Carbiding of the electrodes of electrovacuum devices

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Abstract. Modification of the surface properties of the materials of electrodes or deposition of protective coatings on them are the most effective ways to increase the service life and reliability of electrovacuum devices. Very often for these tasks operations of the carbiding of details are used. In this work results of direct carbiding of W and Mo, carried out in a mixture of the hydrogen stream and the carbon-containing gas on a technological installation of a flow type, are discussed.

Operational properties of parts and components used in the manufacture of electrovacuum devices are determined by the condition of their surface layer. This is due to the fact that the surface layer of the component during its operation is subjected to the external active mechanical, thermal, chemical or other types of impact. Therefore, modification of the surface properties of the material or deposition of a protective coating are the most effective ways to increase the service life and reliability of parts and devices [1–4].

The most widely as wear resistant coatings the refractory compounds of $d$-transition metals of IV–VI groups of the Periodic system of elements with $O_2$, $C$, $N_2$ are applied, due to the peculiarities of their crystallochemical structure [5].

1. Metals, having a lack of electrons in the inner $s$-, $p$- and $d$-orbitals, quite easily gain electrons from any source, as which can serve internode atoms of carbon, nitrogen and oxygen.

2. Most transition metals have sufficiently large atomic radii and during the formation of compounds with atoms $O$, $C$ and $N_2$ can obey the Hagg rule, according to which the ratio of the radius of the nonmetal atom to the radius of the metal atom is less than the critical value of 0.59. For the compounds of metals of IV group (Ti, Zr, Hf) Hagg rule is accurately obeyed, that leads to the formation of simple structures in which prevails the connection metal–to-metal, and atoms $C$ and $O$ can be regarded as inserted into the lattice of metal atoms.

3. Most transition metals have a wide region of homogeneity that allows depending on the content of oxygen, nitrogen and carbon to change the physical and mechanical properties of their carbides, nitrides and oxides quite noticeably.

4. Transition metals and their compounds, primarily compounds with a simple cubic structure of NaCl type (ZrC, ZrN, TiN, VC, TaC), have extremely high melting points. Very often in the manufacture of electrovacuum devices operations of the carbiding of details are used. So the source of the flow of electrons in vacuum devices is a thermionic cathode, which should ensure high durability and stable emission at the smallest possible consumption of energy for its
heating [6]. In addition, the cathode should be resistant to repeated cyclic stress and the working surface of the cathode must not break down when exposed to ions rapidly moving towards the cathode. At the same time, the higher the anode voltage is, the more energy have the ions when they reach the cathode.

During the manufacture of (W–ThO₂–WC) cathodes technological operation of the direct carbiding of the tungsten wire is used: tungsten doped with 1.5...2.0 % ThO₂ or tungsten with additives of 10 % Re and 1.5...2.0 % ThO₂ [7].

The shielding grid is used to improve current takeoff, it is electrically connected to the positive pole of the anode power source and decreases the likelihood of parasitic oscillations at high frequencies by reducing the capacitance between the control grid of the lamp and its anode (figure 1). To increase the service life of devices antiemission coatings are applied [8–10], to improve the adhesion of which, operations of carbiding of the surface of the mesh fabric are also used. To obtain a layer of the substrate material carbide, was used as a technological devices, providing a direct carbiding in an atmosphere of carbonaceous gas, and also vacuum arc plasma sources with integrally cold cathode [11].

![Figure 1. Generator lamp: (a) – design (C – cathode; G₁ – control grid; G₂ – screen (shielding) grid; A – anode); (b) – assembly of a cathode-grid node of a GU-92B lamp](image)

The phase composition of the formed coatings was studied by X-ray diffraction analysis. The elemental composition of the coatings was determined by electron probe microanalysis, based on comparing the characteristic X-ray spectra of the analyzed sample with standards of known composition. Direct carbiding of W and Mo (heavy transition elements of the sixth group with very similar mechanical, physical and chemical properties) [12] was carried out in a mixture of the hydrogen stream and the carbon-containing gas on a technological installation of a flow type.

