

Aluminum Treatment in the Electrolytic Plasma During the Anodic Process

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Abstract

Electrolytic-plasma processes are new highly efficient and environment friendly processing techniques of metals and alloys; they could be applied for polishing and cleaning of the metal surfaces, for thermal and chemical-thermal treatment. The present work is related to the study of modes, established on the active electrode made from aluminum during the anodic process and using of these modes for polishing of its surface, and also for the synchronous polishing of the anode surface and coating removing from the surface of the copper-plated cathode. The copper content and surface roughness of the metal before and after treatment were evaluated by means of the profilometry and energy-dispersive X-ray analysis (EDAX). The composition, microstructure and morphology of the copper coating removed from the cathode surface have been studied depending on treatment parameters.

The results show that electrolytic-plasma processes can be effectively used for polishing of the surface of aluminum, simultaneous polishing of the aluminum anode and removing of the copper coating from the cathode.

Keywords: electrolytic plasma, discharge, electrolysis, polishing, coating.

1. Introduction

The most common material is aluminum, which can be easily machined and shaped by casting, has good corrosion resistance, high thermal and electrical conductivity. High natural corrosion resistance due to the high chemical affinity of aluminum to oxygen, i.e. the surface layer of the aluminum chemically reacts with oxygen, forming oxide film of Al_2O_3 , the thickness of which does not exceed 1 micron. The microhardness and wear resistance of this layer is significantly higher than the base layer has. However, in some cases, it is necessary to have a higher degree of protection (corrosion or chemical), to modify the appearance of surface (color, texture etc.) or to create defined physical properties of the surface (increased hardness, wear resistance or adhesion). In such cases, anodizing of aluminum and aluminum alloys is carried out.

Anodizing of aluminum [1] relates to the electro-chemical processes of formation of the stable oxide coatings (films) on the surface of metals. Anodizing of aluminum and aluminum alloys can occur with the participation of a variety of electrolytes with the use of sources of direct or alternating current or combinations thereof. When using DC the aluminum item is always the anode. When aluminum is exposed to the electro-chemical oxidation, it is possible to obtain the film with thickness from 9 to 20 microns. The supply voltage does not exceed 20V.

Studying of the modes established on the active aluminum anode with increasing voltage [2], has shown, that after the commutation mode the heat mode is established only in aqueous solutions of NaOH or KOH with concentration less than 2% within the voltage 90-140 V. In

other electrolytes or at higher voltages the electrohydrodynamic mode of the anodic process is established. It is found, that depending on the processing conditions, it is possible to carry out the electrolytic-plasma oxidation [3-9], polishing of the surface of aluminum or deburring. It should be noted that in some works, where DC supply voltage is used the electrolytic-plasma oxidation is named as microarc oxidation [3-7] that in terms of electrical discharges properties is fundamentally wrong [2]. To talk about the microarc oxidation is possible only in case if only AC power source is used.

All electro-chemical installations include standard process chain: degreasing, washing, neutralization, electro-chemical oxidation, drying, so when using electrolytic plasma the first three processes could be excluded and treatment can be carried in neutral electrolytes.

In this work, we will consider some regularities of the aluminum polishing process and possibility of the synchronous polishing of aluminum and copper layer removing from the surface of the copper-plated cathode.

2. Materials and Methods

The study of the laws of the various modes establishing on the active electrode was carried out by means of simultaneous oscilloscope and high-speed filming. Current-voltage and temperature characteristics of these modes were studied depending on the molecular properties of aqueous solutions. Aluminum rods with diameter from 1 to 10 mm and length 60-70 mm and plate with thickness 2-3 mm, width 10-15 mm and height 50-100 mm were used as an active electrode.

The method of electrolytic-plasma polishing is based on plasma and electro-chemical processes, arising in the thin gas-vapor shell near the surface of the immersed in the

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solution metal electrode under the high voltage. Unlike the traditional electro-chemical polishing electrolytic-plasma technology uses environmentally friendly aqueous solutions of salts (NH₄Cl, KCl and other) and alkalis: KOH and NaOH of low concentration (3-6%) with various additives, which are rather several times cheaper than toxic acidic components.

