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Desorption of gases from cathode materials in electrovacuum devices during the production process

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Abstract: Desorption of gases from cathode materials in electrovacuum devices (EVDs) is one of the key problems in the production process, which has a significant impact on the performance and durability of devices such as magnetrons, X-ray tubes and vacuum amplifiers. For example, cleaning the surfaces of EVD parts during production inevitably entails their reactions with air components after extraction from the processing zone, and the process of degassing heating during pumping often contributes to an additional complication of the structure and chemical composition of the surface layer, since impurities diffusing to the surface can cause the appearance of new substances. Therefore, even when choosing cathode materials or parts of internal fittings, EVDs are guided by the ability of the material to quickly remove gases, maintain strength at high temperatures and have high chemical resistance. The present paper is a detailed analysis of modern methods of desorption acceleration, the mechanisms of this process and their computational basis, including known physical laws and models of adsorption and desorption. Promising approaches to improving the quality of cathodes at different stages of their production, with an emphasis on the use of new materials and technologies, are evaluated. Calculations confirming the effectiveness of the proposed solutions are analyzed, as well as the influence of various factors on minimizing the impact of desorption processes and increasing the durability of cathodes in EVDs.

Keywords: desorption; cathode materials; thermal desorption; vacuum technologies; gas release; electro-vacuum devices; pumping; emission properties; ion purification; desorption kinetics.

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Десорбция газов из материалов катодов в электровакуумных приборах в процессе производства

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Аннотация: Десорбция газов из материалов катодов в электровакуумных приборах (ЭВП) является одной из ключевых проблем в процессе производства, оказывающей существенное влияние на производительность и долговечность таких устройств, как магнетроны, рентгеновские трубки и вакуумные усилители. К примеру, очищение поверхностей деталей ЭВП в процессе производства неизбежно влечет за собой их реакции с компонентами воздуха после извлечения из зоны обработки, а процесс обезгаживающего нагрева во время откачки нередко способствует дополнительному усложнению структуры и химического состава поверхностного слоя, поскольку примеси, диффундирующие к поверхности, могут вызвать появление новых веществ. Поэтому даже при выборе материалов катодов, деталей внутренней арматуры ЭВП руководствуются способностью материала быстро удалять газы, сохранять прочность при высоких температурах и обладать высокой химической устойчивостью. Приведен подробный анализ современных методов ускорения десорбции, механизмов этого процесса и их расчетных основ, включая известные физические законы и модели адсорбции и десорбции.

Оценены перспективные подходы к улучшению качества катодов на разных этапах их производства, с акцентом на использование новых материалов и технологий. Проанализированы расчеты, подтверждающие эффективность предложенных решений, а также влияние различных факторов на минимизацию влияния процессов десорбции и повышение долговечности катодов в ЭВП.

Ключевые слова: десорбция; материалы катодов; термодесорбция; вакуумные технологии; газовыделение; электровакуумные приборы; откачка; эмиссионные свойства; ионная очистка; кинетика десорбции.

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1. Introduction

The production of vacuum tubes is one of the most complex industries. This is due to the fact that the stability of the electrovacuum device (EVD) depends not only on the preservation of the shape and condition of the parts, the choice of materials, the appropriate technology for their processing and compliance with the entire technological process of manufacturing the device. Fulfillment of the conditions of mechanical precision of manufacture and assembly does not guarantee durability and manufacturability due to the processes of material desorption during the technochemical stages of production and further operation or storage of EVDs. In particular, the materials of electrodes, which ensure the correct functioning of the device, are subject to desorption or spraying.

During various stages of production, a layer of the gas phase inevitably forms on the surface of cathodes. During degassing heating during pumping out EVDs, the structure of oxide films and adsorbed impurities becomes more complex, often changing its chemical composition due to diffusing elements from the volume of materials. This can lead to significant changes in the emission properties of the cathode, contamination of the vacuum environment and complete failure of the device. Therefore, one of the main production tasks is to remove chemically adsorbed gases and impurities such as hydrogen, oxygen and hydrocarbons from the cathode surface. The materials used in production are assessed by their ability to quickly remove gases, low vapor pressure, strength at high temperatures, thermal expansion coefficient, thermal conductivity, electrical conductivity, high insulation resistance even at high temperatures and chemical resistance. The purity of the material also plays a decisive role, since even small impurities can significantly affect the performance characteristics and service life of devices. In particular, when the vacuum conditions in instantaneous magnetrons deteriorate from 10^{-8} to 10^{-7} mm Hg, the current density from the field emission cathode decreases from 7.0 to 5.6 mA·cm^{-2} (Fig. 1) [1]. The use of materials with a minimum gas content can be attributed to the mandatory requirements for the materials of EVD parts, since maintaining low pressure in the vacuum

In recent years, research in the field of adsorption and desorption phenomena on EVD cathodes has focused on understanding the physicochemical processes occurring on the surface and inside the cathode material, as well as on developing new methods for controlling these processes in order to improve the efficiency and stability of devices [2–4]. Thus, modern studies emphasize the importance of not only the chemical nature of adsorption, but also its kinetic aspects. For example, experiments using various spectroscopy methods allow observing changes in the surface states of cathodes in real time when exposed to a gas environment [5]. This helps to refine the interaction models and optimize the operating conditions of devices to minimize the negative impact of desorption. Another important aspect of recent research is related to the effect of adsorption on the emission properties of cathodes [6]. Especially it is noticed in the context of high-precision and highly sensitive applications, where even small changes in the emission level can significantly affect the operation of the device. Studies show that adsorbed layers can cause temporary or permanent changes in the function of the cathode, which requires the development of specialized coatings or evacuation methods to eliminate or minimize this effect. At the same time, promising solutions related to the development of new materials and modifications of cathode surfaces by forming protective layers are increasingly being proposed.

