

FORMATION OF OXIDE THIN PELLICLES BY MEANS OF ELECTRIC DISCHARGES IN PULSE

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Abstract: The article contains the results of theoretical and experimental investigations concerning the formation of oxide thin layers on the surface of metal pieces by means of electric discharges in pulse. The possibility of forming oxide pellicles on metal surfaces is determined by the chemical contents of the passive layer and the type of its conductivity. The pellicles obtained by this method increase the surface active resistance up to 1,2 MΩ and decrease the surface roughness. The productivity of forming oxide pellicles by means of this method depends on the energetic regime of processing and can reach from 1 to 20 cm²/min.

1. INTRODUCTION

Anticorrosive protection of the metal used to produce pieces, items, sub aggregates and aggregates of machines is an important problem in machine building. It presents the totality of measures taken to protect technical materials from the aggressive action of corrosive media. The methods and techniques of anticorrosive protection are various and numerous and they can be grouped into the following categories:

- methods of preventing corrosion;
- use of metals and alloys resistant to corrosion;
- methods of influencing the corrosive medium;
- methods of covering metal surfaces with protective layers;
- passivation of surfaces by depositing oxide or hydroxide pellicles, etc.

The essence of preventing corrosion consists in:

- correct choice of materials used in building devices, industrial equipment from the point of view of resistance to corrosion;
- avoiding the contact of two metals one of which is more electronegative than the other, e.g. aluminium and copper alloys or alloyed steel, bronze and steel, etc.;
- avoiding the contact of cold-hardened metals with annealed or cast metals because due to the difference of electrochemical potential between them the former corrode in the presence of an electrolyte;
- a more careful processing of the metal surface because hollows and scratches favour and accelerate corrosion.

The group of metals and alloys resistant to corrosion contain noble metals and their alloys, but their use becomes difficult because of the high cost. Self-protective metals and alloys will be used instead. These are metals and alloys which after an initial corrosion are covered with an isolating pellicle due to the passivation phenomenon (e.g. the passivation of Ag in HCl by forming the AgCl pellicle of Fe in HNO₃ concentrated through the formation of the Fe(NO₃)₃ pellicle, etc.)

In most cases metals are alloyed with an adequate component. Sometimes the relatively low concentration of the alloyed component considerably reduces the corrosion speed (e.g. the introduction of such elements as Cu of 0,2 %... 0,3 %, Cr or Ni in steels, etc.)

There are many cases when it is possible to influence the corrosive medium to lower the speed of corrosion. There exist many possibilities.

The following can be mentioned [1]:

- modification of pH which means bringing it to a convenient value for the metal that is to be protected. This means elimination from the medium of corrosion using physical, chemical and mechanic methods (e.g. neutralization of waste water with chemical substances);

- removal of gases (O_2 and CO_2) which increase the speed of corrosion in corrosive media, particularly that the water;

- use of inhibitory elements or passivators (organic or inorganic substances) which being introduced in small quantities in the corrosive medium lower or completely annihilate its corrosive capacity;

- cathode protection (electro defence) means the use of galvanic methods of metal protection with the help of auxiliary metal anodes which take over the corrosive capacity of the medium thus protecting the material used for the piece.

The protection realized by applying anticorrosive [1] layers means to cover the metal with a thin layer or self-protective material. The self-protective layer should meet the following requirements: it should be compact and adherent, it should be elastic and plastic enough, and its thickness should be uniform and as small as possible. The protective layer may be metallic or non-metallic. Metallic deposits may be realized through different methods: galvanic, thermal, through plating, laser radiation, bombarding with ions, alloying by means of electric discharges in pulse, etc.

The formed surface layers, except those obtained through plating, usually present a certain porosity which determines the appearance of local portions of corrosion with all the consequences. Non-metallic protective layers may be organic or inorganic, realised with the help of varnish, paints, enamels or plastic thin sheets.

The formation of inorganic thin pellicles (of oxides or hydroxides) on the piece surface is a progressive method of forming superficial layers possessing anticorrosive protection. The oxide being much more passive than the metal proper in the interaction with the surrounding reality lowers the corrosive potential of the whole piece. The thickness, uniformity and concentration of the oxide layer formed on the surfaces of pieces depend on many factors of thermal, chemical and electric nature. The growth of energy of applied processing on the piece surface makes the speed of reaction $Me + O_2 \rightarrow MeO$ raise. It also increases the strong adhesion of the formed oxide and the piece material due to the phenomena of diffusion that take place in the oxide. The key problem that should be solved is the one that deals with the formation of structurally stable deposits with a high mechanic and electric resistance, having a uniform continuity and thickness on the whole surface.

