alloy of aluminum D16 processed via electrical discharges in impulse under different regimes (the condenser battery capacity C is equal to 600 µF = const, the frequency of impulses f is equal to 15 Hz = const, the frequency of piece rotation n is equal to 30 rot/min =const):

1 - U_c = 100 V, S = 1,5 mm; 2 - U_c = 120 V, S = 1,5 mm;

3 - U_c = 140 V, S = 1,5 mm; 4 - U_c = 160 V, S = 1,5 mm;

5 - U_c = 200 V, S = 2,0 mm; 6 - U_c = 240 V, S = 2,0 mm;

7 - U_c = 280 V, S = 2,0 mm

(U_c - the charging voltage of the condenser battery, S - the distance between electrodes)
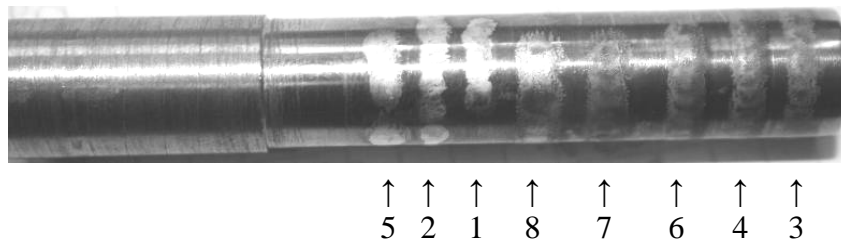

Fig. 4. The general view of the sample made of steel 45 processed via electrical discharges in impulse under different regime (the condenser battery capacity C is equal to 600 µF = const, the frequency of impulses f is equal to 15 Hz = const, the frequency of piece rotation n is equal to 30 rot/min = const):

1 - U_c = 100 V, S = 1,5 mm; 2 - U_c = 120 V, S = 1,5 mm;

3 - U_c = 140 V, S = 1,5 mm; 4 - U_c = 160 V, S = 1,5 mm;

5 - U_c = 180 V, S = 1,5 mm; 6 - U_c = 200 V, S = 2,0 mm;

7 - U_c = 240 V, S = 2,0 mm; 8 - U_c = 280 V, S = 2,0 mm

(U_c - the charging voltage of the condenser battery, S - the distance between electrodes)
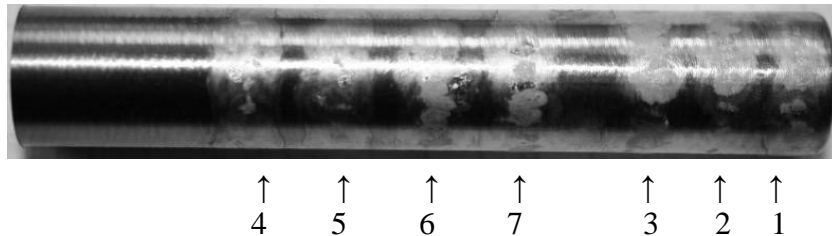

Fig. 5. The general view of the sample made of titanium VT8 processed via electrical discharges in impulse under different regime (the condenser battery capacity C is equal to 600 µF=const, the frequency of impulses f is equal to 15 Hz = const, the frequency of piece rotation n is equal to 30 rot/min = const):

1 - U_c = 100 V, S = 1,5 mm; 2 - U_c = 120 V, S = 1,5 mm;

3 - U_c = 140 V, S = 1,5 mm; 4 - U_c = 160 V, S = 1,5 mm;

5 - U_c = 200 V, S = 2,0 mm; 6 - U_c = 240 V, S = 2,0 mm;

7 - U_c = 280 V, S = 2,0 mm

(U_c - the charging voltage of the condenser battery, S - the distance between electrodes)

3. THE RESULTS OF EXPERIMENTAL INVESTIGATIONS AND THEIR ANALYSIS

The above mentioned works (Topala et al., 1989; Topala, 1993; Topala & Ojegov, 2008; Topala et al., 2009) have stated the sufficient conditions that are necessary to process the surfaces so that no liquid phase should occur on their surfaces. It is necessary to avoid the appearance of the liquid phase because of two reasons: it prevents the erosion process of the processed surface and the formation of craters which leads to an increase of the processed final surface roughness.

