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ON EFFICIENT THERMIONIC CATHODES

A review of scientific works devoted to the most efficient modern thermionic cathodes – oxide cathodes and dispenser cathodes – is made. The main attention is focused on the analysis of emission mechanisms from those electron sources. In addition, the relation between the emission of dispenser cathodes and their physical and technical parameters is considered. The influence of fabrication methods on the cathode performance is discussed.

Keywords: oxide cathode, dispenser cathode, alkaline-earth metal oxides, scandium oxide, thermionic emission, field emission.

1. Introduction

Nowadays, when semiconductor, micro-, and even nanoelectronics, as well as devices created on their basis, conquered various branches of electronic technique, an impression may arise that electrovacuum devices (EVDs) are not useful for applications anymore, and, in time, they will be forgotten altogether. However, it is not so. The matter is that the developers of radio-electronic devices have understood that the solid state has restricted capabilities. In addition, under extreme operational conditions (the outer space, military objects (silos), aggressive high-temperature media), semiconductor circuits work unreliably, or they cannot be used at all. They are 10⁸ times less resistant to neutron radiation and 10⁷ times to gamma rays than EVDs. The maximum ambient temperature for semiconductors cannot exceed 250 °C, whereas EVDs reliably work even at $T \approx 600$ °C. Moreover, for today, the rather appreciable progress can be observed in the so-called vacuum microelectronics. In vacuum microelectronic devices, passive and active (electron sources) elements are fabricated in the same technological cycle, i.e. we may say about vacuum integrated circuits (VICs), in which microminiature cathodes are used.

In addition, there is a group of vacuum devices, which cannot be substituted by solid-state devices in future years. First of all, these are EVDs of ultrahigh-frequency (UHF) range used in long-range radiolocation, radionavigation, space communication receivers, high-resolution picture cathode-ray and image pick-up tubes, and so forth. In other words, EVDs are ap-

plied if electromagnetic signals of high frequency and high power have to be transformed. In addition, the electron emission in vacuum is a unique way to produce free electrons.

The basic element of any EVD is an electron source, cathode (or emitter). Its performance parameters completely govern the characteristics of an electrovacuum device. These are the power, durability, reliability, steepness of the current-voltage characteristic, and other relevant characteristics (specific for every device). For instance, this is the resolution capability for electron-beam tubes or the noise level for UHF devices. In connection with the aforesaid, the activity dealing with the creation of highly reliable, efficient, and economical cathodes continues, including works aimed at the modernization and the optimization of operational parameters of existing electron sources.

At present, thermionic cathodes are used the most often in EVDs. Emitter's task is to maintain the required concentration of electrons near its surface and in the space of electron interaction with electric and magnetic fields. Therefore, the emission current magnitude and the lifetime of a cathode without appreciable deterioration of its characteristics are the major cathode parameters. However, both the emission and the durability of a cathode depend very considerably on its working temperature. It is clear that those characteristics are in the strong contradiction with each other. Among the known types of thermionic cathodes, the best balance with respect to all requirements is reached when the so-called oxide cathodes (OCs) or dispenser cathodes (DCs) are used in EVDs. Moreover, they are the most efficient ones as well. In other words, they are characterized by the best ratio between the emission current density and the specific power spent to heat up the cathode.

2. Oxide Cathodes

The oxide-coated (hereafter, oxide) cathode was invented by A. Wehnelt in 1904. Structurally, this is a metallic substrate (core), most often fabricated from nickel, covered (by the deposition carried out with the use of various techniques) with a solid solution (this is very desirable!) of alkaline-earth metal carbonates, two- ((BaSr)CO₃) or three-component ((BaSrCa)CO₃) equimolar complexes, several tens of microns in thickness. In the latter case, the molar ratio of components BaO:SrO:CaO=47:43:10 was recognized optimal. With the help of a heater located in the core, the carbonates are thermally decomposed in vacuum to the corresponding oxides, with the pumping rate of reaction gas products should be as high as possible. The so-obtained solid solution of oxides has to be highly homogeneous for the subsequent heating of the OC oxide coating at a higher temperature, which is called activation, to bring it within a short time interval into a state with high emission. During 110 years of the OC existence, the tremendous number of researches aimed at elucidating the mechanism of OC emission were carried out throughout the world. As long ago as in 1954, the outstanding Ukrainian scientist, Corresponding Member of the Academy of Sciences of the UkrSSR, the founder and the head of the Kyiv scientific school of physical electronics N.D. Morgulis noticed in his known review "Modern thermionic cathodes" that, "from the viewpoint of physics, the oxide cathode is a very complicated and interesting system" [1]. Already in those days, more than 10 methods were used by researchers. However, during the later 50 years of the active application of OCs in various EVDs, progress took place only in the technology of cathode fabrication. Concerning the ideas about the origin of the thermionic emission from oxide cathodes, N.D. Morgulis wrote about them at that time as "elementary". According to them, the OC was considered as the perfect, structurally homogeneous layer of an electron semiconductor (barium oxide) with an impurity of donor atoms (metallic barium). The emission from this cathode has a character of mere evaporation.

However, the concept of OC as a semiconductor film on a metallic substrate turned out very fruitful. The next 50 years were devoted to the development of semiconductor-related theories for the explanation of the physical principles of OC performance under various vacuum conditions, in a wide temperature interval, and in the stationary and pulse operational modes at collecting emission currents from $100~\rm mA/cm^2$ to $15~\rm A/cm^2$ during thousands and tens of thousands of hours. The results of those researches were repeatedly discussed in the past in various reviews and monographs. The most known of them in our country are works [2–7]. In addition, thousands of scientific papers on this subject were published during those years.