The choice of the method to be used for the production of the protective layer depends on:

- the conditions and working surroundings of the piece;
- the form and dimensions of the protective item;
- the quality of the supportive material or of the protected item;
- the functional technological parameters of the device;
- the way the item to be protected is placed in the device;
- the technologies of application and executive possibilities for anticorrosive protection;

Below we shall present and interpret some results of experimental investigations concerning the formation of oxide layers on the surfaces of pieces made of building steels (steel – 3 and steel - 45) by means of electric discharges in pulse under a regime of sub excitement. This technique of surface processing is little investigated at present though it can ensure technical – technological and economic conveniences due to which it is of scientific interest.

2. METHODOLOGY OF EXPERIMENTAL INVESTIGATIONS

Special equipment was used for the investigation (fig.1). The equipment consists of the following main parts: the block of power pulses which is a generator of RC-type pulses (1), the block of inducing (2) and the block of command [2].

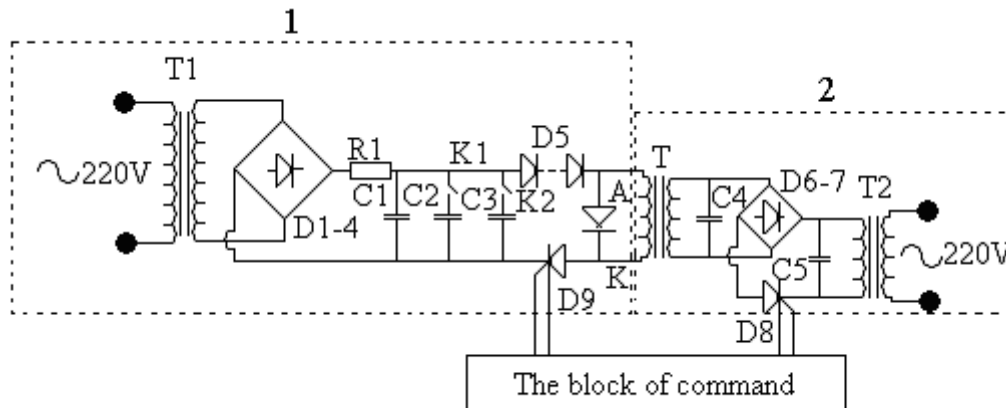


Fig.1. The main electric scheme of the equipment.

The power pulse block is aimed at forming in the interstice of current pulses which realise the processing of the piece surface; the block of inducing causes the creation in the interstice working in an air medium of a conductivity canal that will serve to exhale later the energy accumulated on the condenser battery of the first block, the command block will vary the frequency of electric discharges in pulse and will synchronise in time the inducing pulses and power pulses by opening simultaneously D_8 and D_9 thyristors.

The samples that underwent the processing were fixed in a device realised with the help of an optic microscope, which allow to regulate the size of the interstice and to keep it constant throughout the processing.

The processing of sample surfaces is done under conditions of forming in the canal contact zone of electric discharges in pulse with electrode surfaces of "cold" electrode spots. After the optimum energetic regime was determined (the charging voltage of condensers of the current pulse generator and their capacity were chosen for a certain interstice) the pulse generator was started. The number of passings through which the sample surface processing is done is determined by the continuity of the formed layer. In all the cases when this stopped for a certain inducing voltage of electric discharges in pulse the processing was finished. This means that the continuous passive oxide layer was formed in the processed surface.

3. EXPERIMENTAL RESULTS AND THEIR ANALYSIS

When dealing with superficial processing by means of electric discharges in pulse under a regime of sub excitement it was important to demonstrate if this type of processing is possible in the case of confirmative results to establish certain parameters of entrance and exit of the process. Attempts have been made to determine the dependence of the thickness of formed layers on the processing regime, voltage (or energy) in the interstice). Certain properties of the formed layers were stated: sample hardness before and after processing, the electric resistance of the sample superficial layer, structure and surface analysis.

