Antiemissive coatings

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Abstract. High demands, the implementation of which determines the quality of the products in whole, are presented to the grid electrodes of the generating lamps as the elements that determine parameters and characteristics of electronic devices. The grid is a complex structure with a certain degree of transparency. The choice of material of the grid electrodes is determined by the conditions of their operation and design features of the device. Grid nodes are located in the area of the electron beam and during operation of a lamp they should have high heat dissipation to maintain their geometric characteristics and possess a low coefficient of secondary emission.

1. Introduction

The application of circuitry decisions in radio-transmitting devices allows to increase overall performance of the powerful generating lamps. However, the use of the principles of pulse-width modulation in modulator and radio-frequency cascades caused the essential revision of the requirements to their active elements – powerful generating and modulator lamps. Obvious need in increasing the intensifying parameters of powerful generating lamps (steepness, stability, frequency range and bandwidth) led to transition from the triode to tetrode devices, as more adapted for the specified requirements. The shielding grid electrodes preserve considerable electronic loadings in the conditions of pulse amplification. To achieve their maximum efficiency a problem of thermal stability is needed to be solved.

The grid electrodes of powerful generating lamps are made from molybdenum, tungsten, or a tungsten alloy with rhenium addition. Oxidic or thoriated and carbonized cathodes (figure 1) are used as a source of electrons. The electronic structures of the corresponding lamps providing effective switching of high currents (hundreds of amperes) at the voltage of 20…45 kV must have thin and precise structure working in the conditions of high temperatures (up to 2000 K) and carry out functional tasks of the opposite plan – to provide the highest emission ability of the cathode in hundreds of amperes and the minimum emission ability of both grids at the level of no more than units of milliampere. For powerful generating lamps the norm of undesirable thermionic emission is about 10^{-5} A/cm^2.

Constructive solutions that reduce the temperature of the grid electrodes by increasing their working surface or distance between the grid and the cathode are generally not acceptable because they decrease such technical characteristic of the lamps as steepness; also they increase interelectrode capacities, dimensions and weight. The problem of improving the properties of antiemissive coatings

is researched in many countries, but the main decisions for powerful generating lamps with filamentary thoriated and carbonized cathode only result in using multilayer coatings with end use of platinum (Pt – order number 78; atomic weight 195.08; configuration of the outer electron shells $5d^9 6s^1$; face-centered structure; melting point 2041.4 K; boiling point 4098 K; work function 5.3 eV; effective atomic radius 1.387 Å; ionization potentials 9.0, 18.56 and 23.6 eV). Platinum as an element of the eighth group in the chemical compounds is able to exhibit multiple valences: 0, +2...+6, +8.
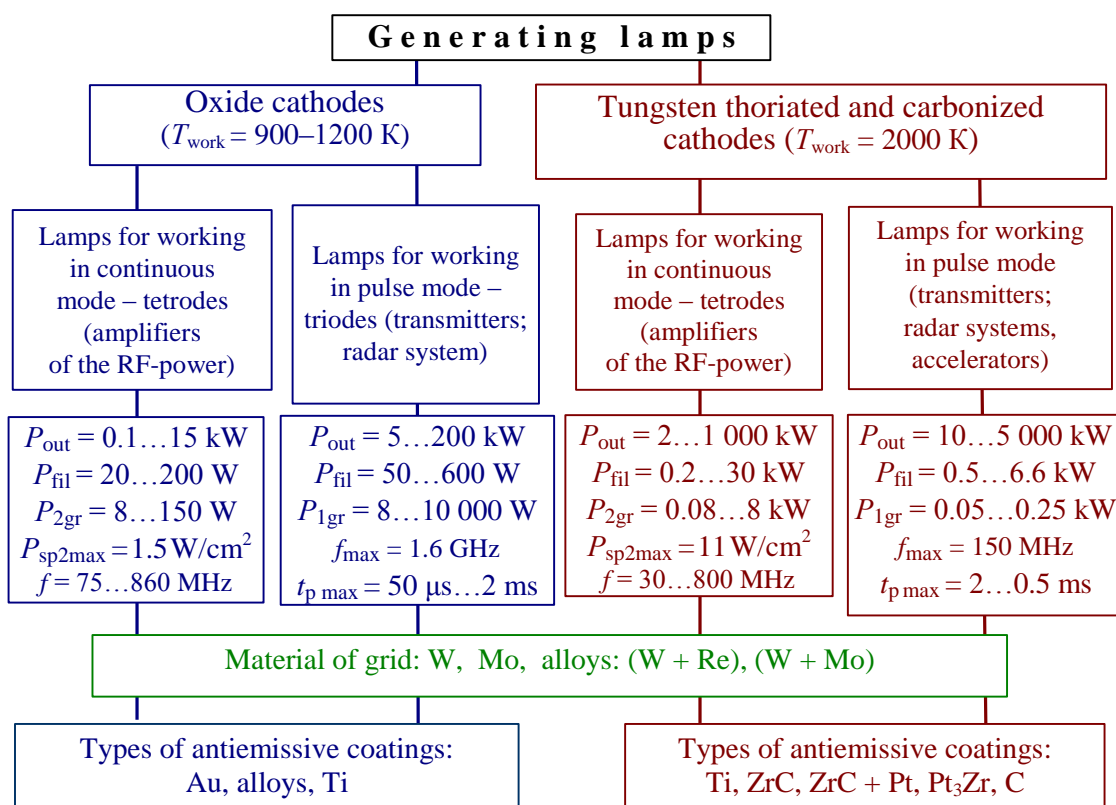