In the late thirty years, a whole arsenal of super-powerful methods was attracted to research thermionic cathodes. They are used for the analysis of the chemical composition and the atomic and electron configurations of the material surface. These are the emission methods of analysis, probing the surface with the use of low- and high-energy electrons, electromagnetic radiation, and ion and molecular beams. (The presented classification of methods was borrowed from work [8].)

Owing to those methods, the large and overwhelming progress in OC researches was achieved. A lot of important and interesting results were obtained, which allowed a new concept of the OC working mechanism to be formulated [6, 9]. P. Zalm and B.P. Nikonov, independently, proposed two almost identical models for the oxide cathode. Those models were based on the data which proved that an excess of metal is formed on the surface of AEM oxide crystals after the corresponding thermal vacuum treatment, and just this excess is responsible for the thermionic properties of the system. The additional sputtering of barium onto the oxide surface from an external source gives rise to an additional reduction of its work function. The ultimate value of work function depends on the type of oxide, which the surface layer was formed on. At a surface state density of 10^{13} cm⁻², the work function of the semiconductor does not depend any more on its bulk properties and is determined by the Fermi level position near the crystal surface and the value of external work function.

The high concentration of surface levels results in the band bending with the corresponding modification of the internal work function. Since barium is in the ionic (or strongly polarized) form on the crystal surface, there must appear a dipole component that changes the external work function. Its value is extremely sensitive to the number of barium atoms on the surface. This means that, starting from a certain Ba concentration, the depolarizing effect of neighbor atoms has to manifest itself, so that the magnitude of external work function should approach the work function value for a thick Ba layer. A situation may arise at that when the increase in the external work function will not be compensated by the corresponding reduction in the internal work function, and the further growth of the barium concentration on the crystal surface will be accompanied by an increase rather than a decrease of the total work function.

B.P. Nikonov assumed the internal work function value in an activated OC to be close to the activation energy of the surface conductivity in crystals and amount to only 0.1–0.2 eV. Then, the main contribution to the OC work function is made by the height of the surface potential barrier, which is determined by the composition and the properties of a near-surface layer in the crystal [9]. The band scheme proposed by P. Zalm at that time [6] predicted that the decrease of the potential barrier owing to the conduction band bending and the dipole-assisted reduction of the external work function only facilitates the escape of conduction band electrons into vacuum.

The results used by the authors of works [6, 9, 10] did not allow them to prefer that or another performance scenario for OCs. The matter is that there was a doubt concerning the formation of a dipole layer on the ionic crystal surface, even if the concentration of one of the lattice components was high. Later, those doubts were dispelled by experiments on the sputtering of a medium with a low concentration $(10^{-4}-10^{-2} \text{ ML})$ onto various oxides. For instance, it was shown that the effective dipole moment of Ba adatoms on the SrO surface is approximately an order of magnitude larger than the dipole moments of Ba adatoms on the metal surface, and barium on the surface can play the role of donor centers with one electron, which can be released at the thermal ionization of the center. In other words, local donor centers are formed on the surface of the oxide layer, and the ionization of those centers may result in the appearance of electrons in the conduction band of the crystal surface layer, as well as at its surface.

Hence, from the viewpoint of B.P. Nikonov [7], the OC is a semiconductor with donor centers located near the bottom of the conduction band. As the donor surface concentration grows, the band bending increases, and the donor level approaches the conduction band bottom. The donor concentration in the surface layer becomes substantially higher than in bulk. This fact allows the crystal surface to be considered as "quasiinsulated" with its own Fermi level. The distance of the latter from the vacuum level determines the height of the surface potential barrier. In the near-surface layer of a semiconductor, a band is formed with local donor centers located close to the bottom of the conduction band, but far enough from the vacuum level. In this case, the complete ionization of an impurity takes place even at relatively low temperatures, and the Fermi level value, $E_{\rm F}$, reckoned from the vacuum level (in essence, this is the work function) is calculated by the formula

$$E_{\rm F} = \chi + kT \ln \frac{N_{\rm C}}{N_{\rm D}} = \chi + \alpha T, \tag{1}$$

where $N_{\rm C}$ is the total number of states in the conduction band, $N_{\rm D}$ the donor concentration, χ the external work function of a semiconductor, and α the temperature coefficient of work function.

As the author of work [7] marked himself, the model of semiconductor with a high density of states at the surface qualitatively corresponds to experimental data and explains the dependence of the emission current on the donor concentration and the temperature coefficient of the work function. However, in the framework of this model, the magnitude of work function remains an experimentally determined quantity and has no relation to the medium properties, as well as to the properties of atoms and molecules that form the near-surface layer in the cathode.

In general, the considered model describing the work of oxide cathodes was supported by many researchers, including the Professors of Taras Shevchenko National University of Kyiv G.Ya. Pikus, V.F. Shnyukov, and G.E. Chaika. The results of their researches concerning the mechanism of stoichiometry break in crystals of chemical compounds at their heating in the vacuum and the application of basic principles of the electron theory of chemisorption on the semiconductor surface and the theory of statistical interaction of defects and electrons in semiconductors allowed them to develop the theory of electron

evaporation and formation of binary semiconductor compounds of the A_2B_6 type at the free evaporation into vacuum [14, 15]. On the basis of this theory, the authors of works [14, 15] formulated a more universal concept concerning the functioning of OCs. This concept made it possible to explain almost all experimental results obtained by various researches during the long period of the oxide cathode application in various EVDs.