The purpose of this review is to comprehensively analyze modern approaches to gas desorption processes from cathode materials used in vacuum tubes with an emphasis on increasing their durability and performance characteristics. The review covers the latest advances in heat treatment, radiation and electron exposure, and the use of nanomaterials, providing an interdisciplinary approach to solving desorption problems. Particular attention is paid to theoretical models based on Fick's

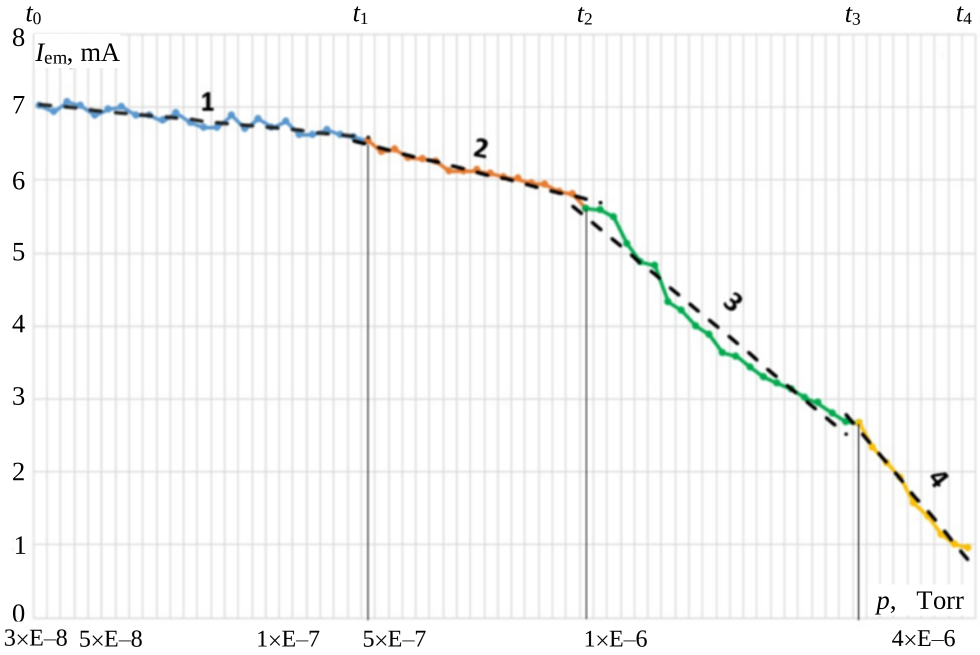


Fig. 1. Dependence of the autoelectronic emission current on the pressure in the chamber [1]

and Arrhenius's laws, as well as practical recommendations for production optimization. The work is aimed at integrating theoretical knowledge and modern technologies to create more efficient and reliable devices.

2. Thermally activated desorption

Thermally activated desorption is widely used in industrial processes to improve the quality of cathodes in EVDs. In most cases, vacuum degassing requires thermal activation of cathodes or additional thermal cleaning. Classical studies of cathode heat treatment [7–9] provided the basis for modern methods of removing impurities through heating. These studies showed that cathode temperature above 1000 °C significantly increases the desorption rate for all materials. Modern studies [10, 11] have confirmed these data and proposed more accurate models to describe the processes of gas diffusion on the cathode surface. For example, the Fick equation for diffusion allowed us to accurately calculate the concentration of impurity gases on the cathode surface and the time required for their complete removal:

$$\frac{\partial C}{\partial t} = D\frac{\partial\ C}{\partial x^2},$$

where C is the impurity concentration, D is the diffusion coefficient. If we assume that the activation energy of capture is identical to the activation energy of diffusion in the lattice the activation of desorption will be equal to the sum of the diffusion energy and the energy barrier, which is in good agreement with the experimental spectrum of pure iron with careful surface treatment [12].

At the same time, more often, modern studies of basic EVD designs give hope for the creation of computer methods for calculating and modeling surface processes for their further generalization to technological units with a more complex elemental composition [13].

