Method and equipment for forming multilayer intermediate structures in the production of antiemission coatings

D K Kostrin
Department of electronic instruments and devices, Saint Petersburg Electrotechnical University “LETI”, 197376, Saint Petersburg, Russia
E-mail: dkkosrin@mail.ru

Abstract. In the paper the method and equipment for forming antiemission coatings based on platinum and zirconium are described. This method is based on the preliminary formation of a multi-layer complex structure consisting of layers of different compositions, with high-temperature annealing of which it is possible to obtain a high-quality layer of zirconium carbide. Later this layer serves as the basis for obtaining one of the most promising types of anti-emission coatings – Pt\textsubscript{3}Zr. To implement this method an electronic device with a microprocessor module was developed that allows controlling the pressure in the working chamber, as well as regulating the voltages and currents in the vacuum arc installation.

The most important condition for the formation of an intermetallic compound Pt\textsubscript{3}Zr is the presence of a qualitatively formed ZrC intermediate layer applied with the use of a vacuum arc installation [1]. The effectiveness of plasmachemical synthesis processes is determined both by the kinetic energy possessed by charged and neutral particles, and by the composition of plasma stream. Increasing the energy of the ions that bombard the processed side of the product makes it possible to modify the properties of the layer on the surface of the part, and also increases the diffusion mobility of adatoms, thus leading to the predominant formation of crystallites in the condensation plane [2].

The most important technological problem in the formation of the ZrC sublayer is the balancing of the ion flux that occurs on the product, caused by the sputtering of the metal from which the cathode is formed, determined based on a given value of the vacuum arc discharge current and the flow of carbon atoms. It is necessary to take into account the fact that synchronously with this, the coating formation occurs together with the decomposition of the original hydrocarbon molecules [3], as well as their radicals directly on the heated up to 800 K product, which causes the appearance of carbon in atomic form and increased carburization of zones near the surface, which significantly affects the structure of the resulting carbide compound [4, 5].

The stoichiometric structure of the ZrC layer can be obtained by diffusion annealing in a vacuum atmosphere of a multilayer structure [6, 7] that includes a set of stepwise deposited Zr nanolayers, a non-stoichiometric carbide compound of a variation composition with a lack of carbon ZrC\textsubscript{1–x}, and a carbide compound with an excessive inclusion of the carbon component ZrC + C.

The formation of these nanolayers is carried out on a preliminarily formed layer of the base metal carbide compound Mo\textsubscript{2}C–MoC [8], which makes it possible to obtain one of the barrier layers that inhibits the process of diffusive migration of Pt into the volume of the grid electrode material, and
reduces the presence of unbound Mo in the near-surface zone, which prevents its free diffusion migration into the intermetallic layer.

The formation of an additional Zr layer makes it possible to form a transitive barrier layer, which is a complex structure consisting of a set of phases (Mo–Mo₂C–MoC)–(MoC–C–Zr), due to the action of Zr ions with high energy, as well as parallel diffusion migration of atoms that gather at the boundary of the surface separation between the base and the coating MoC–Zr.

After pumping out the working volume and obtaining the required vacuum level [9], a vacuum arc discharge with an integrally cold cathode is formed between the dispersed cathode and the anode of the system using the igniting electrode. The plasma stream generated in this way is fed into the vacuum chamber. The movement of charged plasma stream particles occurs in a divergent magnetic field formed by the magnetic system of the plasma generator [10].

The action of the leakage valve is controlled by a micro electromotor as part of a microcontroller electronic device (figure 1), which determines the vacuum level in the working chamber using an ionization pressure sensor. The microcontroller software controls the thresholds for switching operating modes using the buttons on the front panel of the device and is shown on the sign-synthesizing indicator. The specified parameters of the vacuum arc installation are entered in the non-volatile memory of the microcontroller and are available for later use.

**Figure 1.** Appearance, internal structure and a fragment of the electrical circuit diagram of the device developed for process control.
The step-by-step structure of nanolayers formed from metal plasma stream generated using vacuum arc discharge is created by varying the pressure of the reactive gas in the vacuum chamber in a linear form in a certain range from the smallest \( p_1 \) to the largest \( p_4 \) (figure 2).

![Figure 2](image_url)

**Figure 2.** The principle of changing the working gas pressure in the system and the composition of the applied coating layers.