This is followed by the presentation of experimental investigations concerning the formation of oxide pellicles on the surfaces of pieces made of construction steels.
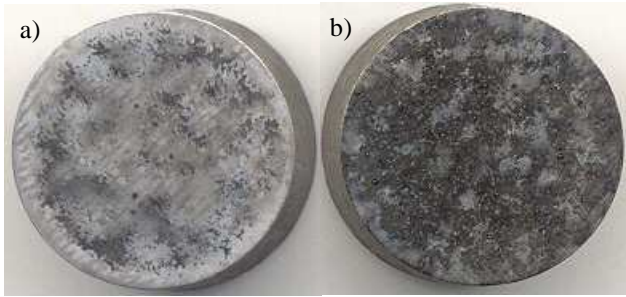
Fig. 6. General view of the surfaces of steel 45 samples after processing with electrical discharges in impulse (the parameters of processing regime: the charging voltage of the condenser battery U_c = 140 V; the capacity C = 600 μF; the distance between electrodes S = 1.5 mm; the impulse frequency f = 15 Hz; the duration of processing τ = 2 min):
a) cathode piece;
b) anode tool

During the experiment the tool and the piece were made of the same material to prevent the transfer of the tool material to that of the piece.

The investigation of the piece surfaces (fig. 6, a) and of the electrode (fig. 6, b) allowed us to state that the latter is also subjected to oxidation.

The layer formed on the tool-electrode is discontinuous with traces of melting and electric erosion. The tool-electrode loses its properties of electric conductibility, modifies its initial character of geometry and requires renovation or clearing the active surface in the process of functioning. Because of these reasons it is necessary to make it of a material resistant both to electro erosion and to oxidation.

The study of surfaces processed under a regime of oxidation by applying electrical discharges in impulse and their chemical analysis allowed us to state that there is a considerable percentage of C, N, O, Fe in them (fig. 7). Out of these elements Fe and C are found in the processed material of the piece, while O and N are implanted in the piece material from the working medium (air).

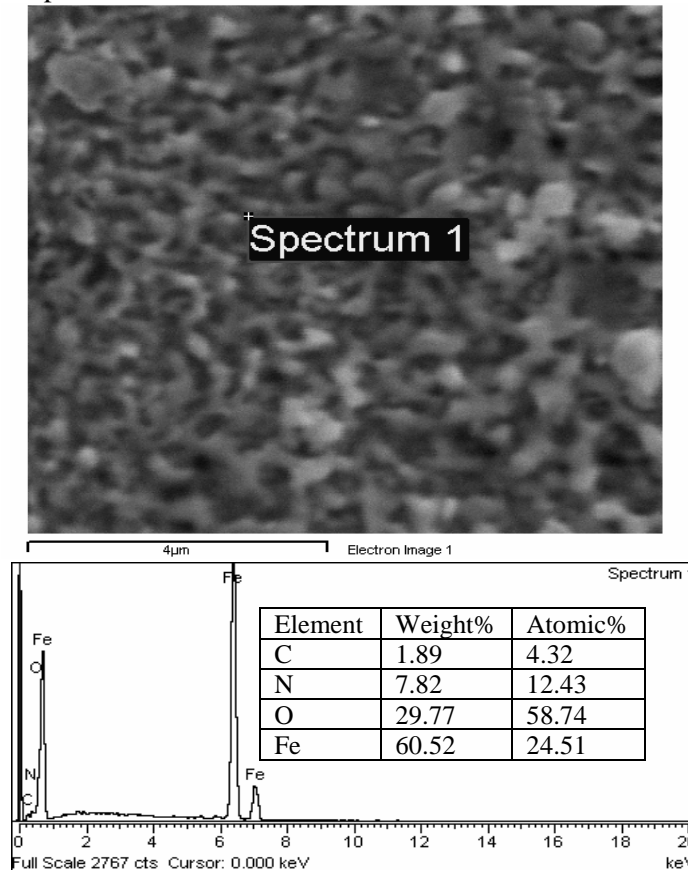| Element	Weight%	Atomic%
C	1.89	4.32
N	7.82	12.43
O	29.77	58.74
Fe	60.52	24.51

Fig. 7. The spectrogram of the cathode piece surface made of steel 45 processed by electrical discharges in impulse (the parameters of processing regime: the charging voltage of the condenser battery U_c=140 V; the capacity C=600μF; the distance between electrodes S=1.5 mm; the impulse frequency f =15 Hz; the duration of processing τ =2 min)

The spectrograms presented in fig. 7 attest an abnormal dissolving of oxygen on the processed surface of the piece under conditions of electrical discharges in impulse. This effect may be explained based on the diffusion phenomena that occur under these conditions and on the chemical reactions of short duration that occur at the interaction of the plasma canal with the processed metal surface.