To exclude the possibility of oxidation of the substrates and their decarbiding in the process of heat treatment the hydrogen was carefully purified from oxygen and water vapors. During annealing of the substrate to a temperature of 1500 K and above in the region adjacent to its surface, the thermal decomposition of hydrocarbons with the formation of the atomic carbon occurs, forming carbide compounds [13], while gaseous components are removed from the chamber and neutralized. The optimum condition for the formation of carbide phases and absence on the surface and in the bulk of the liquations of free carbon, is the achievement of the balance between the speed of the process of formation of atomic carbon and its rate of diffusion into the material [14, 15].

When determining the thickness of the carbide layer the fact that one of the characteristics of the resulting carbides is emerging fragility of the material, increasing with the growth of the carbide layer, was taken into account. The thickness of the carbide layer was evaluated by measuring the electrical resistance before and after the process of carbiding and by studying the metallographic sections.

As the result of carbiding the resistance of a material changes, that allows to assess the degree of carbiding γ using a method of measuring the electrical resistance of the metal before carbiding $R_{me}$
and after the process of carbidizing $R_{MeC}$: $\gamma = [\rho_{MeC} / (\rho_{MeC} - \rho_{Me})] \gamma'/(1 + \gamma')$, where $\rho_{MeC}$ and $\rho_{Me}$ – resistivity of carbide and pure metal, respectively; $\gamma' = (R_{MeC} - R_{Me}) / R_{Me}$ [16].

The advantage of using vacuum arc plasma sources is an opportunity to consistently obtain in a single technological cycle of the substrate material carbide (MoC, WC) and deposit coating of zirconium carbide. In this case, the formation of the coating is realized by deposition of ions with high kinetic energy. Changing the value of the accelerating potential $U$ allows to adjust the energy of the deposited ions, and hence to control the flow of the process of the coating formation. Preliminary condensation of the sprayed cathode material (Mo, W) to a face of an akin metal contributes to achievement of a structural-based coating, which in a subsequent diffusion reaction reduces the interfacial tension related to the difference of the crystal lattices, and improves the strength of the adhesive bond. For the implementation of plasma-chemical synthesis of carbide compounds into the flow of metal plasma of a vacuum arc discharge reactive gas benzene ($CH_2$) is introduced.

Mo has the atomic radius 1.386 Å and W – 1.394 Å, but their atomic masses ($m_{Mo} = 183.8, m_{W} = 95.94$) differ in $m_{Mo}/m_{W} = 1.916$ times, which leads to significantly different processes of interaction with plasma flow. In addition, because of the peculiarities of the electronic structure and complex covalent-ionic-metallic nature of the interatomic interactions the phase diagrams of the carbide systems of Mo and W have several structural modifications, stable in different temperature and concentration intervals. For the selected conditions of carbidizing were obtained layers consisting, respectively, of the phases of molybdenum carbide – MoC and tungsten carbide, formed from the inner layer of half carbide $W_2C$ and surface monocarbide layer of WC with a hexagonal structure. With the increase in time of carbidizing the thickness of the $W_2C$ layer increases, while the thickness of the surface WC layer has changed very little. Growth of the diffuse layers obeys parabolic temporary law [17], typical for the processes of reaction diffusion, which indicates the preferential diffusion of atoms of the nonmetal – carbon, through the lattice of the formed phases into the metal.

For the formed coatings were observed all the lines of maximum intensity characteristic to these carbides. So for lines of $W_2C$ should be noted: (321, 302) – 1.3471 ($ASTM = 1.348$) the intensity of the line 40; (200) – 2.3584 ($ASTM = 2.363$) the intensity of the line 35; (221, 202) – 1.7454 ($ASTM = 1.749$) the intensity of the line 35; (040, 023) – 1.4955 ($ASTM = 1.502$) the intensity of the line 30. In the coating there is WC compound with line: (302, 116) – 1.2836 ($ASTM = 1.281$) the intensity of the line 80. The presence in the coating of the various phases of tungsten carbide is due to the complexity of its formation at these temperatures.

The presence of the sublayer of substrate material carbide $Me_{subst}C$ with thickness up to 1 µm provides during the subsequent formation from the flow of the metal plasma of vacuum arc discharge in the environment of carbon-containing gas achievement of a coating of zirconium carbide $ZrC$ with stable composition. After the deposition in the electrolytic solution of platinum layer during heat treatment in vacuum, in the formed system $Me_{subst}(Mo,W)$–$Me_{subst}C$–$ZrC$–Pt, occurs the formation of an intermetallic compound Pt$_2$Zr.

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