In correspondence with works [14, 15], the process of evaporation of ionic crystal atoms into vacuum at the heating of a crystal has three stages. At the initial stage, the surface ion of the crystal lattice leaves the normal site and forms a Frenkel defect at the surface. This defect is associated with a certain local energy level in the semiconductor energy gap. By exchanging an electron (a hole) with the conduction (valence) band, this defect becomes neutralized at the second stage. Afterward, at the third stage, the neutral atom, which is weakly bound with the crystal, easily evaporates (a neutral atom is bound with the crystal by van-der-Waals forces). The excess atoms formed on the crystal surface can diffuse into the crystal bulk as well.

The surface concentration of neutral atoms and, hence, their evaporation rate are governed not only by the rate of defect formation. Here, a special role is played by the surface electron state: the concentration of free electrons, n_e , of the conduction band in the near-surface region. In the general case, this parameter is governed by the Fermi level position. Any variation in the concentration of those electrons results in a modification of conditions for the ion neutralization and the surface atom evaporation, which is certainly accompanied by a change in the composition of the near-surface layer of AEM oxides. This means that there is a profound feedback between the evaporation of components and the crystal surface stoichiometry break for crystals of the A₂B₆ type, which is implemented by means of free electrons. This feedback is a result of the strong dependence of the component evaporation rates on the free electron concentration for metals and metalloids (for them, the corresponding dependences have opposite signs). In turn, the latter changes when the stoichiometry breaks owing to variations in the concentrations of cation and anion vacancies, which are the intrinsic defects of the donor and acceptor types, respectively. In this case, as the free electron concentration changes, the component evaporation rates shift in a direction such that the further development of a deviation from the stoichiometry is prevented.

Hence, a new property – the electron self-regulation of the stoichiometry breaking in binary ionic crystals - was established. It consists in that a quasistationary state (QSS) of the crystal is attained at the free evaporation of components into vacuum at a fixed temperature. This state is characterized by a constant deviation from the stoichiometry and identical evaporation rates of the components. This is supported by the dynamic balance between the electron subsystem in the crystal with a flux of evaporating component atoms and the defects (vacancies) formed at the evaporation. In the course of heating, a stationary transient layer is formed at the crystal surface, in which the deviation from the stoichiometry is different from that in bulk and strongly decreases into the crystal depth. The degree of crystal surface deviation from the stoichiometry can be precisely controlled by affecting the electron subsystem of the crystal with the help of an electric field, light, or by introducing impurities. Holes can also be considered as free charge carriers on the equal footing with electrons.

On the basis of the concept about the crucial role of the electron subsystem in the formation of the composition and electrophysical properties of A₂B₆ crystals, which was formulated by G.Ya. Pikus, V.F. Shnyukov, and G.E. Chaika, the functioning of an oxide cathode at all stages of its work can be briefly described as follows. The thermal dissociation of AEM oxides, the rate of which substantially depends on their composition, plays a considerable role in the mechanism governing the formation of an excess metal concentration in the oxide cathode at its activation and maintaining this concentration at a sufficient level during a long period of the cathode functioning under high-vacuum and high-temperature conditions. The concentration of the excess metal, which is formed in the course of heating, is close to optimal.

In the course of OC performance in vacuum, a QSS, typical at the given working temperature, with the broken surface stoichiometry of oxide grains and identical evaporation rates of components is established. The stoichiometry break is firstly observed on the surface of oxide crystals and only afterward in their bulk. In the case of thin oxide coverages, quasistationary states are not established, because the coverages have enough time to evaporate completely

prior to the QSS establishment. The QSS depends on some external factors: temperature, anode voltage, composition of residual gases in EVDs, and others. The establishment of quasistationary states explains the stabilization of electronic properties of OCs at their long-term functioning under the condition of permanent evaporation of the active medium into vacuum.

Provided that the partial pressure of oxygen in a device is low, i.e. the oxygen flux from the outside to the cathode is less than the rate of oxygen evaporation in the QSS, the thermal dissociation can be used to obtain OCs with a high emission and a long lifetime. Otherwise, the long-term work of OCs is possible only if there exists an additional source of the free metal, the role of which is played by the activator in the cathode core.

A significant amount of the AEM excess required for the creation of efficient OCs emerges in the cathode coverage even at the early stage of oxide layer formation, i.e. in the course of carbonate decomposition. However, the metal excess, which is formed during this stage of the thermal vacuum treatment of a specimen, turns out in the atmosphere created by released gases. Those gases interact with the metal and, in such a manner, reduce its concentration. As evidence, we may point to the $CO_2 \rightarrow CO$ conversion, which is a consequence of the interaction of CO₂ with the free metal. From experimental data, an important practical conclusion follows: in order to prevent the conversion of carbon dioxide into carbon oxide and obtain cathodes with optimal emission properties, it is necessary to increase the rate of gas pumping, namely, to decrease the CO₂ pressure in the device volume and to lower the maximum temperature under the cathode heating during the process of carbonate decomposition to 1100–1150 K, i.e. to temperatures, at which the conversion is weakly ex-

Of high importance is the issue concerning the localization of the extra AEM which was formed in the course of oxide thermal dissociation. The corresponding analysis showed that the evaporation features of examined oxides are associated first of all with a substantial change in the physicochemical properties of the oxide grain surface. The appreciable role of this surface is confirmed by the character of the oxide layer interaction with hydrogen and carbon oxide: their interaction reactions with the oxide layer runs on the

surface of oxide grains. The interaction of oxides with hydrogen and carbon oxide is accompanied by the appearance of a significant amount of the free AEM on the cathode surface and by a change of the cathode emission properties. In this case, the concentration of the free metal increases on the grain surface first of all, but there is a limiting value for the amount of the metal that can be localized here. The results obtained for the hydrogen and carbon oxide interactions with the oxide layer are especially important because the fractions of those gases in the residual atmosphere of EVDs are the highest.

