



INVESTIGATIONS ON ANTI-CORROSION PROPERTIES OF THE SURFACE LAYERS FORMED BY APPLYING EDI

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Abstract: The results of experimental research on corrosion behavior of the films formed by applying electrical discharges in impulse (EDI) are presented in this paper. It was experimentally established that oxide pellicles formed on metal surfaces increase their resistance to corrosion by 2-10 times beside the unprocessed surface. Graphite pellicle deposition with the use of pyrolytic graphite tool - electrodes increases superficial microhardness, their functional durability and processing productivity of the active piece surfaces.

Key words: oxide films, corrosion resistance, graphite, tool-electrode, electrical discharges in impulse.

1. INTRODUCTION

Corrosion control is one of the oldest technical problems. It appeared once the man began to acquire metals and to use them of everyday life. Over the centuries the acquisition and processing of metals has expanded greatly. Although recently humanity started to use in technique polymer materials, however, metals and their alloys remain primordial building materials in machine, installation, equipment and construction building. Oxidation of metal surfaces has found applications in various fields of technology for corrosion protection [1] and to change the electrical properties of surfaces in electrical and radio engineering [2, 3]. For this purpose, the method of electrolytic deposition of thermodynamically stable pellicles on some metal surfaces is applied, which can be obtained only at the so-called fed metals, which include aluminum, titanium, tantalum, niobium, etc. The spark-anodic electrolysis, also known as micro-plasma or micro-arc oxidation, has been developed [4, 5]. Depositions formed by this method are a large range of structural, technological and operational requirements: micro-hardness, wear resistance, low coefficient of friction, and ability of electro-isolation, erosion resistance, and high adhesive properties. An important advantage of such depositions is that their properties are of complex operational

character. Low-alkaline and acidic electrolytes and metal salt solutions are used to realize this process. Deposition properties depend on the chemical composition of the alloy, concentration, composition and temperature of the electrolyte, electrical regimes of the process and its duration, etc. Coverings mainly consist of solid crystalline phases in the matrix of softer oxide phase of metals that form part of the alloy and the electrolyte. This structure provides a high micro-hardness, wear-proof and corrosion resistance, heat protection and electro-isolation properties of the covering. The application of this technology implies the use of special devices for electrolytic processes and the adoption of measures required to ensure safe working conditions for staff.

Recently, a number of works [6, 7] has been published where the results on the nano-oxidation by applying electrical discharges in impulse (EDI) of metal surfaces under ordinary conditions are presented.

Parallel to this lately, as it is demonstrated in papers [8-13], producing experimental research in order to obtain graphite films on the surface of parts made of metallic materials by EDI in sub-excitation regime in order to increase the hardness of the surface layer, functional durability, to increase the anti-adhesion properties, to reduce the stick phenomenon, etc. Of course, the interest also presents how the aggressive media influences graphite films deposited on metal surfaces by EDI.

2. METHODOLOGY OF EXPERIMENTAL INVESTIGATIONS

Both for films graphite formation and to achieve superficial oxidation by applying EDI in sub-excitation regime their maintenance with surfaces has been ensured under the action of "cold" electrode spots. The condition of the energy balance, in this case, takes the form [8, 14]:

$$Q = \frac{4W_s}{\pi d_c^2 S} < Q_{melt} \quad (1)$$

where Q is the heat emitted on the surface of electrodes per volume unit, J/m^3 ; $W_s = \int_0^\tau u(t)i(t)dt$

is the energy emitted in the interstice, J ; $u(t)$ is the voltage on the interstice at the discharge, V ; $i(t)$ is the instantaneous value of the current in the interstice, A ; τ is the duration of the discharge impulse, s ; d_c is the diameter of the plasma canal, m ; S is the distance between the electrodes (the interstice), m ; $Q_{melt} = q_{melt} \cdot \rho_{melt}$ is the volumetric melting heat of the processed piece, J/m^3 ; q_{melt} is the specific melting heat of the processed piece, J/kg ; ρ_{melt} is the material density at the temperature of melting, kg/m^3 . So, for the ESO of construction steel, the energy emitted in the interstice of (1-2)mm will not exceed (6-10)J.

The impulse current generator [8, 14] with voltage block for interstice pre-ionization was used as a source of energy. The discharge energy emitted in the interstice constitutes (1-6)J. And, thus, establishing the generator energy regime, the superficial piece oxidation for indicated materials without melting of the processed surface can be produced.

The thickness of the oxide pellicle subjected to the condition of the energy balance and according to Palatnik's criterion, is directly proportional, respectively, to the quantity of heat and the energy emitted on the electrode surfaces, [14]:

$$\begin{aligned} \delta &\sim Q \\ \delta &\sim W_s \end{aligned} \quad (2)$$

The power of electrical discharge:

$$P = \frac{dW_s}{dt} = \frac{W_s}{\tau} \quad (3)$$

where τ is duration of electrical discharge.