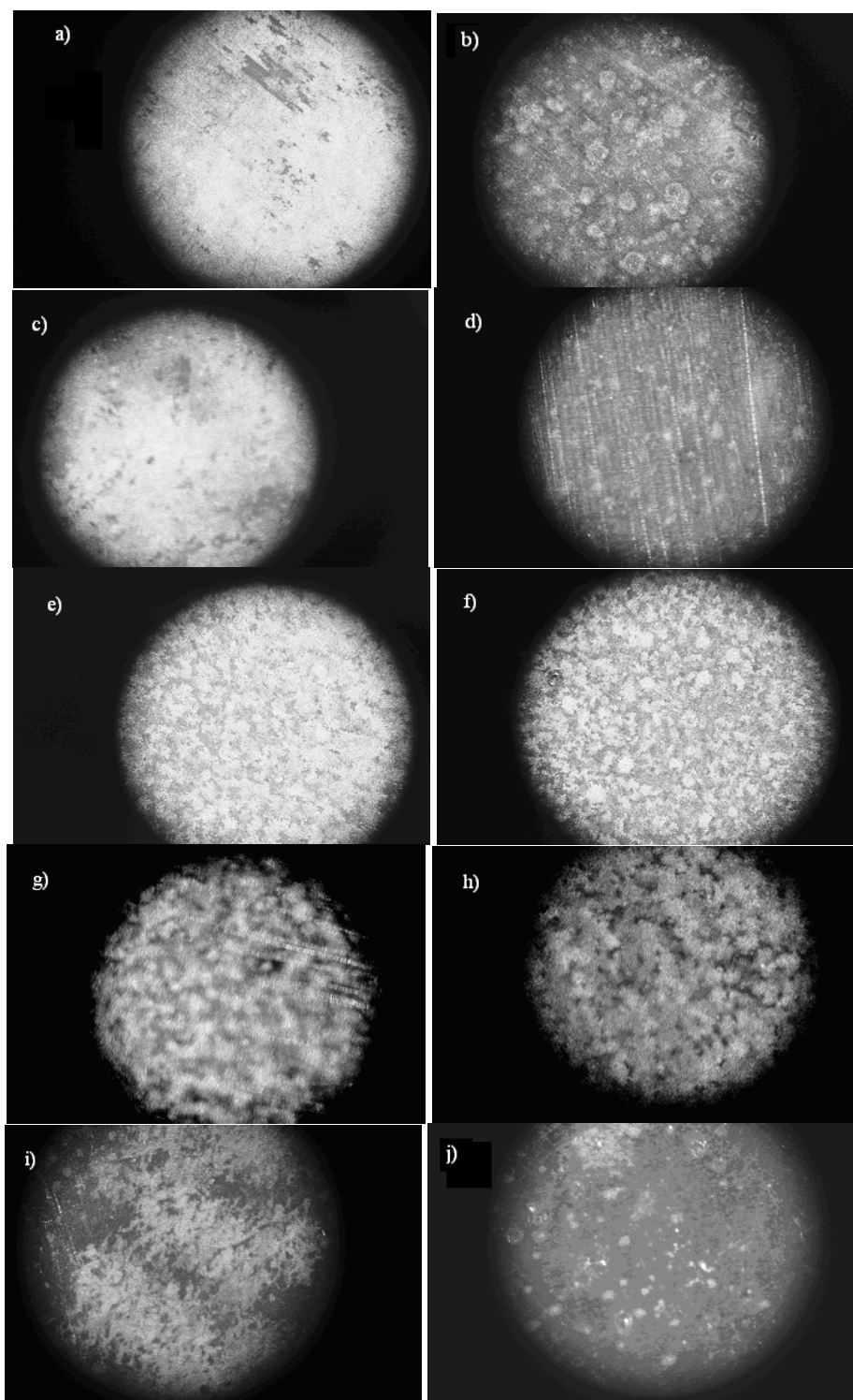


Fig.2. Sample surface after processing (steel-45): $C = 8\mu F$, $f = 40$ Hz;

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|-------------------------------------|-----------------------------------|
| a. cathode-piece, S=1mm, U=400V; | b. anode-piece, S=1mm, U=400V; |
| c. cathode-piece, S=1mm, U=300V; | d. anode-piece, S=1mm, U=300V; |
| e. cathode-piece, S=0,5 mm, U=130V; | f. anode-piece, S=0,5 mm, U=130V; |
| g. cathode-piece, S=0,5 mm, U=100V; | h. anode-piece, S=0,5 mm, U=100V; |
| i. cathode-piece, S=1,2 mm, U=400V; | j. anode-piece, S=1,2 mm, U=400V. |

After the results of the experimental investigation were analysed [2 ÷ 5] it was presumed that the processing should be done with relatively small energies within the limits $10^{-2} \dots 10^0$. The following parameters of the pulse generator were established:

condenser capacity of the power block $C = 8 \mu\text{F}$, pulse frequency $f = 40 \text{ Hz}$, charging voltage of capacities $U = 100 \div 400\text{V}$, interstice size $S = 0,5 \div 0,5 \text{ mm}$.

Various experimental investigations were done to vary the interstice size and the charging voltage of capacities, that is, to vary the energy of electric discharges in pulse. Fig.2 and fig.3 present the general view of sample surfaces of steel-45 and steel-3 respectively after processing under different regimes.