The solution temperature was varied in the range from 20 to 80°C. The treatment time varied from 20-30 seconds to 10 minutes. The voltage on the bath electrodes was 280-360V, anodic current density 0.4-0.6 A/cm².

Studies of the mechanisms of polishing of the aluminum anode and synchronous dissolution of copper coating from the surface of the cathode was conducted using the cathode made of stainless steel, which has previously been covered with copper coating, obtained during the polishing of the copper-containing anode [10]. The cathode was made in form of a half-cylinder with dimensions 150×80×0.3 mm.

After the treatment the surface of the samples were examined by means of scanning electron microscopy (SEM), characterizing the morphology of the surface. The thickness of the copper coating was determined by microstructural analysis using microhardness tester PMT-3. The chemical composition of the anode and the cathode surface before and after treatment was determined by X-ray analysis with microanalyser KYKY-2800V. The clearness of the anode surface was determined using the profilometer model 130 produced by "Plant Proton-MIET."

3. Results and discussion

Electrolytic-plasma polishing occurs only if the processed product is a positive electrode (anode). Under the high voltage and high current density, the electrolyte ebullience occurs near the anode surface, thin gas-vapor shell forms, consisting of the water vapor and the ions contained in the electrolyte. The electrical current flowing through the gas-vapor shell causes the occurrence of the plasma processes, typical for the gas discharge. Under the influence of electrical discharges and active ions the modification of the processed product surface occurs.

Metal polishing occurs within the voltage 200-350V and current densities 0.2-0.5 A/cm² [2, 11], i.e. when establishes the electro-hydrodynamic mode of the anodic process. When the voltage is more than 200V, around the anode forms stable thin (50-100 microns) gas-vapor shell, characterized by small oscillations at a constant voltage. The electrical field intensity in the shell reaches 10⁶-10⁷V/cm. This electrical field intensity causes the ionization and excitation of the elements included in the electrolyte, as well as the emission of ions and electrons, necessary for maintaining an electric discharge in the shell. Near the microprotrusions of the part surface, the electrical field intensity is highest, so pulsed electrical discharges occurs in these areas. In places of the closest approach of the electrolyte to the metal anode, the spark discharges occur, which are registered in form of points on a background of the glowing stationary electric discharge. An independent discharge, existing in the gas-vapor shell and responsible for the glow and conductivity of this shell, is either the unipolar corona discharge or glow discharge. Analyzing the properties of these discharges [2], we can conclude that it is possible to talk about the specific glow discharge in the gas-vapor shell between metal and electrolytic electrodes regardless of their polarity.

Basic quality indicators of the electrolytic-plasma polishing, which include the roughness and reflectivity of the surface, depend on the number of factors: voltage on the electrodes, composition and temperature of the electrolyte, the treatment time. Depending on the chemical composition of the anode material, it is necessary to choose the composition and concentration of the electrolyte. Given the diversity of metals and alloys, electrolyte compositions vary in wide limits. Furthermore, in some cases, takes place the use of additive of substances significantly affecting the basic properties of the solutions: surface tension and kinematic viscosity. These include glycerin, acetone, triethanolamine, etc., which change formation conditions of the gas-vapor shell and shift the current-voltage boundary of the electrohydrodynamic mode.

Temperature conditions in the near electrode zone and in the electrolyte play a significant role in the process of polishing of metals and alloys, and high quality of the surface can be achieved only in the certain range of the electrolyte temperature. The connection of the microrelief with the temperature of aqueous solution is explained by the temperature dependence of such properties of the fluid as electrical conductivity, surface tension, wetting angle, viscosity, which affect the stability of the vapor-gas shell and which are responsible for the mechanism of the microroughness removal.