Detailed studies of thermal desorption are presented in [14]. An extensive analysis of the temperature and pressure effect on the desorption characteristics of various cathode materials was carried out. In the process of thermal vacuum treatment of cathodes, an incorrectly selected pressure can lead to insufficient or excessive desorption. Thus, a pressure of 10^{-3} mbar leads to an increase in the desorption flux for scandate-based cathodes by 25 % compared to a pressure of 10^{-2} mbar. With regard to thermal treatment, scandium oxides are preferable in production, since they reduce the work function to 1.6–1.8 eV compared to traditional cathodes, for which this figure is 2.0–3.0 eV. The addition of scandium oxides to cathodes made of other materials helps to improve the thermal stability of cathodes at high temperatures (up to 1500 K). In particular, Sc_2O_3-based cathodes demonstrate stable emission characteristics for 1000 hours of continuous operation at temperatures up to 1200 K, which is superior to most similar materials [15]. Tungsten and thorium-based cathodes also demonstrate the efficiency of thermal desorption under high-temperature conditions. For them, a characteristic increase in desorption begins at a temperature of 1200 K, contributing to an increase in gas evolution by 40 % compared to a temperature of 1000 K [16].

From a physical point of view, the activation of desorption and diffusion processes during pumping out EVDs through long-term thermal vacuum treatment can effectively remove a significant amount of gas components from the internal surfaces and from the volume of the device parts. However, long-term thermal vacuum treatment can entail a decrease in the emission characteristics of the cathodes due to additional chemical transformations on the surface or destruction of the surface layer. Improvement in the work function of tungsten, molybdenum and barium oxide cathodes was noted only when heated in a certain temperature range [17]. Samples made of nickel, after preliminary long-term 12-hour thermal degassing at a temperature of 800 °C in a vacuum, released CO at each bombardment pulse with energy of 270 eV at room temperature. Further investigation revealed that the surface of the nickel samples was covered with a thin but strong insulating film of carbon-containing nickel oxides [18]. In addition, the possibility of mass transfer of metals inside and outside the finished devices should be separately highlighted. Quite a few cases of the manifestation of the volatile properties of metal oxides have been described in the literature [19–21]. Some volatile properties of molybdenum MoO_3 and copper CuO oxides have been considered in detail. The partial pressures of these oxides when heated to 600 °C are approximately 10^{-3} and 10^{-2} Torr, respectively. It is also noted that BaO molecules evaporate without decomposition at low temperatures, despite the high boiling point of this compound. At approximately 800 K, dissociation of BaO_2 molecules begins, which leads to further evaporation of metallic barium [20].

It is known theoretically that the cathode temperature can be affected by several factors simultaneously: the heating model and the temperature coefficient of heater resistance. To solve the problem of excessive desorption during heating, they resort to optimizing temperature conditions [22] and monitoring the current cathode temperature during thermionic emission [23] or using a synergistic effect with new approaches to stimulating desorption and diffusion processes [24–26]. The paper [26] shows that the cathode temperature decreases as the current collected by the anode increases. When the emission current was 180 mA, which corresponded to a current density of 2.92 $A{\cdot}cm^{-2}$ the cathode temperature decreased by 29 °C in the constant voltage heating mode and by 35 °C in the constant current heating mode.

3. Ultraviolet radiation and ion cleaning

At certain stages of vacuum tube production, methods such as ultraviolet irradiation or ion cleaning are used to accelerate desorption processes. Compared to traditional heat treatment, calculated data indicate an increase in the rate of desorption processes during UV treatment by several times [27]. The threshold energy for neutral desorption can be quite low, down to 5 eV (far ultraviolet radiation). At higher energies (15 eV), ion desorption can be expected [28]. The promise of this method lies in its effectiveness when used at the final stages of cathode production, when it is necessary to remove remaining impurities before installing the cathodes in devices. In addition to removing contaminants at the atomic level, UV radiation, due to its local effect of high energy density, made it possible to carry out controlled nanostructuring [29].

Research in this area over the past 10 years has been aimed at finding modes and criteria for cleaning electrodes. The optimal ratio between the ignition voltage, working gas pressure, DC glow discharge current and the distances between the EVD components made it possible to reduce the pumping time by 2.0–2.5 times with lower energy costs about 15 years ago [30]. However, with the advent of new cathode materials and more stringent operational requirements for devices, it became necessary to improve the classical methods. Cathodic plasma electrolytic treatment is a new technology for preparing a surface for further processing or creating surfaces with specified properties [31]. Using a plasma discharge caused by electrolysis and the cooling effect of the electrolyte, metal cleaning and subsequent deposition of a thin metal film are effectively achieved. The most common methods of film creation in production are physical or chemical vapor deposition [32, 33]. These methods require separate preliminary treatment of materials, while the spraying process itself is quite lengthy. The plasma electrolytic processing process, having four simultaneous effects from a strong electric field, oxidizing free radicals, ultraviolet light and a shock wave, turns out to be cost-effective and environmentally friendly [34].

However, its application in the field of electronics still needs to be adjusted in relation to the modes and conditions of the process. The most practically oriented developments are pumping technologies for EVDs with secondary-emission cold (non-heating) cathodes [35]. The main feature of the method is a combination of ion cleaning with sequential degassing of the device components, which includes the use of high-energy ions to remove adsorbed gas molecules. In the process of ion cleaning, ion flows are created directed at the surface being cleaned. This helps remove contaminants at the molecular level, including residual molecules such as hydrogen and oxygen, and reduces the preparation time of devices by 40 %. Other studies show the same results [29], which reinforces the prospects of the method in its application for mass production. The most successful examples of combined technologies to date include the processing of cathodes in instantaneous devices such as magnetrons. In these devices, the use of combined methods ensures low levels of desorption in the vacuum cavity and stability of thermionic emission.