In the range of operating pressures \( p_0 \ldots p_1 \ldots p_2 \) \((8.7–33–45 \text{ mPa})\) coating layers applied from metal plasma stream are created from both Zr ions and atoms sprayed under the influence of the cathode spot of the vacuum arc discharge.

Increasing the concentration of reaction components (\( C_6 H_6 \)) in the vacuum chamber in the pressure range \( p_2 \ldots p_3 \) transforms the phase composition of the plasma stream and provides the required parameters for initializing and performing the operation of plasmachemical synthesis of a chemical compound with the formation of a carbide of a variable composition with a lack of carbon Zr\(_{1-\alpha}\). The applied carbide compound has an extended homogeneity zone (Zr\(_{0.62...} \ldots \text{ZrC}\)), within which carbon is embedded in the crystal structure of the formed coating without the appearance of new phases.

A layer of carbide compound with an increased concentration of the carbon component in the coating (Zr\(_C + C\)) is created at a pressure value in the range \( p_3 \ldots p_4 \) (more than 45 mPa). Further, when the pressure in the chamber becomes equal to the set pressure value \( p_4 \), the gas inlet is suspended and it is pumped out of the vacuum chamber to the initial pressure value \( p_1 \).

The characteristics of the resulting thin layers differ significantly with identical parameters of the monolayer, which is due to phenomena that occur during the formation of an internal structure with a large number of connections. The formed multilayer coating of a variable composition includes a set of layers applied in stages Zr–Zr\(_C \ldots -(\text{ZrC + C})\) (figure 3(a)), in the composition of which, with a variable distribution of the C content over the depth of the layer, the amount of Zr sprayed is unchanged.

When creating a multilayer structure, the length and frequency of control pulses are set based on the parameters of the vacuum chamber pumping system. The final thickness of the resulting coating was 5...6 \( \mu \)m, the duration of the application process was 50...60 min; the discharge current was 75...90 A; the bias potential set on the part was \(-100...-150 \text{ V}\).

Taking into account the atomic theory may be noted that during high-temperature chemical treatment in a vacuum structure that includes the generated set of nanolayers with variable composition Zr–Zr\(_C \ldots -(\text{ZrC + C})\) due to diffusion caused by high temperature from areas with excess C in areas with predominant content of unbound Zr, intensive chemical reaction takes place with the formation of ZrC of stoichiometric composition (figure 3(b)):

\[
\text{Mo} + [(\text{Mo}_2\text{C} + \text{MoC}) + \text{Zr}] + n[\text{Zr} + (\text{ZrC}_{1-\alpha} ) + (\text{ZrC} + \text{C})] \rightarrow \text{Mo} + [\text{MoC} + \text{ZrC} + \text{C}] + [\text{ZrC}].
\]
In the course of the research, it was found that the created ZrC coating has a high-quality crystal structure with a predominant crystallographic orientation (111). Of the lines found in X-ray diffraction patterns, all the most important lines attributed to ZrC were found: (200) || (220) || (311) || (222).

Figure 3. Schematic structure of coatings: (a) – preliminary multilayer Zr–ZrC1–x–(ZrC + C) coating; (b) – ZrC coating formed after annealing in vacuum; (c) – Pt layer deposited from hexachloroplatinate acid; (d) – final Pt3Zr coating formed after annealing in vacuum.

Next, a Pt layer with a width of no more than 10 μm was applied to the resulting ZrC outer layer of the final system in an electrolyte based on hydrogen hexachloroplatinate (IV) (hexachloroplatinate acid) H2(PtCl6)·6H2O (figure 3(c)).

During further high-temperature processing (1150...1450 °C) during structural transformations, a chemical reaction of elements with the formation of intermetallic compounds is observed in the formed structure Mo–MoC–ZrC–Pt (figure 3(d)). Of the lines found in X-ray diffraction patterns, all the most important lines attributed to Pt3Zr were found: (200) || (201) || (004) || (202) || (203) || (122) || (204) || (205) || (206) || (224).

Based on the results obtained, it can be argued that the considered technology with the use of a preliminary created Zr–ZrC1–x–(ZrC + C) multilayer system and further high-temperature annealing in a vacuum environment make it possible to form a ZrC coating layer with a stoichiometric composition and, as a result, achieve a high-quality Pt3Zr intermetallic layer and thus obtain the required performance characteristics of the antiemission coating [11].

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