Thus, the thickness of the oxide pellicle is directly proportional to the power of electrical discharge emitted in the interstice.

The direct determination of operating properties that affect the functionality of pieces has required intensive investigations. Therefore, this task has been allocated for the performance that best suits the peculiarity of the work and does not require the use of lengthy and expensive techniques and equipment.

For evaluating and determining the operating properties of oxide coverings that characterize corrosion resistance, active surface resistance and other properties, the results of measuring the following characteristics of the coverings are presented: surface morphology, chemical and phase

composition of coverings, the total pellicle thickness.

Technique XPS (X-ray Photoelectron Spectroscopy) was used for qualitative and quantitative analysis of the processed surface.

To determine the corrosion of graphite and oxide films the electrochemical research method was chosen. We used this method because it allows the acceleration of corrosion, which is not something other than anodic dissolution and thus saving the time to study the evidence.

The electrochemical installation was composed of an electrolysis cell which contains 1% NaCl solution where we placed two electrodes: steel cathode and steel anode with unprocessed surface or covered with graphite or oxide film on its active surface, which are connected with a voltmeter and an ammeter to continuous power source adjustable in the range of 0-40V. Also a number of samples were studied in 30% H₂SO₄ solution.

The speed of corrosion was determined by the reaction, [15]:

$$K_m = \frac{\Delta m}{A \tau} \quad (4)$$

where Δm is the difference of metal mass in time τ after removing the corrosion products, A is the surface supposed to corrosion.

3. RESULTS AND DISCUSSIONS

In the case of graphite film formation it was established that they effectively form whereby the workpiece is connected contour discharge current pulse generator as anode, [8]. It was found that the film formed can achieve micrometer thickness at full continuity and a porosity of mode synthesis conditional on the machined surface deposition. Experiments with graphite film formation on the surface of the glass mold plunger made of iron have proved being processed surface morphology analysis confirmed that the formations on the surface of micrometer size not exceeding; apart from the initial components of the processed material there has been a considerable amount of carbon (about 80%) in atomic content, [9]. As the processing takes place in the air, there is an accumulation of oxygen of about 17-19% and respectively (3-4)% of nitrogen on the piece surface. These components allow the hardening of the superficial layer, by about (2-8) times [13] in comparison with the basic material, through its diffusion inside it and the thermal treatment due to rapid cycling warming and cooling of the superficial layer.

Experimental research shows that the cathode in the case of the tool-electrode in addition to the graphite film is formed in the white layer which is higher than

the microhardness of the core material of about (1.5-2) times, the use of the tool under the anode electrode showed an increase in hardness of about (2-5) times the surface oxidation is observed, but without forming a graphite film, [13].

To determine the potential of dissolution is necessary to build volt-ampere characteristic of sample steel anode 45 and anode sample - 45 steel coated with graphite cathode material for both cases - 45 steel. First samples are polished and washed with distilled water and then are introduced into the electrolyte solution at a distance of 10 mm, apply a DC voltage of 0.4 V with a step of 3 min holding time (figure 1).

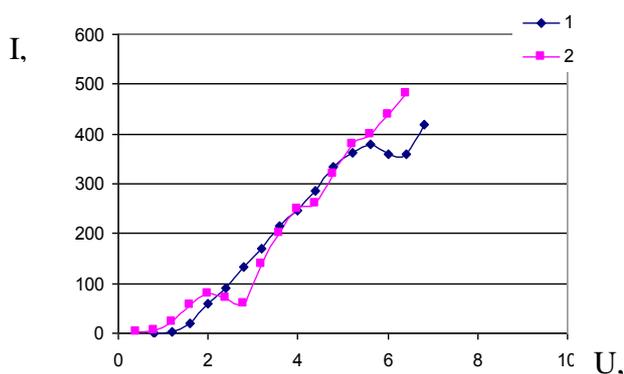


Fig. 1. Volt-ampere characteristic of the electrochemical process: 1 – steel C45 coated with graphite; 2 – the unprocessed steel C45 surface

When placed in the electrolyte in the absence of evidence from the external circuit current is determined stationary potential. For the case when both electrodes are made from the same type of steel it is almost zero, and for the case when the anode is covered with a graphite film forms the stationary potential of 0.1 V. The application of an external potential may obtain the curves in Fig. 1 (curve 2), this sample can be seen that the steel is increased with the increase in the potential of the current intensity to the value of 2V, followed by a decrease attesting portion where the current up to a voltage of 2.9V. This effect may be due to the action of chemical reactions that lead to oxidation and passivation hydro-oxidation sample surface without graphite film. Once this value, as can be seen from the graph that with increasing voltage the corrosion current decreases, and the corrosion process is conducted at low speed, that is, the passive film appeared allows active dissolution of the anode. Passive state is maintained until the potential of 2.8 V then current intensity increases considerably accelerator anodic dissolution process.