We may also assert that when surfaces are processed under an oxidation regime by applying electrical discharges in impulse there is no significant deterioration in the processed surface; there we find under micrometric irregularities (fig. 7).

Unfortunately these analyses did not allow us to state

the phase contents. Papers (Topala et al., 1989; Topala, 1993; Topala et al., 2009) deal with the formation of steel oxides and hydro-oxides in an amorphous state that is later confirmed by experiments in corrosion.

In order to check the resistance of samples (processed with oxide pellicles formed on the active surface by applying electrical discharges in impulse) to chemical corrosion an electrolyte was made of distilled water and salt NaCl of 1% concentration at room temperature. The oxide pellicles were made through electrical discharges in impulse with the following parameters: U_c=140V, C= 600μF, S=1,5mm, f=15Hz. The samples were fixed in a special device so that only one part in the form of a circle from the processed surface is subjected to dissolving. This one is included in the circuit of anodic dissolving as an anode. The trials were done under a regime when the experimental installation functioned in continuous power and the applied power was modified step by step by 0.1 V. These trials helped to build the volt-ampere characterization of samples both with and without oxidized surfaces (fig. 8).
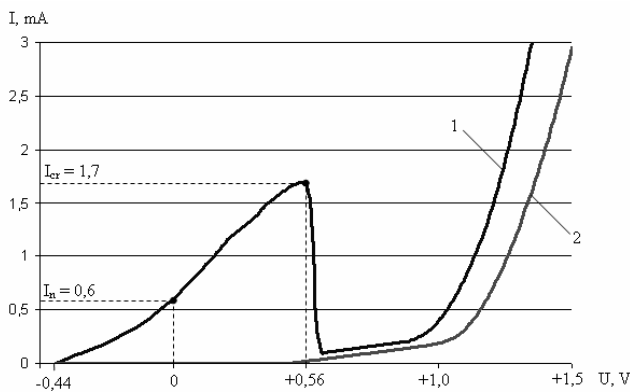

Fig. 8. Volt-amperic characterization of the corrosion process in samples made of steel 45 in electrolyte (watery solution of 1% NaCl):
1 – raw surface;
2 – processed surface

If we compare the results presented in fig. 8, we may notice that the anodic dissolving potential of the processed sample has increased by 6 times compared to the one of unprocessed sample.

When increasing the voltage applied between electrodes the picture of anodic dissolving of pieces subjected to trials is modified. For example, when voltage U=2V, the current in the circuit is 300mA for the unprocessed piece and 161mA for the sample with oxide pellicles.

The volt-ampere characterization in fig. 9 shows that the volt-ampere features of the unprocessed sample and of the one that was processed within the voltage interval 1.5-2.5 V are practically parallel. This confirms the presence of an isolating pellicle on the surface of the processed sample that increases its active resistance.
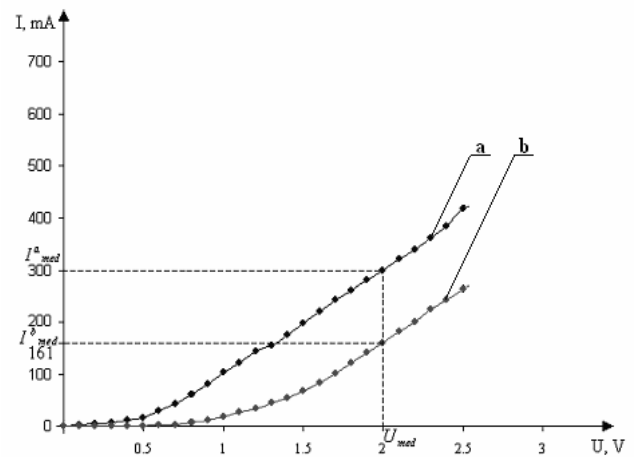

Fig. 9. Volt-ampere characterization of the electro-chemical corrosion process:
a – unprocessed surface; b – processed surface

If we take into account the previously obtained results (Topala & Ojegov, 2008; Topala et al., 2009) concerning the measuring of the surface active resistance, we could conclude that the oxide layers formed on the surfaces of samples are not totally continuous; because of this their anodic dissolving process is more intensive than it was expected.