Figure 1. Operating parameters and materials of the grid electrodes.

Platinum and intermetallic compounds of platinum group metals make interest while creating high-temperature alloys and a compound based on platinum and zirconium (Zr) has proven its effectiveness when used as antiemissive coating of the grid electrodes of powerful generating lamps [1]. In such devices antiemissive coating consists of a layer of platinum and a layer of zirconium carbide (ZrC), acting as a diffusion barrier between the platinum and the core grid. To reduce the thermionic emission, the grid electrode is coated with a metal of the VIII group of the periodic system, in particular platinum. To reduce the diffusion of platinum into the core grid between the base metal and platinum an intermediate layer consisting of compounds Zr–Pt or Ti–Pt is applied.

2. Technology of receiving antiemissive coatings

The technology of obtaining antiemissive coatings consists of the following technological operations: by the method of cataphoresis a powder intermetallic compound Zr–Pt or Ti–Pt with a thickness of 5…10 μm is deposited onto the grid, after which it is baked for 20 minutes at a temperature of 1773…1873 K in an inert atmosphere or in vacuum; the next three microns layer of Pt is formed by electrolysis, after which the grid is again annealed in vacuum. By adjusting the particle size of the powder of the intermetallic compounds the surface roughness can be accurately determined and thereby secondary emission of grid electrode can be purposefully influenced.

The grid electrodes of generating lamps with a big capacity of thermal load made from Mo, W or Ta have the antiemissive coating, including the intermediate layer formed by metalloid and metal of which the grid is made, and a platinum blanket. Preferable thickness of an intermediate layer with a small roughness makes about 15 % of width of a metal wire. Thickness of a superficial metal layer of platinum reaches 30 μm.

In [2] possibility of receiving an antiemissive intermetallic coating of Pt$_3$Zr is shown. In this technological process for deposition of carbide of zirconium coating the plasma arc method is used, which is carried out by a plasmatron with self-established arc length in argon with a pressure of 10 kPa.

In recent time improving the parameters of the devices is only possible by the use of more efficient technological processes and by achieving new performance properties of the used materials by creating complex systems of multilayered structures of alloys or chemical compounds. The most perspective method for surface treatment of materials is the method of using the fluxes of metallic plasma generated by vacuum arc discharge with integrally cold cathode. This type of technological equipment provides high efficiency when receiving the ionized and high-speed flow of substance, opens the possibility to control technological process of deposition from plasma of various pure metals, implement plasmachemical synthesis of simple and complex compounds, reproduce alloys and obtain complex combined coatings. The technological process in vacuum ensures the purity of the obtained coatings and high adhesion on materials with various physical and chemical parameters.