The process of OC activation consists not only in the creation of a certain metal excess – first of all, barium - in bulk and, especially, on the surface of oxide crystals, but also in the creation of a certain concentration ratio between the oxygen and metal vacancies, when the former exceed the latter (a certain ratio between the concentrations of cations and anions on the surface and in bulk of the crystals). The work function minimum corresponds to a strictly definite ratio between the surface oxygen and metal concentrations. Therefore, a reduction of the work function at the metal excess growth, which is identical both in the course of oxide reaction with hydrogen and at the sputtering of the metal from an external source, follows from a decrease of the metal vacancy concentration, first of all, on the crystal surface. In addition, the work function minimum takes place at a certain concentration ratio between cation sites occupied by barium and strontium ions. Since the temperature of the OC activation, at which the required ratio between vacancy concentrations is realized, is much higher than the working one, the transition of oxide crystals into the QSS corresponding to a lower temperature and a lower excess of oxide vacancies (metal atoms) should be accompanied by a deterioration of OC emission parameters even in the absence of other factors negatively affecting its emission. This issue is important in connection with the problem of OC durability.

In addition to a change of the concentration ratio between oxygen and metal vacancies, another important role in the recession of the OC emission during the lifetime is played by a variation of the barium and strontium concentration ratio in the total metal excess, both as a consequence of the known prevailing evaporation of the barium component (mainly, in the form of BaO molecules) from (BaSrCa)O crystals and

owing to the difference between the evaporation rates of Ba and Sr, especially in the regime of emission current take-off, i.e. if the anode voltage is applied.

While creating durable EVDs, the application of oxide coverages several tenths of microns in thickness is inexpedient, because the evaporation of free AEMs grows drastically as the coverage thickness decreases. If the oxide layer thickness is small, the work function can be substantially reduced by the anode voltage application and the electron bombardment of the coverage.

At the same time, in the case of thin oxide films on active cores, the evaporation rates of Ba and Sr are higher than that of BaO. Moreover, they increase, if an electric field is applied. From whence, it follows that the total rate of active medium loss may be large enough if the anode voltage is applied. It cannot be excluded that, owing to a small amount of the active medium in the thin oxide coverage, this effect can give rise to an appreciable reduction of the cathode lifetime.

In accordance with the basic ideas concerning the mechanism of formation of QSS in ionic crystals in vacuum, a substantial influence of this process on the kinetics in the case of AEM oxide crystals has to be made by fine-dispersed particles of some metals which are in contact with them. Those particles must be chemically passive with respect to oxides, but form stable compounds with oxygen or AEMs. This issue is of interest from the viewpoint of elucidating the role of fine-dispersed additives to OCs with a metallized oxide layer, which are introduced into the cathode coverage in order to prevent the active component from the additional evaporation, when the high-density emission current is taken away. A research of this issue showed that fine-dispersed particles of nickel and copper make a considerable impact on the kinetics of component evaporation and the formation of the oxide layer composition. For example, the nickel additive, if it does not undergo a substantial oxidation in the course of oxide layer formation at the carbonate decomposition, considerably accelerates the metal excess production and, accordingly, improves the emission properties of OC at the initial stage of its activation.

Bearing in mind the concept of QSS in AEM oxides, the additives to the OC coverage should be chosen with regard for the peculiarities of their interaction with components of the cathode active layer such as a metal and oxygen under high-vacuum conditions. The most suitable for this purpose are metals that, like Ni, form stable compounds with oxygen, which are well soluble in a metal. The corresponding choice of the carbonate decomposition regime should minimize the oxidation of additive particles at the carbonate decomposition stage.

Both the surface and the bulk of AEM oxide crystals are responsible for high emission properties of OCs. The change of the work function in oxide crystals with a change of the excess metal concentration in them roughly resembles the concentration dependence of the work function in metal film systems: the work function is minimum at a certain concentration of an excess metal, which is strongly bound with the surface. This minimum stems from the extreme dependence of the external work function on the surface concentration of the excess metal, because the internal work function of a semiconductor monotonically decreases to its limiting value as the concentration of donors (atoms of the excess metal) grows.

The formation of QSS in mixed (BaSrCa)O crystals becomes considerably complicated owing to a permanent depletion of the Ba component in the nearsurface layer as a result of the prevailing evaporation of BaO molecules. Therefore, even provided a balance, typical of the QSS, between the escaping metal and oxygen atoms, the surface and bulk compositions of mixed crystals permanently change toward a larger fraction of cation sites occupied by strontium ions. As a result, the mixed crystals, by their physicochemical and electronic properties, such as the kinetics of component evaporation and the work function, approach SrO crystals covered with barium adatoms. Since the work function of mixed crystals strongly depends on the ratio between the Ba and Sr components, their continuous enrichment with the latter is one of the mechanisms driving a slow deterioration of emission properties of OCs during their lifetime.

