Formation of coatings from the flow of metal plasma of a vacuum-arc discharge

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Abstract. Modification of the surface properties of a material or application of a protective coating are the most effective ways to improve the service life and reliability of parts. For the production of coatings vacuum-arc discharge with integrally cold cathode is widely used. The advantages of this method are high degree of purity of the coating, the possibility of changing the structure of the coating and obtain complex multicomponent coatings. In this paper, we consider the production of anti-emission coating based on titanium; the results of metallographic studies of this coating are presented.

1. Introduction

In many cases, the performance properties of parts are determined by the state of their surface layer, as it is exposed to external active mechanical, thermal, chemical or other types of effects. Therefore, modification of the surface properties of a material or application of a protective coating by ion-plasma method are one of the most effective ways to improve the service life and reliability of parts [1, 2].

Method of surface treatment by forming the coating allows precision dimensional surface treatment, significantly increase wear resistance, mechanical strength and thermal protection of parts, improve anti-corrosion properties, change the hardness and friction coefficients.

Of great scientific and practical interest is the development of technological processes based on the formation of film structures from metal plasma of a vacuum-arc discharge, allowing the most effective control of the state of the surface layer of a solid body [3–8]. Operational properties of parts are determined by all stages of the process: evaporation of the material, its transportation and deposition on the treated surface [9, 10]. Comprehensive study of the conditions of coatings formation and study of the surface layer taking into account operating conditions is a progressive trend in improving the quality of structural materials, in solving the problem of achieving high structural strength and compatibility with the environment. Analysis of the behavior of the surface layer of a solid body in the process of ion-plasma treatment, and in the process of operation, with the goal to study the physical nature of the relationship of structure, composition and construction with the physical, mechanical and chemical properties of materials and the development of scientific foundations for the management of these properties is an urgent scientific problem.

2. Results and discussion

One of the important applications of surface layer modification is the deposition of anti-emission coatings on grid electrodes of electrovacuum devices to protect them from thermoelectronic and
secondary electron emission [11, 12]. The vast majority of modern radio transmitting devices operating at frequencies up to 30 MHz, with an output power level of more than 40 kW, as the amplifying devices of the end stages use powerful generator lamps, which are structurally complex products. The main directions of development of this type of devices are to increase the specific power while increasing their durability. The maximizing efficacy parameters required the solution of problems of thermal resistance of the shielding grids of the tetrode, withstanding in the conditions of pulsed gain significant electronic loads. This problem becomes very relevant when creating powerful generator lamps using overstressed modes and high specific power dissipation on the grids up to 20 W/cm² or more, with a corresponding increase in their operating temperature. Therefore, the anti-emission properties of the grid coatings will determine the quality and reliability of the devices.

The most effective is the use in the manufacture of grid electrodes of materials and coatings with high values of the integral coefficient of radiation and the work function, and in some cases representing a complex system of multilayer structures consisting of alloys or chemical compounds. To reduce the thermoelectronic emission, the grid electrode is coated with metal of group VIII of the periodic system, in particular with platinum. To reduce the diffusion of platinum into the core of the grid and increase the radiating capacity between the base metal and platinum, an intermediate layer consisting of Zr–Pt or Ti–Pt compounds is applied. The most effective compound is Pt₃Zr [13].

Titanium is distinguished from the group of metals used in the production of electronic vacuum devices. It allows creating protective coatings serving to prevent evaporation and also blackening and anti-emission coatings having a sufficiently high adhesion with a substrate. The properties of titanium include high mechanical strength, lightness, high melting point, low coefficient of secondary electron emission, good getter properties and stable characteristics to oxidation and interaction with alkali metal vapors. The mechanism of operation of titanium as an anti-emission coating consists in the desorption of atoms of the active cathode substance from the mesh surface under sufficient thermal load. The estimated temperature of the thorium desorption from the surface of titanium is 900 K. The work function from the titanium coating, under the conditions of spraying the active substance from the cathode, at a temperature of 1000 K is 3.0 eV, at 1200 K – 3.16 eV and at 1400 K – 3.35 eV. The emission factor for these temperatures is 0.53, 0.56 and 0.58, respectively.

In addition to these properties of titanium, it should be noted that in the working modes of operation, titanium coatings present a gettering surface, actively contributing to the maintenance of vacuum conditions in the device. Titanium absorbs active gases and keeps them in a wide temperature range starting from 473 K. Sorption capacity of titanium coatings depends on the thickness, roughness and porosity of the coating, and, to a large extent, is determined by the method of its production.