The formation of intermetallic compound Pt–Zr occurs at high temperature in vacuum on a refractory substrate (Mo, W) in the presence of a stable layer structure of ZrC in the existence of platinum. Unlike the solid solutions intermetallic compounds usually have a complex crystalline structure different from the structures of initial materials and properties unlike to the original components. The composition of the intermetallic compounds does not always obey the rules of valency and therefore any formed compound is characterized by its crystal structure and its individual properties.

For modifying the phase structure of the processed surface and formation of a ZrC coating vacuum arc plasma sources of coaxial and extended designs were used. The zirconium carbide coating (with thickness 5…8 μm) was synthesized in a flux of metal plasma in the environment of carbon-containing gas (C$_6$H$_6$). Platinum with thickness of 10 μm was deposited in an electrolytic solution containing hexachloroplatinic acid (H$_2$(PtCl$_6$)·6H$_2$O), disodium hydrogen phosphate (Na$_2$HPO$_4$) and diammonium hydrogen phosphate ((NH$_4$)$_2$HPO$_4$) at a current density of 0.015…0.045 A/cm^2.

Chemical heat treatment was carried out in vacuum at a temperature of 1300…1700 K. In the created system reactions of interaction proceed in a certain functional order. As a result of the high-temperature diffusive processes, defining kinetics of change of materials properties and nature of phase transformations, and also exchange chemical reactions, occurs an interaction of elements forming intermetallic connection

$$\mathrm{ZrC} + \mathrm{Pt} \xrightarrow{T} (\mathrm{Zr} + \mathrm{C}) + \mathrm{Pt} \xrightarrow{T} \mathrm{Pt}_x\mathrm{Zr}_y + \mathrm{C} \,.$$
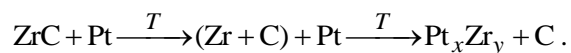
The composition of the formed intermetallic compound depends on the quality and thickness of the formed layer of zirconium carbide, the thickness of the layer of platinum, the surface properties of the substrate (the presence of a transition layer and barrier layer), as well as on time and temperature of vacuum annealing.

3. Characteristics of intermetallid Pt–Zr coatings

The X-ray phase analysis showed that at the chosen temperature of formation of an intermetallid Pt–Zr varying the time of vacuum annealing allows to change structure of the formed coating. It was found that each couple of elements (in certain limits of structure and temperature) is capable to form some types of nonstoichiometric compounds, in each of which in the field of homogeneity a number of transitional phases is observed. Structure of an intermetallid with 15…20 at. % Zr is characteristic for Pt$_4$Zr compound; with 20…30 at. % – Zr–Pt$_3$Zr; with 60…65 at. % – Zr–Pt$_3$Zr$_5$; compound PtZr in high-temperature (β-PtZr, structure of CsCl) and low-temperature (α-PtZr, structure of CrB) phases contains 47…54 at. % Zr. At temperatures of annealing of 1400…1600 K the main phase as a part of a

coating is intermetallic connection Pt_3Zr which in the range of working temperatures is capable to chemically connect thorium (Th).

In a crystal lattice of a metallid Pt_3Zr atoms of metals hold strictly certain positions, as if creating some sublattices inserted one into another. In these sublattices there is a significant amount of unoccupied sites that provides creation of connections with high valency. Intermetallic compounds based on platinum retain stable properties in a narrow temperature interval, which is associated with high polarizing effect of platinum and effect developing when heating its compounds that results in destruction of chemical bonds and the restoration of the metallic state. This leads to the gradual decomposition of Pt_3Zr followed by the formation of compounds $Pt_{11}Zr_9$ and Pt_9Zr_5. Thus the processes of counter diffusion which are characterized by different coefficients of diffusion of atoms (atoms of free platinum in a substrate and substrate material in a coating) migrating towards each other start proceeding actively (Kirkendall's effect). This effect is caused by the chaotic thermal movement of atoms and existence of the gradient of concentration directed towards decrease of this concentration.