According to the aforesaid, the role of activators introduced into the OC core in the mechanism of OC functioning has to be reconsidered. The concentration of the metal excess, which is formed at the thermal decomposition of oxides and is strongly bound with the lattice, is close to optimal. Therefore, under the conditions that provide the efficient course of this process, only an insignificant part of the metal chemically reduced by the activator is used to activate the oxide cathode. All the remaining part of the reduced metal

is evaporated. The role of the activator under those conditions is actually reduced to a decrease of the vacancy concentration in the metal sublattice, and this role can be considerable only at the initial stage of OC activation, e.g., at a high rate of metal oxidation by carbon dioxide or at a high pressure of residual oxygen in the device.

The attained QSS is characterized by a certain temperature-dependent concentration ratio n_0/n_M between the oxygen (n_0, donors) and metal $(n_M, \text{acceptors})$ vacancies, which is considerably different on the surface and in the bulk of crystals. In the course of heating, the excess of a metal in crystals of AEM oxides increases. Therefore, n_0 is always larger than n_M , and their difference grows with the temperature. In the course of heating of AEM oxides in vacuum at a certain temperature, both oxygen and metal vacancies are formed.

According to the electron theory describing the evaporation and the formation of a composition of AEM oxide crystals at their heating in vacuum, the regularities of this process in the case of specimens, whose thickness is comparable with or less than the screening length in semiconductors, differ from those typical of thick crystals. This circumstance is related to the fact that no transition layer with a thickness comparable to the screening length and with the free electron concentration gradient that would provide equal evaporation rates for metal and oxygen atoms can be formed in a thin specimen in the course of its heating. This effect is of special interest from the viewpoint of the durability of OCs on the basis of thin (less than 1 μ m) films of AEM oxides obtained by the molecular sputtering.

Detailed researches of the regularities in the kinetics of component evaporation and formation of the composition of AEM oxide crystals under the influence of an electric field at parallel measurements of thermoemission properties demanded a significant revision of the concepts concerning the physical nature of phenomena that occur in the oxide layer at the thermionic current take-off, as well as their role in the mechanism of OC current activation. The results of those researches were a direct experimental proof of the hypothesis that the current activation of OCs is not a result of electrolytic processes in the oxide layer. In other words, there is no spatial component separation in the crystals under the action of an electric field. Therefore, the state of the oxide layer at

the passage of an electric current through it is a new QSS with a higher metal excess than that in the no current QSS at the same temperature. In addition, they demonstrated that the increase of the metal excess in the OC oxide layer results from a reduction of the free electron concentration at the crystal surface at the thermionic current take-off. This process is the most efficient in the case where the emission current approaches the saturation. The metal excess obtained at that is localized first of all on the surface of oxide crystals, with its concentration in the QSS being a little higher than the optimum one, which corresponds to the oxide layer work function minimum. In addition, in the case of (BaSrCa)O crystals, the efficiency of the strontium excess formation at the current takeoff is considerably higher than that of the Ba excess formation.

With regard for the extreme dependence of the oxide layer work function on the metal-oxygen ratio at the crystal surface, on the one hand, and the barium-strontium ratio, on the other hand, those results explain the major regularities in the kinetics of OC emission change in the course of current activation. For instance, they explain the fact that the process of current activation is a self-stimulating process that runs at the highest rate at those sections of the oxide layer surface, where the work function is minimum (the highest density of the collected current). As a result, the work function at those sections reaches a minimum value more rapidly; then, it grows a little as a consequence of both the excess of the metal amount over its optimum value and an increase of the Sr fraction in the total metal excess. The emission inhomogeneity over the OC surface has a substantial influence on those processes.

The rate of metal excess production is maximum at the most active sections of the oxide layer surface. However, starting from the moment when the corresponding work function becomes minimum and begins to increase owing to a decrease of the collected current, this parameter and, accordingly, the rate of OC activation slow down. The process can be considerably accelerated if it is not executed in the continuous but the periodic regime by alternating the saturation current collection and pauses (when the electric field is switched-off). During the pause stage, the Sr excess formed at the current take-off stage is removed more quickly. Therefore, at the current take-off stage, the optimum ratio between the Ba and Sr concentra-

tions in the total metal excess on the most active sections of the oxide layer surface is attained more rapidly. Moreover, the metal excess on less active sections is formed more quickly owing to the strontium flux interception in the porous oxide layer. As a result, the duration of OC activation in this regime becomes 3 to 5 times shorter, which makes it especially promising for the activation of OC with a passive core.

In view of the inhomogeneity of the oxide layer surface, those results make it possible to explain the peculiarities in the change of OC emission, when the high-density thermionic current is collected, e.g., in the pulse regime. At last, the substantial difference between the rates of barium and strontium formation stimulated by the current take-off is one of the main causes giving rise to an irreversible increase of the OC work function at the long-term functioning in the emission regime as a result of increasing the Sr fraction in the total metal excess, first of all, on the surface of oxide crystals.

3. Parameters of Modern OCs

The structure of the oxide layer (density, porosity, surface roughness, layer thickness, the shape and dimensions of the crystals that form the layer) and the cathode core material were proved to have no substantial influence on the thermionic characteristics of a cathode if it is activated at a pressure below 5×10^{-7} Pa [7]. However, the functional characteristics of OCs are directly connected with the functional parameters of the oxide layer. Friable porous coverages consisting of large crystals become degased and activated more quickly and easily. At hard enough treatment regimes, they can lose a considerable amount of their active medium and change their composition with corresponding modifications in emission properties. At the same time, the cathode emission depends very substantially on the initial composition of the OC active medium.