Experiments have shown that high quality of the surface polishing can be achieved only in a well-heated electrolyte. When the electrolyte temperature is lower than 50°C the quality of polishing decreases. An increase in the electrolyte temperature above 90°C causes the same result. In addition, some electrolytes, containing ammonium salts, hydrochloric acid and other substances, decompose when heated over the 85°C, forming volatile products that require frequent adjustment of the composition of the solution.

The most important parameter that determines the quality of the polishing is the operating voltage. It was experimentally established that there is a minimum voltage value for each metal, below which the quality of the polishing begins to deteriorate noticeably. The minimum voltage thresholds values have been identified for polishing of the various metals: stainless steel – 220V; copper and copper alloys - 260V; aluminum alloys - 270-290V [2].

The value of the aluminum surface roughness and reflection coefficient depending on the value of voltage across the electrodes of the electrolytic cell are shown in table 1, 2. Not only from energy considerations but also from technological considerations, the increase in voltage more than 340 volts is undesirable, since there is a possibility of entering into the area of contact electrical discharges [12], when the disruption of the gas-vapor shell is possible and the electrolytic-plasma treatment is more difficult.

Table 1. The influence of voltage on surface roughness of aluminum alloys

Polishing duration, sec	Voltage, V			
	250	300	350	400
	Roughness, μm			
30	0,25	0,20	0,21	0,26
60	0,19	0,16	0,16	0,21
90	0,16	0,13	0,14	0,18
120	0,12	0,12	0,12	0,14

Table 2. Influence of voltage on the reflection coefficient of aluminum alloys

Polishing duration, sec	Voltage, V			
	250	300	350	400
30	42	46	49	40
60	50	62	67	48
90	64	78	81	55
120	72	83	83	67

It is natural to assume that the quality of the surface polishing is proportional to its duration (table 3). With the increase in the duration of the polishing from 30 to 120 seconds, the surface roughness decreases significantly (from 0.24 to 0.10 microns), and the reflectivity rises from 42 to 74%. The rapid decrease in the roughness during the first 120 seconds, apparently, related to the fact that there is an active local smoothing of the microrelief in places of highest projections. The further increase of the polishing duration doesn't give such significant change of the surface roughness, but only gives a mirror gloss to the surface.

Table 3. Influence of the polishing duration on the surface roughness (R_{a}) and reflection coefficient (K) at voltage 280 V.

Polishing parameter	Polishing duration, sec					
	30	60	90	120	180	240
$R_{a, \mu k}$	0.24	0.18	0.15	0.13	0.11	0.10
$K, \%$	42	51	64	72	73	74

Best results for polishing of the aluminum surface and synchronous removing of the copper coating from the surface of the cathode were received using the aqueous solution containing 10% NH_4Cl , 4% KCl and 3% oxalic acid at a voltage of 300V on the electrodes and temperature of the electrolyte of 60–80°C. At that, the aluminum surface had a shiny appearance, and the surface of the cathode was completely cleared from the copper coating.

Brief specifications of the technological modes of the electrolytic-plasma polishing:

- The minimum attainable surface roughness of $R_a = 0.03-0.015$ microns;
- reduction in surface roughness is determined by the level of initial roughness, duration of treatment and occurs in economically feasible processing time for 2-3 classes, for example, from $R_a = 1.25-0.63$ microns up to $R_a = 0.16-0.015$ microns;
- The duration of deburring and contamination removing is 10-20 seconds (depending on the height of the burr).

Copper coatings are generally not used as a standalone coating or for ornamental purposes or for the protection against corrosion of steel parts. This is because copper is easily oxidized in atmospheric conditions, becoming covered with oxide coating. However, due to the good adhesion of deposited copper with different metals is used in multilayer protective-decorative coatings as an intermediate sublayer, and also to protect steel parts from carburization, and deposited as a foil on printed circuit boards.

The method of the anodic dissolution in various solutions is used to remove copper coatings. In work [13] to remove copper coatings, deposited as a foil on the printed circuit boards, an aqueous solution is used, containing

ammonium sulphate, copper sulphate, hydrogen peroxide, thiourea, sulfuric acid, dimethylformamide, at a current density 30-40 A/dm^2 .

