

## Formation of dispersed particles during plasma oxidation

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Microplasma oxidation is a promising method of producing ceramic coatings for various purposes [1–5]. At present theoretical models of breakdown and coating growth are being actively developed and new application areas suggested [6–8].

We already know the mechanisms of growth of microplasma coatings due to electrochemical and chemical oxidation of metals and inclusions of electrolyte elements in the course of thermal reactions on the surface [9]. In the place of microarc discharge on the solution-metal interface during a short period of time (about 200–1000  $\mu\text{s}$ ) high temperatures of  $10^3$ – $10^4$  K and pressure of  $10^2$ – $10^3$  MPa are developed [10] which result in the formation of a vapor-gaseous medium in the space and the local fusing of the base metal, which is ejected by the arc process into the solution where part of it is hydrated and the rest of it remains there in ionic form [11].

The present article shows additional mechanisms of inclusion of electrolyte components into the microplasma coating composition as a result of crystal formation in the electrode layer.

Specimens of 2024 aluminium alloy (4.4% Cu, 0.6% Mn, 1.5% Mg) with a total area of 0.02 dm<sup>2</sup> served as anode. They were first etched in potassium hydroxide solution and then purified in nitric acid solution. A plate of stainless steel 3 dm<sup>2</sup> in area, served as a cathode. The treatment was carried out in electrolyte based on sodium phosphate (20 g·l<sup>-1</sup>) with inclusions of ferrous citrate (10 g·l<sup>-1</sup>) and surface—active substances (triethylamine - 15 g·l<sup>-1</sup>). A potentiostatic processing regime with unipolar sinusoidal or pulse voltage ranging from 300 to 520 V was used.

The coating formation time took from 20 to 40 min, with an electrolyte temperature of 298–318 K. The micrographs and the element composition data on the coatings were obtained using a JSM 84 scanning electron microscope with a link adapter at the magnification of 1000 times. Average concentrations of components were obtained from an area of 200 × 200  $\mu\text{m}$  using three measurements. The concentrations in the crystal region were determined by focusing a beam to 5  $\mu\text{m}$  in size.

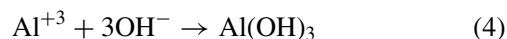
A morphology study of the surface after microplasma processing has revealed, in a number of cases, dispersed formations on the coating, including those of a regular geometric shape (Fig. 1). It indicates the crystalline nature of the above structures. The presence of dispersed particles on the coating surface is caused by the characteristic features of microarc oxidation. Ejection of melt, which accompanies a breakdown, and its interaction

with electrolyte, result in the formation of both fused parts around pores and various dispersed particles of the amorphous structure weakly connected to the surface. Crystallisation on the coating surface under given physical conditions (high temperatures and pressures) is unlikely. The formation of crystals deep in the solution is also highly improbable as it is not supersaturated in any component, and is heated during the microplasma process. In order to explain the mechanism of appearance of dispersed formations of a crystalline structure, the following approach has been suggested.

When a unipolar electric current passes through the specimen surface, intensive decomposition of water occurs:



Therefore, the electrode layer always contains a great number of hydroxide ions. It leads to oxidation of the aluminium particles present in the layer, that were ejected by a microplasma discharge, to charged colloid particles of hydroxide, e.g., according to reactions (3) and (4) [12]:



Additionally, numerous chemical and electrochemical reactions with electrolyte components take place in the electrode layer which are difficult to investigate. The presence of various ions, free radicals and colloid particles results in the formation of dispersed particles of a complex crystalline and amorphous structure. The ion concentration in the electrode layer can lead to supersaturation of the solution and crystal formation, with the colloid particles of aluminum hydroxide being the crystallization centers. The growth of the nucleation centers to critical size is promoted by the surface—active substances and phosphorus present in the electrolyte, which decrease the crystal surface tension. After the critical size has been achieved, the process of growth becomes spontaneous.