The disadvantages of the method include the possibility of initiating a chemical reaction with impurity gas molecules on the cathode surface or an uneven temperature distribution, which becomes especially noticeable in nanoscale areas. Nanosecond pulses of UV radiation are capable of transferring energy so quickly that the material does not have time to transfer heat to deeper layers. Due to this, it is possible, if necessary, to controllably limit the surface effects of evaporation and desorption [36–38]. This ability additionally opens up possibilities for using these effects in microelectronics and nanotechnology, especially for the creation of thin films or controlled modification of surfaces [39, 40].

4. Electron desorption and radiation effects

Electron desorption was actively studied back in the 1960s, which made it possible to establish the mechanisms of this process [41]. It was found that even low-energy electrons can effectively desorb gases adsorbed on the metal surface, and the desorption rate increases with increasing electron energy and increasing irradiation time. Thus, when exposed to electrons in the range from 1 to 30 eV on tungsten, copper and platinum under conditions of maintaining a pressure of 10^{-9} Torr, desorption of oxygen and carbon dioxide occurs. Cold cathodes made of nickel and cobalt when exposed to electrons with energies from 1 to 50 eV demonstrate acceleration of hydrogen and argon desorption.

Among modern studies, there are works that examine in detail the effect of all types of radiation on the desorption capacity of the surface [42, 43]. Experimental data show that radiation can significantly change the desorption mechanisms, accelerating or slowing down this process depending on the type and intensity of radiation. In addition, it has been shown that an applied electric field can change the distribution of charged particles and increase the repulsive force between the adsorbed molecules and the cathode surface. This is especially noticeable at high voltages, where electric fields promote acceleration of desorption. For example, when molybdenum cathodes were exposed to intense ionizing radiation, a significant activation of desorption was recorded, increasing by 30 %. Moreover, this method not only increases the quantum efficiency of the cathodes, but also does not affect the surface roughness, which is especially important for the operation of cathodes under high vacuum conditions [44].

Later, a model of gas and radiation desorption during initial high-voltage conditioning in vacuum was created [45]. The applied voltages varied from 20 to 100 kV for stainless steel electrodes, as a result of which intense desorption of impurity gases (mainly hydrogen and oxygen) began at voltages above 60 kV. According to the author, the increase in the desorption rate before reaching the threshold voltage of 80 kV is associated with the accumulation of energy in the surface layers of the metal. For example, at a voltage of 80 kV, the measured desorption rate reached 10^{16} molecules$\cdot$cm$^{-2}\cdot$s^{-1}, while at 40 kV it was about 10^{14} molecules$\cdot$cm$^{-2}\cdot$s^{-1}. It was also noted that desorption reaches a peak in the first few minutes of processing, after which the desorption rate decreases, indicating saturation of the process. A feature of this model is that it takes into account the radiation effect caused by accelerated electrons and ions, which additionally contribute to desorption. This radiation effect increases the local surface temperature to values about 200 °C, which stimulates thermally activated desorption of molecules. It is confirmed that under such conditions, radiation desorption can account for up to 20 % of the total number of released molecules in the early stages of high-voltage processing.

Thus, high radiation load leads to significant improvement of vacuum conditions in EVDs, due to active desorption of ions and molecules from the cathode surface. Desorption intensity increases sharply under radiation exposure, especially in the case of hydrogen molecules, which is associated with their high mobility and penetration into materials. At the same time, vacuum recovery after irradiation occurs slowly, which indicates prolonged activation of desorption processes in the material after exposure.

5. Cathode materials

With the increase in frequency ranges and power of modern devices, more stringent requirements arise for heat resistance, durability and stability of cathodes to external factors, such as high temperatures and intense electric fields. The manufacture of cathodes from traditional materials such as nickel, tungsten, alkaline earth metal oxides requires precise control over the conditions of all stages of their manufacture, operation and storage [46, 47]. Moreover, the structure of the cathode surface or the morphology of its coatings due to the presence of microroughness, defects or variable resistance to external influences relative to the chemical composition can also have an accelerating or decelerating effect on the desorption of the material [48]. In this case, it is necessary to take into account not only the stability of cathode emission, but also degradation processes [49]. The latest developments in this area suggest the use of new materials for cathodes, such as oxides of rare earth metals (e.g. scandate) and nanostructured coatings.

However, depending on the required operating modes, the state of all technological units of the devices should still be constantly monitored [50]. Being the most popular for high-temperature applications, scandate cathodes during long-term operation promote active accumulation of desorbed particles on the inner surfaces of EVDs [51]. Therefore, it is proposed to use more stable coatings on the cathode surface or to create multilayer structures that prevent the interaction of active elements of the cathode with the environment. The most widely used are the deposition of thin layers of atoms of alkali, alkaline earth elements and polar molecules of barium oxide [52].