For example, the emission of cathodes with an oxalate coverage [16] (AEM oxalates are $\mathrm{MeC_2O_4}$ compounds, where Me is an alkaline-earth metal: Ba, Sr, Ca) is much higher than that of standard, optimally activated OCs:: it reaches a value of 15–20 A/cm² in the pulse regime at T=1050 K, which is 3–5 times higher than for OCs with a carbonate coverage. As the temperature decreases, this difference grows even more.

The effective work function of oxalate cathodes determined with the help of the total current method amounts to 1.2–1.35 eV in the temperature interval of 750–1050 K. For the best specimens of ordinary OCs, this quantity equals 1.5–1.55 eV. To a great regret, the authors of work [16] did not obtain data concerning the durability of their specimens. By analyzing the emission evolution, the temperature dependences of the evaporation rates of coverage components and the work function of cathodes, and the filament current-voltage characteristics, only a prediction of a long lifetime was made.

The marked good properties of OCs on the basis of AEM oxalates result from the formation conditions of the single-phase solid solution of oxides (BaSr)O, which are more favorable at the thermal vacuum treatment of oxalates in comparison with those applied at the fabrication of usual oxide cathodes.

Appreciably better parameters in comparison with those for usual OCs were obtained at the introduction of rare-earth metals (REMs) into the REM oxide layer of cathode. For example, OCs with the $\rm Sc_2O_3$ or $\rm Eu_2O_3$ additive generated an emission current density of 2–3 $\rm A/cm^2$ for 4000–10000 h at a temperature of 800–830 °C in comparison with 1000–1500 h for ordinary OCs [17, 18]. However, the physics of OCs with REM additives remains unclarified at present.

One cannot but mention an interesting invention made in the 1970s, the so-called M-cathode or the cathode on the basis of a sputter-deposited film of oxide molecules (SDFOM) [19, 20]. Its active medium, being the same as in the ordinary OC, is also deposited onto the same cores. However, the deposition technology is absolutely different: SDFOMs are obtained by sputtering a target made of AEM oxides taken in the standard proportion, which is mostly used in the cathode-based equipment, with the help of argon ions. For the film to be resistant to the deposition atmosphere, the M-coverage is deposited in the carbon dioxide environment. The fabricated SDFOMs have a high density (up to 4.5 g/cm³ instead of 2.8 g/cm³ obtained at the standard deposition of the oxide layer). They consist of an oxide carbonized to 60–80%. From the viewpoint of the developers of this method, it is quite enough in order to provide a required stability to the action of atmospheric air, which contains water vapor, carbon dioxide, and other gases chemically active with respect to AEM oxides.

Those coverages also have a very smooth surface, because the latter is composed of grains no more than 0.1 μ m in diameter [21]. As a result, they are characterized by a high uniformity of the emission current over the surface: the spread of the electron work function from point to point does not exceed 0.01 eV against 0.3–0.5 eV in ordinary OCs. The emission parameters of the M-cathode are close to those of the standard OC. However, because of the coverage specificity, the former has a number of specific features; the most important of them for practical applications is the emission, which is higher in the low-temperature interval (below 900 K) and lower in the high-temperature one.

The lifetime of M-cathodes depends quadratically on the SDFOM thickness and drastically decreases at high temperatures [22]. For example, this quantity achieves 10000 h for a working temperature of 870 K, at a collected current equal to 0.1 A/cm² and a cathode thickness of 0.8 μ m. At 920–990 K, the take-off current density reaches 0.4–1.0 A/cm², and the lifetime diminished to 4000-1500 h for a thickness of 0.7–1.8 μ m. The increase of the SDFOM thickness results in its worse adhesion to the core.

Restrictions on the durability of M-cathodes are not connected with a substantial evaporation of the active medium, but mainly with the depletion of the Ba component at the oxide layer surface [22]. According to work [23], the depletion is associated with the restriction on the barium diffusion through the oxide layer to the surface. In the opinion of the authors of work [24], the loss of the Ba component - mainly, by evaporating barium hydroxide $Ba(OH)_2$ – is a more probable reason that reduces the lifetime of those cathodes. The presence of Ba(OH)₂ in the M-cathode is most likely connected with an insufficient level of SDFOM carbonization. This opinion is based on the results of mass-spectrometry researches [25–27], according to which the amount of BaO evaporated during the cathode lifetime equals only 0.01% of the Ba content in the SDFOM. At the same time, the barium loss owing to the evaporation of $Ba(OH)_2$ reaches 5-10% of the total Ba amount even at the initial stage of the cathode work, which results in a premature change of the optimum ratio between the Ba and Sr components at the M-cathode surface and hence to a considerable decrease of the cathode emittance [28].

The authors of work [29] called in question the possibility of the $Ba(OH)_2$ evaporation from M-cathodes. They suppose $BaCl^+$ to be evaporated and associate its emergence in SDFOMs with the technological process of EVD manufacture. However, they agree that a substantial fraction of the Ba content in SDFOMs can be lost through this channel.