As soon as dispersed particles are formed in the electrode layer, they are affected by the electrophoretic forces and move toward the specimen surface entering the pore and crack regions along the lines of maximum electric field strength. As is seen in the micrograph of the surface (Fig. 1), the particles are observed near the pore boundaries as well as inside the pores. Further,

TABLE I Element composition of microplasma coatings in the region of accumulation of dispersed formations and the comparison with the mean concentration values

Number of measurement	Average concentrations on the surface of the microplasma coatings (wt%)			Concentrations in the region of accumulation of dispersed formations (wt%)		
	P	Al	Fe	P	Al	Fe
1	4.9	16.9	8.9	5.0	34.1	10.1
2	3.9	23.2	8.6	3.0	37.7	6.4
3	5.7	13.4	14.8	10.8	6.6	8.5
4	5.7	13.4	14.8	2.1	41.3	2.1
5	5.7	13.4	14.8	10.5	5.5	15.3
6	10.5	14.8	24.0	8.2	31.9	11.2
7	10.5	14.8	24.0	11.9	23.5	16.4
8	10.5	14.8	24.0	6.9	7.5	8.3
9	10.5	14.8	24.0	17.1	4.9	30.3
10	9.5	19.8	23.1	7.2	2.1	21.7

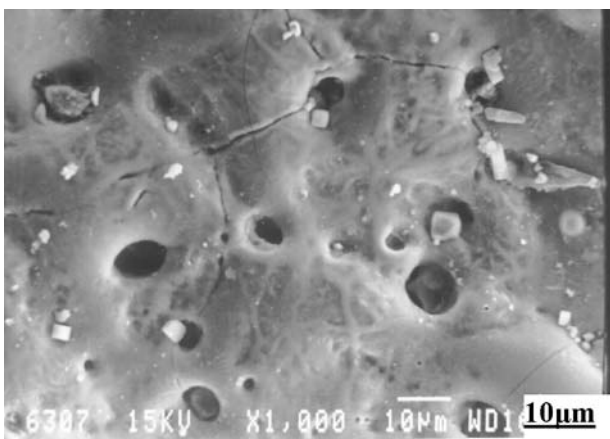


Figure 1 Microphotograph of dispersed particles on the microplasma coating surface at a magnification of  $\times 1000$ .

they partially fuse as a result of the microplasma process enter the coating. Thus, a coating is formed which has a heterogeneous multiphase and multicomponent composition on the surface.

The above mechanism is supported by the element analysis data on microplasma coatings in the region of accumulation of dispersed formations and comparison with the mean concentration values (Table I). The data in Table I refer to the microscopy of the coatings produced in the series of phosphate electrolytes with various concentrations of components.

The concentration sum in Table I does not equal 100%. The light elements such as oxygen and hydrogen, which are not determined according to the given method, account for the remainder. The traces of elements contained in the processed aluminum alloy are also present in the coating.

From the data in Table I one can single out cases of variations of concentrations in all basic elements in the coating. The contents of the elements can be several times larger or smaller than the mean values. Thus, analysis of the region of the dispersed formations indicates a large aluminum content in cases 1, 2, 3, 4, 6 and 7, which suggests the impossibility of the formation of such particles in the depth of the solution. The particles may contain aluminum oxide of the various compositions or aluminum hydroxide formed at the interaction between the ejected aluminum and hydroxide ions. The comparison of the element concentrations in

the surface of one specimen (cases 3–5 and 6–9) shows a considerable variation. It fits the pattern of the formation of dispersed particles near the electrode surface due to various interactions between oxidised aluminum and dissolved compounds under nonequilibrium conditions of the microplasma process. In case 10, with the minimum content of aluminum, crystallization occurred in which the electrolyte compounds took part.

A mechanism of growth of microplasma coatings due to inclusion of dispersed particles from the electrode surface has been suggested. The particles are formed at simultaneous crystallization of the oxidised aluminum ejected from the base material by the plasma process and the electrolyte elements. The dispersed particles enter the surface defects of the coating due to electrophoretic forces contributing to the formation of a multicomponent and multiphase coating. The mechanism is supported by the investigation data on the morphology and coating composition. In our opinion, it has a general character and allows one to understand the entire physico-chemical pattern of the microplasma oxidation process.

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