The dependence of the work function on the thickness of the deposited layer is characterized by a curve in which a minimum is observed at a layer thickness of 0.6–0.7 monolayers, which is typical for various materials. The exact reason for the appearance of this minimum continues to cause controversy: it may be due not only to a decrease in the positive moment on the surface due to the bond between adatoms, but also to the presence of traces of electronegative contaminants in the device. These atoms, binding with electropositive adatoms, can enhance the emission. For example, films containing Cs–O–W or Ba–O–W demonstrate a lower work function (1.6–1.9 eV) compared to Ba–W and Cs–W films (2–2.5 eV). According to [53], the mechanism of this phenomenon is that a group of metallic adatoms is formed around the oxygen ions on the surface. Their effect compensates for the increase in the work function caused by oxygen adsorption, thereby reducing it.

The valence state of the deposited atoms can significantly affect the work function, especially if the covalent component plays a role in their interaction with the substrate. Studies described in [54] showed that when barium is deposited on a clean iridium surface (Ir(111)) the barium atoms are uniformly distributed over the surface until a monolayer is formed. However, in the presence of a small amount of carbon, the adsorbed Ba atoms tend to form island structures. This is due to the weakening of the electron interaction of adatoms with the carbon substrate, which in turn strengthens the bonds between the adatoms themselves. The opposite effect was recorded during the adsorption of barium on a tungsten surface coated with a germanium film [55]. In this case, the deposition of barium on the W surface coated with germanium led to a greater decrease in the work function compared to pure tungsten.

As noted earlier, the introduction of scandium into the tungsten base of cathodes significantly improves their thermionic characteristics. This allows for a decrease in operating temperatures, improved emission efficiency and increased durability of cathodes under operating conditions. After a more detailed analysis of the physicochemical processes on the cathode surface, it was found that the introduction of scandium helps to reduce thermal desorption, due to which the cathodes demonstrate high stability even when exposed to radiation and mechanical loads, which confirms their high reliability under harsh operating conditions.

Currently, many industrial enterprises, including JSC Pluton, manufacture microwave vacuum tubes using dosing cathodes based on tungsten sponge impregnated with barium-calcium aluminate $2.5BaO \cdot 0.4CaO \cdot Al_2O_3$. The thermionic current density of such a cathode at a temperature of 1050–1100 °C is 10–15 $A{\cdot}cm^{-2}$ [56]. Studies of the chemical composition using electron spectroscopy methods confirmed the solubility of calcium, aluminum, tungsten, and scandium in cathode materials. It was shown that the emission properties of dispersing and scandate cathodes are determined by the properties of barium oxide crystallites formed in the cathode material at the stage of its manufacture and activation, as well as the type and concentration of point defects in barium oxide. Thus, the use of thin-film coatings based on oxides and nitrides effectively blocks the penetration of gases to the active centers of the cathodes and reduces the likelihood of desorption [56].

The use of plasma technologies, such as plasma etching or ion plating, for the purpose of modifying the surface of cathodes additionally contributes to increasing the resistance of cathodes to thermal and mechanical destruction [57, 58]. Due to the precise control of the process of ion flow formation by heating the cathode to high temperatures, thermionic emission of electrons is initialized and a dense plasma discharge is created. These discharges play a key role in ion plating processes, providing a high degree of control over the parameters of thin films, such as thickness, composition and structure [40]. And plasma etching of cathodes is useful for creating specific microstructures [59, 60].

The paper [61] is a significant study devoted to the development of tungsten-based thermionic cathodes activated with nanothorium (ThO_2). The cathode fabrication involved a sintering method, which resulted in a uniform distribution of nanothorium over the surface. Such cathodes provide a lower work function and improved thermionic emission compared to traditional cathodes. For example, after activation and sintering, the operating temperature of cathodes was reduced by 200 K. An additional sintering or high-temperature annealing step to achieve better thermal stability and electrical properties of the coatings has proven useful for other materials as well [62, 63].