During the combustion of a vacuum-arc discharge with an integrally cold cathode, droplets exist in the erosion products of the cathode material, which lead to a rough coating with a developed surface (figure 1). This condition has a favorable effect on the gas-absorbing properties of the titanium coating, which most effectively absorbs the residual gases of the active group: hydrogen, oxygen, nitrogen prevailing in vacuum systems.

**Figure 1.** The appearance of the mesh fabric with anti-emission titanium coating (a); morphology of a gas-absorbing titanium coating (b) (average particle size ~2.0 µm, the coating is loose (porous) and agglomerated).
The generation of droplets is due to the formation of erosion craters on the cathode surface. The localization of the electric field in the area of microscopic inhomogeneities on the cathode surface leads to the flow of an autoemission current, the density of which can exceed the critical value. In this case, an explosion of a microscopic protrusion occurs, leading to the melting of the surrounding surface and the formation of a plasma cloud over the cathode spot.

The quantitative composition of droplets is associated with changes in the operation of the integral cathode temperature. With the growth of the cathode operating temperature, the percentage of neutral steam and droplets in the flow increases. With the decrease of the cathode temperature, the growth rate of the coating is determined by the positively charged component of the plasma flow. It should be noted that the percentage of the droplet fraction in the generated plasma flow depends on the melting temperature of the cathode material. So for refractory metals such as molybdenum and tungsten, these values are at the level of units of percent, while for copper this value is about 50 \%. The results obtained in the experiments suggest that as the vacuum-arc device works, the angular distribution of the droplets in space and the number of generated droplets with dimensions up to 1 µm practically do not change, while the quantitative composition of larger particles undergoes significant changes.

The pulse operation mode of the evaporator significantly reduces the portion of the droplet fraction in the generated plasma flow, which is due to the thermal and mechanical inertia of their formation. The flow rate of the plasma-forming material is easily controlled by changing the pulse repetition frequency. During the arc burning for no more than 5 s, drops not exceeding 1 µm were mainly recorded. At the same time, the total number of them was 4–5 times less than in the ten-second interval of the evaporator functioning. The decrease in the arc burning delay time led to an increase in the number of droplets having larger sizes, since with a decrease in the pause, the initial temperature of the cathode for the subsequent combustion stage increases.

The intensity of generation of droplets increases with increasing discharge current. However, only by reducing it, it is impossible to decrease the content of droplets to an arbitrarily small value, since stationary arc combustion is possible only with a discharge current of not less than some critical value for this material, which significantly depends on the thermal properties of the cathode material. The maximum number of droplets evaporates from the cathode working surface at an angle of 20...30° to its plane, and for the formed flow a pattern of radial symmetry is observed.

Metallographic studies of coatings in the process of operation of electrovacuum devices showed that for titanium at a cathode temperature below 1000 K, the obtained coatings had a complex structure. The growth of the negative bias (in absolute value) on the treated substrate leads to the creation of a coating with strongly pronounced components, while at a cathode temperature of more than 1000 K the orientation effect was weak and the coating had a loose rough character. As it is known, the reduction of the secondary emission coefficient is achieved by increasing the roughness of the coating, which is explained by the difficult output of the secondary electron in a layer with a labyrinth structure than from a smooth layer. Figure 2 shows the section of a grid coating with thickness up to 10 µm and more.

Figure 2. Metallographic section of an anti-emission titanium coating.
During operation at high temperature of the grid mesh, there is a counter diffusion of the mesh material and titanium coating (figure 3), leading to deterioration of the operational properties of the grid electrode. However, a characteristic feature of the diffusion of molybdenum and titanium is that they do not enter into a chemical reaction and do not form intermetallic compounds, while solid solutions are observed.

3. Conclusion

With the growth of the cathode operating temperature, the percentage of neutral steam and droplets in the flow increases. With the decrease of the cathode temperature, the growth rate of the coating is determined by the positively charged component of the plasma flow. The results obtained in the experiments suggest that as the vacuum-arc device works, the angular distribution of the droplets in space and the number of generated droplets with dimensions up to 1 μm practically do not change, while the quantitative composition of larger particles undergoes significant changes. The pulse operation mode of the evaporator significantly reduces the fraction of the droplet fraction in the generated plasma flow, which is due to the thermal and mechanical inertia of their formation.

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