An analogue behavior is observed in the research sample steel coated with a thin layer of graphite,

except that a passivation zone the analog voltage is obtained at about 5.6V. In this range of 5.6 to 6.2 V is observed film deposited destruction followed again corrosion current magnification. The behavior of the graphite film of the sample (Fig.1, curve 1) demonstrates that the presence of active carbon on the surface of the sample greatly increases the surface passivation potential (approximately 3.2V). Possibly, the presence of graphite surface area de-oxidation reactions involving the interaction and film porosity graphite provides electrical contact between electrolyte and sample surface environment.

While the nature of corrosion products change, probably formed oxides with lower oxygen content (Fe_3O_4) ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$), which are more stable. At the same time, it is acceptable that corrosion products formed on the metal surface film that insulates the metal from contact with corrosive agent, so the curves showing the variation of corrosion rate in function of time shows a flattening trend. These films are not sticky and compact enough so that the corrosion process diminishes over time, but not annihilate. It should be noted that determinations were performed in static. In dynamic mode, the film consists of corrosion products can probably come off the metallic surface and corrosion processes will take place in this case, with higher speeds.

For the case there is carbon steel coated with lower speeds at the inception phase and then start to rise due to the gradual removal of carbon from the surface and then the destruction of that film.

SEM and EDX analysis results from samples processed according to the technology of formation of oxide films in the optimum dissolution is observed abnormal processing (supersaturated) of oxygen in the metals investigated, [14]. It is shown that the dissolution of oxygen in sample processing steel construction reaches almost 60% at.

The total spectrum of the surface layer of the surface (XPS analysis), [14] were recorded spectrum peaks oxygen (O 1s), carbon (C 1s), iron (Fe 2p, 3p Fe) and silicon (Si 2p, Si 2s), last three being the component of the alloy investigated (Steel 45). XPS signal analysis shows the presence of oxygen O 1s in three types of chemical compounds: a) component O^{2-} ; b) OH^- component; c) the structures of the type C-O and O-C=O. Chemical analysis showed the concentration of each of the components may be expressed as: C (a): C (b) C (c) = 0.89: 1.00: 0.50, [14], which means that the film is formed in the mostly of metal oxides and hydroxides core sample. Detailed research on surface electrical resistance and resistance to corrosion of pellicles formed on steel C45 surfaces with electrical discharges in impulse [14] have shown that, due to the formation of oxides and hydroxides in the amorphous state, the

surface electrical resistance of the samples increased from hundredths of Ω/mm^2 until $\sim 1 \text{ M}\Omega/\text{mm}^2$, the potential of corrosion increased from -0.44 to $+0.4 \text{ V}$, the resistance to corrosion has increased by about 2 times in 1% NaCl solution, and by about 10 times in 30% H_2SO_4 solution (Table 1).

Due to simplicity of technology and lower costs of electricity, the formation of oxides and hydroxides pellicles using electrical discharges in impulse can be successfully applied in manufacturing of resistors for microelectronics and radio-techniques and in corrosion protection of drinking water pipes.

Table 1. Variation of the corrosion speed, $\text{g}/\text{m}^2\text{h}$ during immersion time (τ) of the samples in steel C45 with the surface and the raw oxide film according to the type of electrolyte

Electrolyte		τ , min							
		30	60	90	120	150	180	210	240
1% NaCl	Unprocessed surface	864	812	812	796	768	748	721	714
	Surface with oxide films	470	450	421	410	410	402	385	378
30% H_2SO_4	Unprocessed surface	1426	1331	1262	1180	1124	1065	1038	1010
	Surface with oxide films	142	128	122	120	113	104	102	100

Experimental investigations demonstrate that micro-oxidation processes occur simultaneously on the surface of the tool-electrode too, but they proceeded with an intensity of about three times lower than for the workpiece. Electrode-tool surface oxidation and erosion cause breach of the workpiece surface processing technology that is why the special conditions required for their elaboration. During the machining of the rotary surfaces and, in a particular case, cylindrical and conical surfaces (exterior or interior) condition of continuous work of the apparatus is to maintain constant the size of the discharge interstice. Therefore, it is proposed to manufacture electrode-tools with conjugated to the workpiece surface configuration and their coaxial positioning in relation to the processing surface. At the same time, it is required that their active part must be manufactured of a less active material to oxidation.

4. CONCLUSIONS

Finally, comparing each other both methods of forming thin films on the surfaces of the parts and the deposition of graphite oxidation of the active surfaces we can conclude that:

- Both processing methods lead to the formation on the surfaces of the parts of the new compounds and structures;
- Deposits of graphite oxide films condition considerably decrease the corrosion rate in aggressive media;
- Protects the surface oxide film by direct passivation, then a graphite film protects him by taking upon himself oxidation processes acting as reducer.

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