Electro-chemical removal of the copper coatings [14] is carried out also in the aqueous solution containing sodium nitrate and acetic acid at a current density of 4-5 A/dm^2 and voltage of 2.4-2.5 V on the bath, in this aqueous solution was succeeded to prevent etching of the steel substrate.

Within the process of the polishing of the aluminum active electrode during the electro-hydrodynamic mode of the anodic process at a voltage of 290-320 V across the electrodes in the electrolytic bath in the mentioned above electrolyte synchronously occurs the removal of the copper coating from the steel cathode (Fig.1, before treatment). Depending on the duration of the process the copper layer can be removed partially or completely (Fig. 2). The time of removing of the copper layer can vary from one up to several minutes. In other compositions, used for polishing of aluminum [10], copper-plated coating on the steel cathode was removed less intensively. It was suggested that the removal of the copper coating is caused only by the chemical reactions. For this purpose, the plates with copper coating were kept for three days in this electrolyte. However, any significant dissolution of the copper-plated coating was not observed, i.e. the dissolution occurs only during the flow of the electrical current. And it is still unclear, what is the mechanism of the simultaneous polishing of aluminum anode and dissolution of the copper cathode.

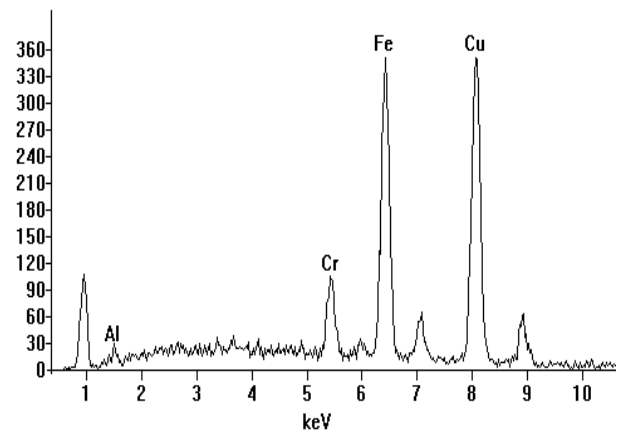


Fig.1. X-ray spectral analysis of the cathode (stainless steel) before treatment.

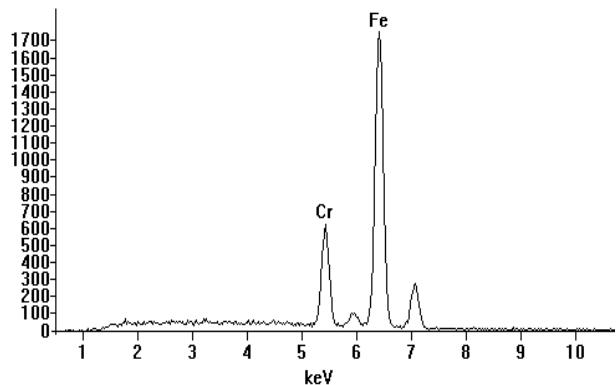


Fig. 2. X-ray spectral analysis of the cathode (stainless steel) after polishing of the aluminum anode. Processing time - 6 minutes.

4. Conclusion

Using the electro-hydrodynamic mode of the anodic process allows performing synchronous (simultaneous) polishing in the electrolytic plasma of aluminum anode and removing of the copper coating from the surface of steel part serving as the cathode. At that the copper coatings could be removed from the surface of the cathode only during the flow of direct electrical current. Unlike the traditional electro-chemical polishing, the electrolytic-plasma treatment uses environmental friendly aqueous solution of salts of low concentration (2-10%), which are significantly cheaper than

toxic acidic electrolytes. The disposal of waste electrolytes does not require special treatment facilities. Besides, processes of surface cleaning, deburring and polishing could be combined in one operation. It is possible to implement full automation of the command and control of the process parameters.

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