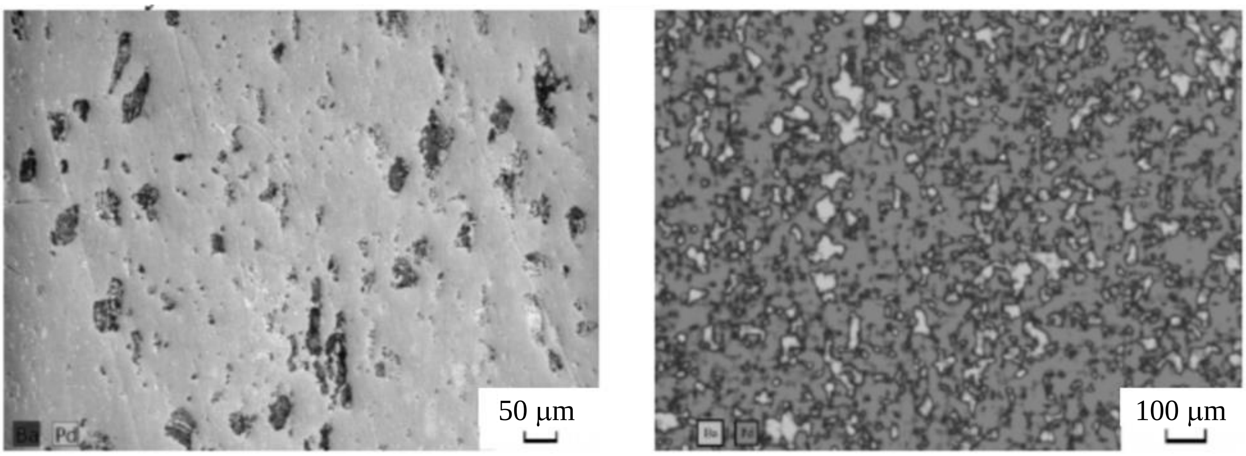
Palladium-barium based cathodes have also demonstrated superiority over traditional materials. Metal-alloy cathodes of this type are a dense form-forming matrix based on palladium containing the intermetallic compound Pd_5Ba distributed in the volume [64]. Their high emissivity is explained by the fact that when heated, a thin layer of the active element or its oxide is formed on the cathode surface, which helps to reduce the work function. Also, the presence of active elements in the volume of the material helps to maintain an emission layer on the working surface of the cathode, which provides secondary electron emission. However, the emission properties of such cathodes strongly depend on the surface structure. It is known that dispenser hot cathodes made of tungsten sponge impregnated with barium-calcium aluminate when heated to temperatures in the range of 1100–1400 K due to decomposition and thermal diffusion form a submonolayer film of Ba and BaO, which reduces the work function. The application of a thin layer of such elements as rhenium, osmium, iridium or their alloys with tungsten enhances the effect, acting as activators. It is known that the emission properties of pure BaO crystallites are determined by oxygen vacancies, which form acceptor-type surface states on the oxide surface. This leads to a significant curvature of the energy bands [65]. In this case, the electronic structure of barium oxide changes according to the synergistic effect of all the impurities present at once [66, 67]. To study the arrangement of atoms surrounding the Ba atom on the surface, a method for determining the extended fine structure of X-ray absorption by the surface was used in [68]. This method makes it possible to obtain information on the distances to the nearest neighboring atoms along the oscillating part of the absorption coefficient beyond the main band. The spectra of such absorption by three types of dispenser thermionic cathode (without coating, with Os–W and Pt – W coatings) were studied using a synchronous radiation source. The results showed that in the first two types of cathodes, barium atoms form clearly defined short-range bonds with oxygen with the Ba–O distance equal to 2.62 Å. However, in thermionic cathodes with the Os–W coating, the barium atom is bonded to two oxygen atoms, which leads to an increase in the surface dipole moment and a more significant decrease in the work function. In the case of cathodes with the Pt–W coating, the Ba–O distance turned out to be greater, and the bond between the atoms was less pronounced. In [69], the classical dipole theory of thermionic emission from dispenser cathodes was challenged by spectroscopic data obtained at a later time. The role of oxygen in providing the increased emission activity of the cathode was noted. However, in [70], when studying the secondary emission properties of impregnated tungsten cathodes using the same spectroscopy methods, as well as thermionic microscopy and high-resolution contact potential difference, a violation of the correlation of the secondary emission and thermionic properties of individual “active” surface areas was discovered. In particular, with increasing temperature corresponding to the process of heat treatment of the cathode, the secondary emission properties eventually worsen, and the thermionic properties improve, which the authors associate with a decrease in the amount of oxygen on the surface and with a change in the nature of the chemical bond of Ba with the substrate for this reason. The effect of carbon impurities on the secondary electron emission coefficient is noted. The effect of various methods of preliminary surface treatment on the emission properties of the cathode is studied. The greatest effect is achieved with sandblasting. It is shown that an increase in the pore size in the tungsten matrix reduces the secondary electron emission coefficient due to the effects of surface charging. At the same time, it should be noted that the secondary emission and thermionic properties of emitters based on metals and metal-oxide film systems depend significantly on the heating temperature, which limits the range of their use in electronic devices.

At temperatures in the range from 1000 to 1300 K, the efficiency of thermionic emission increased significantly due to the reduced work function of the barium coating (2.1–2.4 eV compared to 4.5 eV for tungsten). It was also found that secondary electron emission has a maximum quantum yield of electron emission at primary electron energies from 100 to 500 eV, which improves the performance of cathodes in microwave devices where it is important to maintain a stable electron flow. According to the proposed model of the surface structure of the palladium-barium cathode, it was calculated that the emission properties of the palladium-barium cathode significantly depend on the emission properties of the barium oxide crystallites and on the relative surface area of the cathode they occupy [71]. Quite often, various versions of the design of metal-alloy palladium-barium cathodes, which are a Pd matrix in which the intermetallic phase Pd_5Ba is distributed [72, 73], exhibit a decrease in the secondary electron emission coefficient due to the uneven distribution of the Pd_5Ba phase in the Pd matrix [74]. For the same reason, the greatest number of alloy defects and diffusion welding defects (lack of fusion, “swelling”, “delamination” of the alloy foil from the core) occur [75]. In order to eliminate the above-mentioned shortcomings, a pressed metal-alloy cathode was proposed for the industrial production of magnetrons with non-heater start-up. Activation of the surface of the working edges of field-electron cathodes (FEC) during the activation of secondary emission cathodes (SEC). After pressing and additional sintering of the cathodes in a vacuum furnace, a homogeneous and uniform distribution of barium on the working surface of the palladium-barium cathode was achieved, as shown in Fig. 2 [76, 77].