Due to the high diffusion mobility of the components the diffusion zone reaches significant proportions: molybdenum is fixed throughout the depth of the formed coating Pt_3Zr; and the diffusion of platinum, passing along the edges of the crystals, is fixed at a depth of 20 μm or more (figure 2).
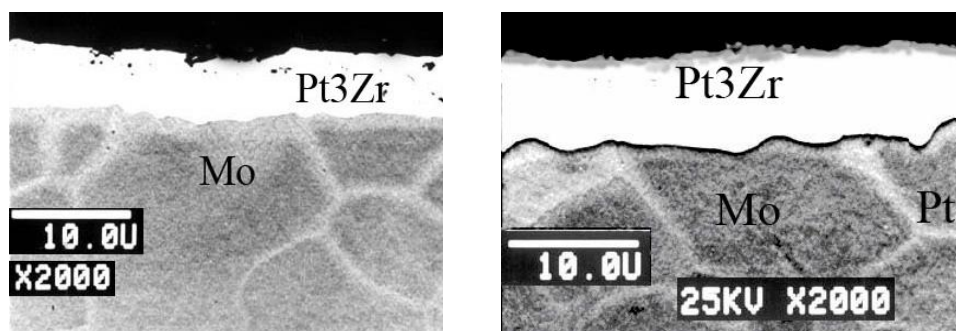

Figure 2. Metallographic sections of an intermetallic coating Pt_3Zr on a molybdenic substrate with traces of diffusion of platinum in molybdenum (scale: 10.0U = 10 μm).

Diffusion along the grain boundaries occurs many times (sometimes by several orders of magnitude) more intensively than in the bulk of grains due to the lower activation energy of the diffusion. Observation of such large grains of molybdenum of variable size indicates that sample is in the temperature region above the recrystallization temperature. Grain growth occurs by the addition of atoms from the surrounding deformed volume to the crystal lattice of the growing grain. Because of the relatively small differences in the sizes of atoms of molybdenum and platinum (Mo – 1.45, Pt – 1.39 Å) in the diffusion region, in a considerable range of concentrations the unlimited formation of solid solutions and such metal compounds as MoPt and Mo_2Pt is typical.

With increasing temperature and time of operation the factor of dissolution diffusion of the intermetallic coating into the substrate material becomes dominant. Increase of the initial thickness of the coating is not able to stop a counter-diffusion of the substrate material into the coating. For inhibition of these processes it is necessary to use an additional barrier layer. When choosing a solution it was assumed that the rate of diffusion in multilayer coatings is significantly lower than in single layer, so any phase boundary represents the energy barrier for the diffusing atoms. Thus the rate of diffusion will be lower the more densely structure is packed and the higher is the value of the bond energy between atoms. Previously it was shown that carbides of transition metals are able to perform the barrier layer function.

4. Deposition of a carbide layer

With regard to the mesh material of which grid is made, the following technological processes of carbidization were used: for items made of pure molybdenum and tungsten or a combination of molybdenum and tungsten direct carbidization in the atmosphere of carbon-containing gas was used; for

items, in manufacture of which niobium was used, with the aim of reducing the time of interaction of niobium with hydrogen, was used carbidization in vacuum with a partial supply of carbon-containing gas into the working volume. Direct carbidization of molybdenum and tungsten was carried out in a mixture of the hydrogen stream and carbon-containing gas on the technological flow-type installation. To exclude the possibility of oxidation of the substrates and their decarbidization during the heat treatment, the hydrogen was carefully purified from oxygen and water vapor. During annealing of the substrate at a temperature of 1500 K and above in the region adjacent to its surface, hydrocarbon is thermally decomposed with the formation of atomic carbon, that reacts and forms carbide compounds [3]; gaseous components are removed from the chamber and neutralized ($Me + C_nH_n \rightarrow MeC + H_2\uparrow$). The optimum condition for the formation of carbide phases and avoiding the formation on the surface and in the volume of liquate free carbon is to achieve a balance between the speed of the process of formation of atomic carbon and its rate of diffusion into the material.