In order to determine the corrosion speed, 5 pairs of samples unprocessed and processed under the same conditions of anodic dissolving were subjected to trial. The measuring helped to complete tables 1 and 2. The corrosion speed is determined by weighing the samples before and after trial using the analytic scales VL-200 with a precision of 10^{-5}g.

The index of corrosion speed is determined (Alai et al., 1979) through the relation (3):

$$K = \frac{\Delta m}{A \cdot t} \qquad (3)$$

where
K is the corrosion speed (mass indicator), g/m²·h;
A is the area of the working surface of the sample, m²;
t is the trial duration (working time), h;
Δm is the loss (or addition) of mass, g;

$$\Delta m = m_i - m_f \qquad (4)$$

where m_i is the initial mass of the sample, g;
m_f is the final mass of the sample, g.
If we analyze the obtained results, we may state that for processed samples the corrosion speed at applied voltage of 2 V is practically always twice as small as the one of the samples that is not processed by oxidation.

When we take into account the fact the potential of natural corrosion is dozens and hundreds of times smaller than in the case of realized trials then the efficiency of applying oxide pellicles will increase considerably.

Thus, if we go back to fig. 8 we may state that for voltage applied within the limits 0 and 0.4 V there is no current in the circuit formed by the processed piece, so the corrosion speed will be zero while for an unprocessed piece under the same conditions there is considerable current and the corrosion speed is significant.

Finally we may admit that the application of oxide pellicles on metal surfaces with electric discharges in impulse is beneficial for the increase of their active resistance and of the corrosion resistance.

The conditions under which the corrosion speed was determined are as follows: anode – sample; voltage between electrodes U=2V; distance between electrodes d=10mm; electrolyte (watery solution 1% NaCl); processing time at each measuring level t = 0.5 h; sample material – steel 45; area of working surface (of contact with electrolyte) S = 50.24 mm^2.

The width of the oxide pellicle strip was measured with the help of the computer METAM with the measurement scale: the measurement accuracy ±0,025 mm, the measured values (20 for each regime) were verified according to the criterion of Student at the trust interval appurtenance, and then their average value was measured. The relative digression of results did not go beyond 2%. The results of experimental investigations are presented in tables 3 and 4.

Table 1. Speed of anodic dissolving of samples with unprocessed surfaces

No	Initial mass of the sample m_i, g	Final mass of the sample m_f, g	Δm, g	Corrosion speed K, g/m^2·h
1	12,8441	12,8237	-0,0204	812,10
2	13,1458	13,1254	-0,0204	812,10
3	13,3225	13,3025	-0,0200	796,17
4	14,0610	14,0417	-0,0193	768,31
5	13,0248	13,0031	-0,0217	863,85

Table 2. Speed of anodic dissolving of samples with oxidized surfaces

No	Initial mass of the sample m_i, g	Final mass of the sample m_f, g	Δm, g	Corrosion speed K, g/m^2·h
1	12,8569	12,8441	- 0,0128	509,55
2	13,1605	13,1458	-0,0147	585,19
3	13,3338	13,3225	-0,0113	449,84
4	14,0717	14,0610	-0,0107	425,95
5	13,0366	13,0248	-0,0118	469,74

Table 3. The dependence of the strip width on the energy emitted in the interstice

The energy emitted in the interstice W_S, J	The width of the oxide strip b, mm		
	The sample material		
	D16	Steel 45	VT8
2,29	2,15	2,45	4,75
2,72	2,5	2,85	5,2
3,15	2,85	3,2	5,55
3,58	3,15	3,6	6,1
4,01	3,4	3,95	6,45
4,52	3,6	4,15	6,85
5,27	3,9	4,4	7,2
6,58	4,45	4,9	7,5

Table 4. Experimental data
The condenser battery capacity – C = 600 μF
Impulse frequency – f = 15 Hz
Piece rotation frequency – n = 30 rot/min