In order to increase the stability and reproducibility of generation initiation, a structurally similar cathode based on palladium with barium (Fig. 3) was subjected to special activation in the temperature range T~970–1370 K, observing the condition $T{\cdot}t \sim 1.0{\cdot}10^6–1.5{\cdot}10^7$ (K s) [78]. In this case, filiform crystals of palladium with a length of ~50–100 nm and a cross-sectional size of ~5–20 nm, partially or completely covered with barium, are grown on the end surface of the FEC.

The presence of filamentary crystals on the FEC surface significantly increases the value of the field emission current, thereby ensuring the failure-free operation of the magnetron (Fig. 4). In such a cathode design, various metals and alloys with stable secondary emission properties and resistant to the effects of ion and reverse electron bombardment can be used as SECs, along with palladium-barium emitters, for example, impregnated or oxide cathodes, iridium, platinum, osmium, intermetallic compounds, platinum with barium, iridium with lanthanum, iridium with cerium, osmium with lanthanum, etc.

The search for solutions to ensure stable electron emission has led researchers to develop alloys and composite materials. The most suitable materials for the matrix of composite cathodes are palladium, platinum, silver, copper, nickel, molybdenum and tungsten, while cesium, magnesium, lithium, barium, aluminum and their oxides are used as additives.



(a) *(b)*

Fig. 2. Samples of palladium-barium emitters with fractional compositions of the initial powder *a*) 20–45 μm, *b*) 45–63 μm [76]

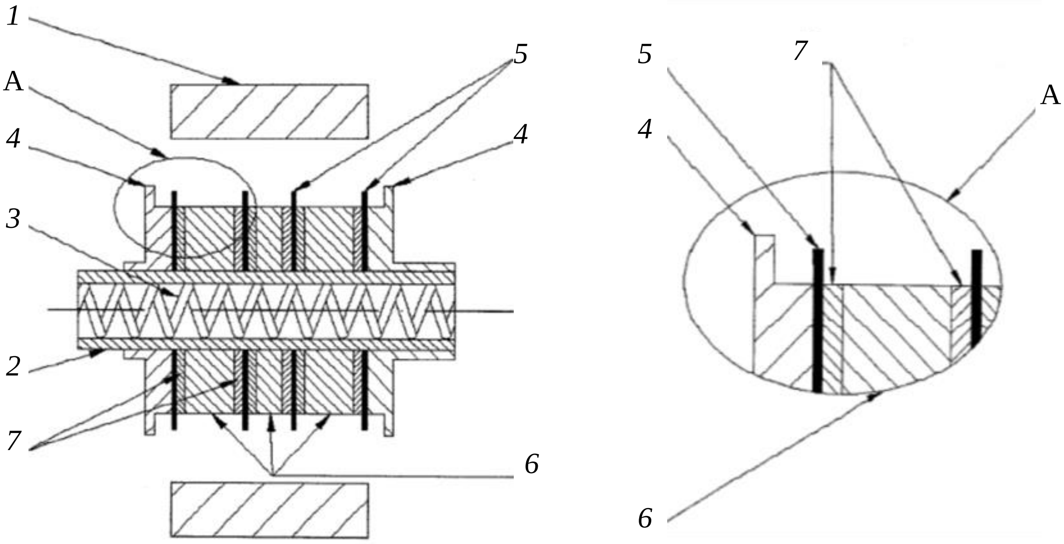


Fig. 3. Schematic representation of the magnetron structure: *1* – anode; *2* – cathode core; *3* – heater; *4* – screens; *5* – autoelectronic cathodes; *6* – secondary emission emitters; *7* – AEC activator washers [78]

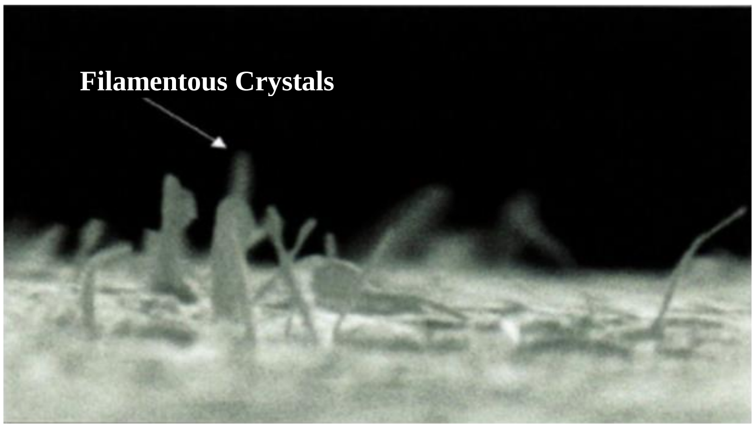


Fig. 4. Micrographs of fragments of the FEC end surface at magnification of M ~ 50000×
(inside the image: filamentous crystals) [78]

Of particular interest are alloys that can demonstrate high emission properties after activation due to the adsorption of a surface-active component located in the volume of the alloy. For example, alloys of platinum and palladium with metals of group II of the Periodic Table demonstrate good emission characteristics. In these experiments, the content of low-melting components in the alloys ranged from 0.5 to 2 weight percent. Activation of platinum alloys was carried out at temperatures of 1350–1480 K, while palladium-based alloys were activated at 1200–1300 K [79].