Compounds of carbon with hydrogen differ in the nature of bonds, number of atoms in molecules and molecular composition. With increasing number of carbon atoms in the homologous series of hydrocarbons their melting and boiling points usually increase. Thus, the composition of the feed gas determines the yield of carbon from the compound and speed of reaction. As a carbon-containing gas, depending on the chosen method of carbidization, natural gas or benzene was used. To obtain stable results in the process of carbidization it is necessary to provide a constant feed rate of hydrocarbon into the working volume.

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 estimated by measuring the electrical resistance before and after the process of carbidization, and also by studying metallographic sections [4]. As a result of carbidization the resistance of a material changes, which allows to assess the degree of carbidization γ with a method of measuring the electrical resistance of the metal before (R_{Me}) and after (R_{MeC}) carbidization: $\gamma = [\rho_{MeC} / (\rho_{MeC} - \rho_{Me})][\gamma' / (1 + \gamma')]$, where ρ_{MeC} and ρ_{Me} are the electrical resistivity of the carbide and pure metal respectively; $\gamma' = (R_{MeC} - R_{Me}) / R_{Me}$.

The advantage of using vacuum arc plasma sources is the ability to consistently obtain in a single technological cycle the carbide substrate material (MoC, WC) and zirconium carbide [5]. In this case the formation of the coating is carried out by deposition of ions with high kinetic energy. Changing the value of the accelerating potential U allows to adjust the energy of ions and hence to control the flow of the process of coating formation. Preliminary condensation of sputtered cathode material (Mo, W) to the edge of related metal helps to ensure a structurally oriented coating that in a subsequent reaction of diffusion reduces interfacial tension caused by differences in the crystal lattices and improves the strength of the adhesive connection.

Because of the peculiarities of the electronic structure and complex covalent-ionic-metallic nature of the interatomic interactions carbide phase diagram of systems of Mo and W have several structural modifications which are stable in different temperature and concentration intervals [1]. For the selected conditions of carbidization layers were obtained, consisting of the phases of molybdenum carbide – MoC and the tungsten carbide formed from the inner layer of semicarbide W_2C and surface monocarbide WC layer with hexagonal structure. With increasing time of carbidization thickness of W_2C layer increased, while the thickness of the surface WC layer has changed slightly.

For coating deposition on a grid with height more than 150 mm the plasma source with extended design with length of 450 mm was used, operating in a pulsed mode and generating a directional tape flux. Developed plasma sources provide a lower operating temperature of the cathode, thereby achieving a reduction in the number of droplets generated into the plasma flux and increase in the quality of the coating. For molybdenum grids not exceeding a height of 150 mm vacuum arc plasma sources of coaxial structure with the diameter of the cathode 100 mm were used [6]. The presence in the technological installation of two evaporators with molybdenum and zirconium cathodes allows conducting a consistent deposition onto the grid of a sublayer of molybdenum carbide and then a coating of zirconium carbide.

For the synthesis of carbide in vacuum arc plasma source a wide range of gases was used – from methane (CH_4) to cyclohexane (C_6H_{12}). Experiments have shown that with increasing relative molecular weight of hydrocarbon molecules the yield of carbon increases. Aromatic compounds give a higher percentage yield of carbon compared to the naphthenic molecules (cyclohexane C_6H_{12}) or paraffin (*n*-heptane). The most effective yield of carbon is achieved by using methane, which has the lowest relative molecular mass of these compounds, while the hydrocarbons of high molecular weight have an increased output of carbon black [7]. During experiments Pt_3Zr coating obtained on a refractory substrate (Mo) with a barrier layer of molybdenum carbide MoC (system: $Me_{subst}(Mo,W) - Me_{subst}C - ZrC - Pt$), was subjected to heat treatment and the changes in the composition of the coating were monitored [8].