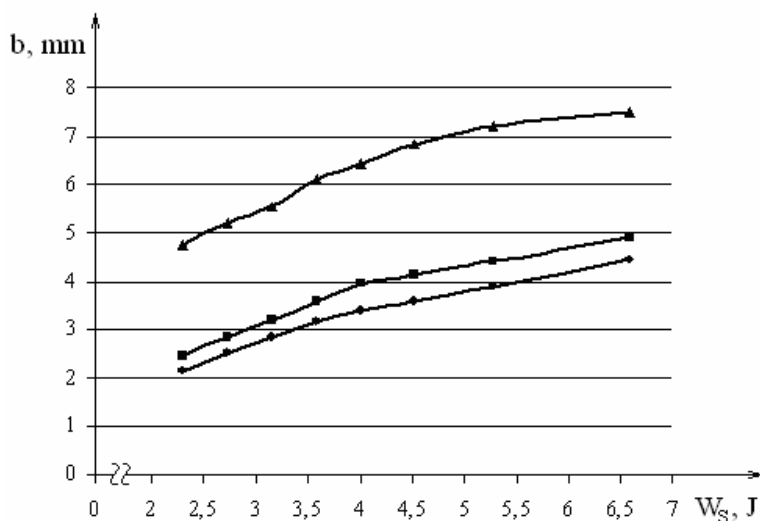| The charging voltage of the condenser battery U_c, V	The interstice size of the interstice S, mm	The piece/electrode material	The average width of the oxide strip b, mm
100	1,5	D16	2,15
		Steel 45	2,45
		VT8	4,75
120	1,5	D16	2,50
		Steel 45	2,85
		VT8	5,20
140	1,5	D16	2,85
		Steel 45	3,20
		VT8	5,55
160	1,5	D16	3,15
		Steel 45	3,60
		VT8	6,10
180	1,5	D16	3,40
		Steel 45	3,95
		VT8	6,45
200	2	D16	3,60
		Steel 45	4,15
		VT8	6,85
240	2	D16	3,90
		Steel 45	4,40
		VT8	7,20
280	2	D16	4,45
		Steel 45	4,90
		VT8	7,50

Fig. 10. The dependence of the oxidation strip width on the energy emitted in the interstice for the samples executed in:
● – D16; ■ – steel 45; ▲ – VT8

We can see in fig. 10 that the dependence of the width of the strip processed on the cathode piece surface in terms of the energy emitted in the interstice presents an exponent for all processed materials. The process is more intensive on the sample surfaces made of aluminum, titanium and, finally, steel. These effects may be explained on the basis of properties of electron emission by these materials and on the avidity of their constituent elements in relation to oxygen.

Table 5. The surface resistance of oxide pellicles for samples made of steel 45

Sample	Surface resistance, $\times 10^6$ Ω				
	Experimental data				Average value
Cathode	0,88	0,72	1,46	0,71	
	0,97	1,52	0,68	0,72	
	0,73	1,09	0,76	0,83	0,98
	1,33	1,10	1,04	0,73	
	1,07	0,88	1,21	0,78	
Anode	0,81	0,26	0,46	0,31	
	0,11	0,14	0,56	0,34	
	0,29	0,11	0,62	0,38	0,33
	0,87	0,38	0,11	0,15	
	0,12	0,13	0,27	0,17	

Using the analysis of results presented in table 5, we can state that in all the cases we have a substantial increase of the surface resistance of electrodes that participated in the process of electrical discharges in impulse, but the active surface resistance of the anode electrode is about three times lower than that of the cathode. The latter observation may be explained by the fact that a greater quantity of energy is emitted on the anode surface under the same conditions and the vaporization processes are more intense; due to this the intensity of the process of oxide pellicle formation is slower. The results of experimental investigations referring to the formation of oxide pellicles can be applied in microelectronics in the production of resistors, in the chemical industry to form passive surfaces on pieces functioning in corrosive media.

4. CONCLUSIONS

Judging by the above said we may conclude that:
− oxygen abnormal dissolving is attested on the metal surface of the piece in conditions of electrical discharges in impulse;
− the active resistance of the metal piece surface increases by about 10^6 times;
− oxide pellicles formed by means of electrical discharges in impulse allow a considerable increase of the corrosion potential and decrease of the corrosion speed;
− to make the tool-electrode function well it is necessary to make it of rustproof material.

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