The authors of works [30–32], recognizing that the carbonization degree of the as-fabricated M-cathode coverage is a very important characteristic of SD-FOMs, carefully analyzed the influence of conditions at the M-coverage sputtering in order to provide the maximum degree of its carbonization. They showed that this coverage parameter is very sensitive to the position of the cathode core with respect to the ionoptical axis of the sputtering system. In the near-axis region, the carbonate content is minimum, and the carbonization degree does not exceed 0.25-0.3. The carbonization degree depends also on the cathode core temperature at the oxide deposition. Moreover, if it is lower than 30%, the M-coverage is not stable in air and becomes easily hydrated; i.e. it transforms into hydroxides, crystalline hydrates, and hydrocarbonates, which causes the coverage destruction.

The authors of works [30–32] succeeded in finding an optimum regime for the active layer deposition in M-cathodes: they selected a required rate of target sputtering and arranged the cathode core outside the zone, where the oxides prone to the hydration when being exposed to air are mainly deposited. This regime allowed them to obtain M-coverages with almost 100%-carbonization. In addition, they managed to create M-cathodes, the coverage of which is a solid, highly homogeneous solution with a composition congruent to that of the targets. This achievement formed a basis for the fabrication of SDFOMs with a high emission and a high reproducibility of operational parameters. As a result, those cathodes are now used in monolithic multicascade amplifiers based on vacuum integrated circuits [33].

The analysis of the discussion between the authors of works [24–27] and [19–23, 29] concerning the presence of Ba(OH)₂ in SDFOMs and the account for the results of works [30–32] allowed the following conclusions to be drawn: (1) the possibility of the Ba(OH)₂ formation in the coverage of M-cathodes during their manufacture from AEM oxides using the plasma method is not excluded; (2) the fabrication of M-cathodes with a high degree of coverage car-

bonization using this method is not a simple task, so that a well-elaborated fabrication technology is required. This means that there always exists a certain probability to fabricate specimens with a phase content shifted toward oxides.

Despite a high efficiency of OCs, which allowed them to be used in many EVDs and even in EVDs of the UHF range, e.g., on the board of satellites in running-wave tubes at frequencies of 3.7–4.2 GHz and an output power of 20 W [34], oxide cathodes are also characterized by appreciable shortcomings. First of all, this is their lifetime, when the take-off currents equal a few amperes per square centimeter. In addition, they have a low resistance to the poisoning by oxygen-containing gases and to mechanical loadings. After the activation, they cannot be held in air. The latter shortcoming does not allow oxide cathodes to be used in special-purpose devices.

The modern development of science and technique needs UHF devices with a higher output power and a lifetime of tens thousands of hours: for the satellite communication, radar stations and electronic countermeasure facilities, especially in the millimeter wave range (frequencies above 30 GHz). For such devices, the cathodes capable of providing the emission current density up to tens of amperes per square centimeter and a lifetime of one thousand hours are required. Among the emitters of all types that are used today, dispenser cathodes (DCs) are the most promising ones for the application in such devices.

4. Dispenser Cathodes

The story of dispenser cathodes (DCs) has begun from barium-tungsten cell cathodes or, as was accepted to call them in the literature, L-cathodes, which were invented by H. Lemmens and collaborators at Philips in 1950. Any L-cathode contains a cell with active medium [4]. The cell is tightly closed by a porous sponge, the external side of which is an emitting surface. As an active medium, AEM carbonates, or Ba-Ca tungstates, or aluminates were used. The sponge of the cathode is its most important part. Usually, it was fabricated from a tungsten powder with definite granularity in order to obtain a required pore size. When heating in vacuum, the active medium decomposes and releases Ba and BaO, which diffuse through the pores to the surface of grains and activate them. L-cathodes had a high emission: the density of the take-off emission current was 5 A/cm²

in the continuous regime and several tens of $\rm A/cm^2$ units in the pulse regime with the restriction of the emission current by a space charge at a temperature not exceeding 1500 K. They were highly resistant to large thermal and mechanical loadings and to the influence of oxygen and water vapors at their installation in EVDs. In addition, the L-cathodes are unpretentious to storage conditions.

However, such shortcomings of L-cathodes as their manufacturing complexity and hence a high cost price, a long-term activation, rather a high working temperature, and the non-uniformity of the working surface heating, which resulted in an appreciable inhomogeneity of the emission, stimulated works aimed at their improvement. Therefore, already in 1954–1957, R. Levi, I. Brodie, and F. Guber proposed and studied impregnated and pressed dispenser cathodes (IDCs and PDCs, respectively).

5. Impregnated and Pressed Dispenser Cathodes

Those cathodes consist of a porous sponge made from powdered metals like W, Re, and Mo (or their mixture), with the pores being filled with an active medium. In IDCs, the active medium is used to impregnate the preliminarily fabricated sponge, whereas the sponge in PDCs is pressed and sintered together with the active medium [4]. By the composition of the active medium, aluminate, tungstate, aluminosilicate, and other DCs are distinguished. When heating in vacuum, complicated processes of interaction between the active medium and the sponge material take place. The thermal dissociation of some compounds occurs with a release, as was in the case of L-cathodes, of Ba and BaO, which diffuse to the grain surface and activate it.