5. Results and discussion

The phase composition of coatings was studied by X-ray diffraction analysis. Studies were conducted on X-ray device DRON-2 in the $Cu_{K\alpha}$ radiation at a voltage of 50 kV and using the four slotted nickel monochromator. The elemental composition of the coatings was determined by electron probe microanalysis, based on the comparison of the characteristic X-ray spectrums of the test sample with standards of known composition. The integral sensitivity of the method is approximately 0.5 weight %.

On the obtained diffraction patterns all the lines specific to the compound, but of lesser intensity compared to the original were recorded, while no other connections or loose components were observed. The plot of one of the diffraction patterns of the Pt_3Zr coating has the following registered lines: (201) – 2.3622 (ASTM-2.3601); (004) – 2.3076 (ASTM-2.3061); (202) – 2.1616 (ASTM-2.1616); (203) – 1.9125 (ASTM-1.9120); (205) – 1.4741 (ASTM-1.4719); (206) – 1.3026 (ASTM-1.3009).

Analysis of metallographic sections of the coatings showed the presence in all of the studied samples of a thin edge carbide layer of the substrate material with a thickness of about 1 μm and in some cases it was observed the presence of characteristic contrasting areas saturated with carbon, also reproduced on the distribution profiles of the elements. For comparison figure 3 presents the distribution of molybdenum and platinum on samples with a barrier layer (figure 3, a) and on similar samples, but without carbide layer of the substrate material (figure 3, b).
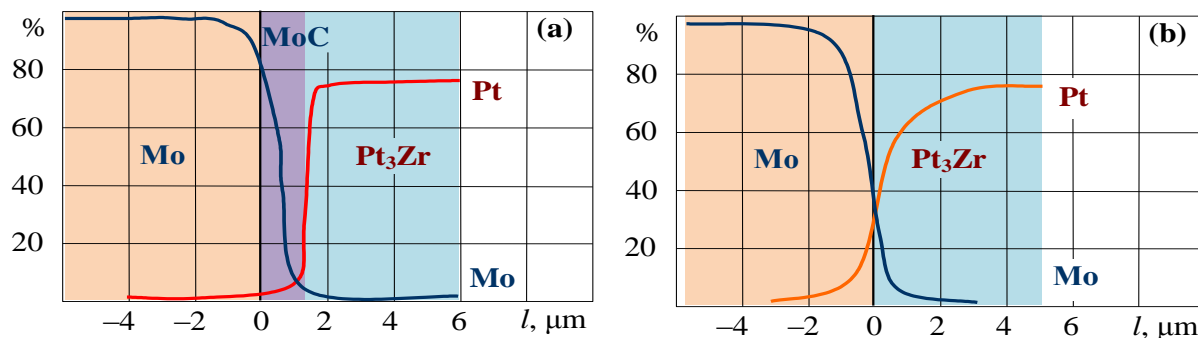

Figure 3. Distribution of elements across the depth of the metallographic section of the Pt_3Zr coating on a molybdenum substrate with (a) and without (b) the underlayer of the molybdenum carbide after 75 h of operation.

In the presence of the barrier layer of the carbide of substrate material on the phase boundary it is observed an abrupt drop in the concentration of diffusing metals in the transition from one layer to another (figure 3, a). In molybdenum, base metals included in the composition of antiemissive coating were not observed and molybdenum was not found in the coating.

Thus, the proposed technology allowed obtaining a multilayer antiemissive coating containing as the underlayer carbide of refractory material, which creates favorable conditions for obtaining a high quality intermetallic compound Pt_3Zr and prevents the counter flow diffusion processes; and improves the lifetime performance properties of antiemissive grid coatings in powerful generating lamps.

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