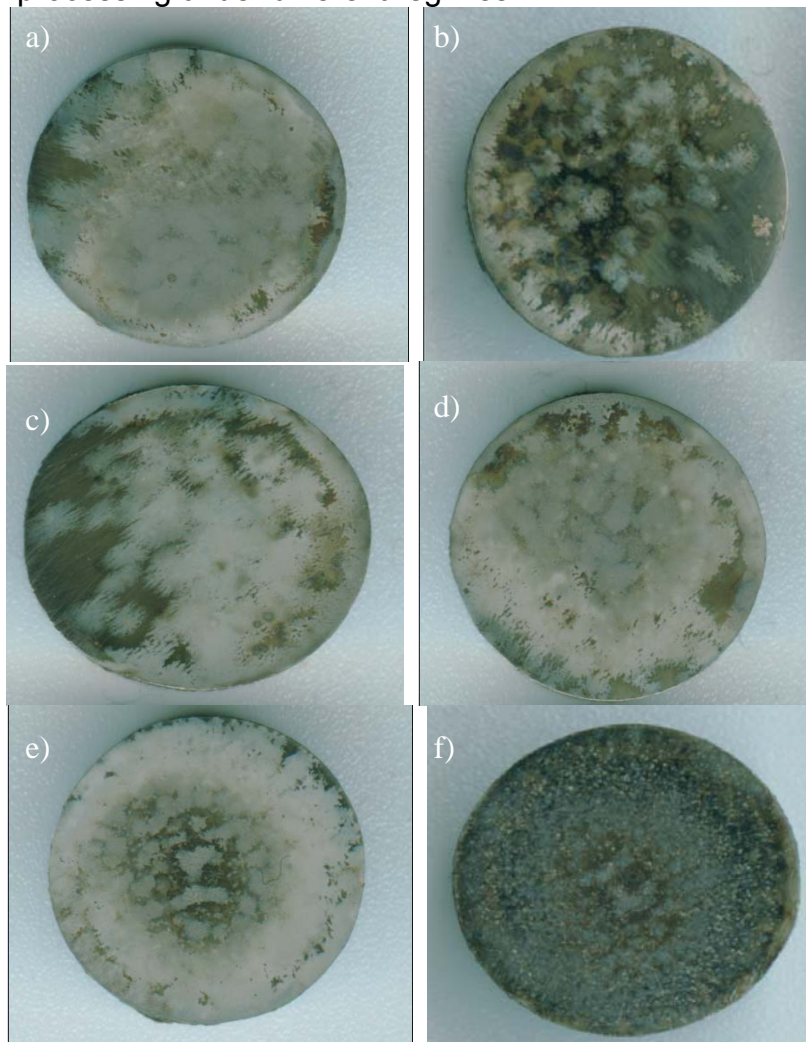


Fig.3. Sample surface after processing (steel-3), $C = 8 \mu\text{F}$, $f = 8 \text{ Hz}$:

- a. cathode-piece, $S=1\text{mm}$, $U=400\text{V}$;
- b. anode-piece, $S=1\text{mm}$, $U=400\text{V}$;
- c. cathode-piece, $S=1,2 \text{ mm}$, $U=500\text{V}$;
- d. cathode-piece, $S=0,75 \text{ mm}$, $U=300\text{V}$;
- $C=8 \mu\text{F}$, $f=16 \text{ Hz}$:
- e. cathode -piece, $S=0,5 \text{ mm}$, $U=250\text{V}$;
- f. anode-piece, $S=0,5 \text{ mm}$, $U=250\text{V}$

During the analysis of the processed surfaces it was noticed that a much more uniform oxide layer without any perforations was formed on the samples that were connected in the discharging circuit cathodes. It is worth mentioning that more qualitative surfaces of a complete continuity are attested for the charging voltage of the condenser battery of 400V in 1mm interstice. This phenomenon may be explained by the big contact spot of the plasma canal with the processed surface and the optimum value of energy density emitted in the interstice on the one hand, and by the fact that the plasma that was formed in the interstice contains positive oxygen ions which move towards the cathode

processed surface under the influence of the electrodynamic forces of the electric field in the interstice. The cathode surface being activated by electrode spots favour the process of oxidation and diffusion of medium elements in the depth of the piece. Craters formed as a result of oxide layer perforation are noticed on the surfaces of anode samples (on the surfaces of which the fall of voltage is higher). At the same time the oxidation process on the oxide layer is less intense because it is bombarded with electrons emitted by the cathode. This is also due to the fact that besides the anode with positively charged electrons are accumulated, the latter processing a high energy manage to heat the dielectric thin layer on the anode surface and to perforate it.

4. CONCLUSIONS

The superficial oxidation on processing surfaces by means of electric discharges in pulse under ordinary conditions is more efficient when the piece is connected to the discharging circuit as the cathode as there are craters formed on the anode during the perforation of the dielectric plasma discharges.

The pellicles obtained by means of this method increase the active resistance on the surface up to 1,2 MΩ.

After the processing the corrosion potential of the surface enlarges and this leads to a better protection of the piece from corrosive media.

The final surface has a roughness smaller than the original one.

The productivity of oxide pellicle formation by means of this method depends on the energetic regime of processing and can reach from 1 to 20 cm²/min.

The sample hardness of the processed surface increased from HB125 up to HB137 due to the superficial micro hardening at the interaction with the plasma canal of electric discharges in pulse.

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