However, in some vacuum tubes it is impossible to achieve such high temperatures, or they may be undesirable. Low-temperature treatment of cathode assemblies does not allow for the complete removal of gas impurities and activation of the Pd–Ba alloy, so in this case activation can be carried out at lower temperatures, but in the environment of certain gases (usually H_2, N_2 or their mixtures) [80,81].

In addition to surface and structural modifications, attention has recently shifted to the latest nanomaterials that demonstrate a high density of active centers, a large specific surface area and increased catalytic activity. For example, cathodes based on nanostructured carbon nanotubes (CNTs) have improved gas desorption characteristics due to high surface activity and the presence of multiple active centers for adsorption of impurities [82, 83]. This allows for a significant reduction in desorption time and an increase in the vacuum quality in EVDs. In addition, nanostructured cathodes improve the thermal stability of materials, which is especially important at high operating temperatures of cathodes in vacuum tubes. Nanomaterials demonstrate resistance to thermal destruction and have higher durability compared to traditional metal-based cathodes.

Table 1. Summary characteristics of modern cathode processing methods

Method	Reduced pumping time (compared to basic vacuum degassing), %	Rationaluse inproduction	Disadvantages
Heat treatment	10–20	Suitable for mass production, especially when processing traditional materials (tungsten, nickel)	Risk of surface damage due to overheating; activation of chemical transformations on the surface of the material; long process; high energy consumption
Ion cleaning	30–40	Effective for removing deep contaminants. Ideal for high-precision devices	May damage the cathode surface; requires complex equipment settings; not suitable for delicate materials
Ultraviolet irradiation	20–30	Recommended for processing delicate materials and nanostructured cathodes	Less effective for heavy contamination; requires strict control of wavelength and intensity
Laser treatment	20–50	Useful for limited quantities or complex cathodes such as carbon nanotubes	High equipment cost; risk of local damage to the material due to improper settings
Plasma treatment	40–60	Ideal for processing cathodes with high thermal and mechanical loads	High energy consumption; difficulty maintaining stable plasma parameters; possible damage to the structure
Use of nanostructured materials	10–30	Rational for use in high-precision and unique devices	High production cost; difficulty in applying nanostructures

In order to improve the characteristics of CNT cathodes for their use in vacuum tubes, laser irradiation is used to treat the surface [84]. This method is used to modify the surface structure, improve electron emission and remove contaminants that may arise during the production stage. At the same time, the correct choice of gas environment during laser processing significantly affects electron emission. It was found that the presence of oxygen in the gas atmosphere during laser processing helps remove carbon impurities and improves the structural and emission properties of the cathodes. At the same time, the vacuum atmosphere preserves the structure of the nanotubes without causing significant destruction. Such treatment in an oxygen atmosphere resulted in an increase in the emission current density by 30–40 % compared to cathodes treated in a nitrogen atmosphere or vacuum.

Various carbon nanoclusters [85–87], recently used to modify metal-porous cathodes [88], seem promising from the point of view of obtaining high emission characteristics. The results of the studies indicate that nanocarbon materials improve the structural stability of cathodes and contribute to an increase in the emission current density due to an increase in the active surface area. Along with this, the durability and resistance to degradation of the cathode under thermal influence are improved [89].

Thus, in this work, a review of existing methods for controlling desorption of impurity gases necessary to increase the durability of cathodes and the stability of their operation under high vacuum conditions was conducted. Table 1 provides a summary of the characteristics of modern cathode treatment methods.

An evaluation of the literature data has demonstrated that synergy between traditional physical and chemical models and the latest scientific developments and experimental data is necessary to increase the productivity, durability and reliability of vacuum devices.

6. Conclusion

Desorption of cathode materials remains one of the main problems in the production and operation of vacuum tubes. Over the past 15 years, many methods have been proposed to improve these processes, including heat treatment, electron and radiation exposure, ion cleaning, and ultraviolet irradiation.

The importance of controlling desorption of impurity gases to ensure the durability of cathodes and the stability of their operation under high vacuum conditions has been confirmed by both experimental and calculated data. Today, depending on the practical focus and the requested requirements for the design details of various vacuum tubes, many promising approaches are available for upgrading production technologies. Studies have shown that the combined use of classical physicochemical models and modern experimental data opens up new opportunities for improving the emission characteristics of cathodes. This, in turn, helps to increase the productivity and reliability of vacuum tubes, which is especially important for high-tech applications such as microelectronics, medical equipment, and telecommunications.

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8. Conflict of interest

The authors declare no conflict of interests.

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