It is clear that the operational parameters of dispenser cathodes of all types depend on both the sponge parameters and the active medium composition [4]. The sponge material determines, first, the generation efficiency of the free Ba component from the initial active medium and, second, the binding energy of Ba and BaO on the working surface of the cathode and, consequently, the rate of their evaporation, which the cathode lifetime depends on. In addition, the binding energy actively affects the Ba component amount on sponge grains and, accordingly, on the aggregate state of an adsorbate: whether it cov-

ers the sponge grains in the form of a two-dimensional film or as bulk entities, crystallites. In other words, the sponge material actively affects the emission of DCs. The sponge porosity, as well as the pore diameter, directly governs the rate of evaporation of the active medium. The dependence of the evaporation on the sponge thickness also takes place. The dimensions of sponge grains and pores, as well as their distribution over the sponge surface, determine the emission uniformity of DCs.

The task of the active medium is to lower the work function of a sponge material as much as possible and provide the highest emission activity of a cathode for thousands of hours. At present, a considerable number of emission-active media are developed. These are Ba-Ca tungstates, aluminates, aluminosilicates, Ba scandates, Sr tungstates, and others. Moreover, aluminates, as an example, are classified into several types [4], an so on.

The practical application of that or another composition of the active medium depends on the performance conditions of the electron source in EVDs. In addition, while manufacturing devices, it is very important that the cathode parameters should be identical. In this connection, one cannot but mention Ba-Ca aluminate of the content $2.4 \text{BaO} \times 0.6 \text{CaO} \times \text{Al}_2 \text{O}_3$ [35], which practically does not contain free barium oxide, so that the influence of atmospheric air is nullified.

The evolution of DCs is a permanent motion to their improvement by developing the corresponding mechanism of emission. The most important stages in the development of dispenser cathodes are: the deposition of films of refractory metals and metals of the platinum group on their emitting surface [36] and the introduction of scandium oxide Sc₂O₃ into DCs [37]. The first improvement consisted in that a submicron osmium film was sputtered onto the cathode surface. It allowed the emission to be raised practically by an order of magnitude at a temperature of 1100 K. The second improvement – e.g., Sc_2O_3 is introduced into the DC sponge, and then the latter is impregnated with Ba-Sa aluminate – allowed the working temperature of cathode to be lowered by 100 K in order to provide a constant emission current [38]. Later, the parameters of Sc–Ba cathodes were increased to a record level in the whole history of thermocathodes: to 460 A/cm^2 at a temperature of 1030 °C [39].

However, despite such amazing success, there is no common viewpoint in the literature concerning the emission mechanism in DCs, and especially in DCs with the Sc_2O_3 additive. At present, disagreements in this issue are the largest, although the ground hypotheses about the probable structure and the element composition of the emitting surface of dispenser cathodes were put forward in the first years of their application [40]. There are three main hypotheses: (1) the DC is a metal-film cathode, i.e. the main contribution to the cathode emission is made by the surface of sponge grains covered with a submonolayer film of the activator [41]; (2) the high activity of DCs is provided by three-dimensional structures of an active medium on the cathode surface [42], which are identified with high-temperature oxide microcathodes [43]; (3) the main source of electrons is the surface of pores filled with Ba-Ca aluminate [44]. The first two viewpoints on the structure of the emitting layer in DCs dominate at present (see works [45–47] and [48,49], respectively). Another viewpoint was expressed by P. Zalm [50] and supported in works [51, 52]. According to it, the cathode surface has two electron sources: crystallites and the film of the Ba component. As was proved later, if the cathode works in ultrahigh vacuum of about 10^{-7} Pa, the cathode emission pattern is not uniform. At pressures corresponding to actual working conditions in EVDs, the high emission from the DC surface takes place only in regions with a thick coverage [53].

In view of difficulties faced by the adherents of the film model of DCs while explaining some experimental facts, having analyzed vacuum conditions, under which experiments were carried out, having compared the technological parameters of cathodes, the technologies of their manufacture and preparation for researches by different authors, and basing on the results of the previous researches in this direction executed at the Taras Shevchenko National University of Kyiv [54–59], a conclusion was drawn that the role of three-dimensional structures, crystallites of the active medium, in the emission mechanism of dispenser cathodes was groundlessly underestimated. The origin of all that lies in the underestimation of the influence of a porous matrix, the technology of cathode manufacture, and the conditions of a thermal vacuum treatment on the structure of the DC emitting layer. Therefore, a comprehensive analysis of a wide scope of dispenser and oxide cathodes was carried out with

the use of mass- and Auger spectometries, emission and scanning electron microscopies, x-ray microanalysis, and emission measurements in diode systems [60–66]. The study of the influence of hydrogen on the evaporation and the activity of specimens was an additional method of researches [57, 58].

DCs with various technological parameters were used as specimens. They differed from one another, first, by the sponge parameters, namely, the sponge material (tungsten and rhenium-tungsten powders), the sponge porosity (varied in wide limits), the granulometric sponge composition (varied from 1 to 40 μ m), the microgeometry of the working surface (mechanical treatment of the surface against the ion etching after the fabrication), and the presence or absence of a film of refractory metals of the Os-Ir-Al type. Second, they differed by the active medium. In particular, Ba-Ca aluminate with the content $3BaO \times 0.5CaO \times Al_2O_3$ was used for DCs with the Re-W sponge and the same aluminate, but with a higher content of calcium oxide with respect to BaO, namely, 2.4BaO \times 0.6CaO \times Al₂O₃, for DCs with the W sponge. More information concerning the fabrication technology of those DCs can be found in work [67]. All cathodes for researches were fabricated at the scientific research institution "Orion" (Kyiv).

After studying the physicochemical and emission properties of DCs with different technological parameters, the following conclusions were made.

- 1. In the course of thermal vacuum treatment, three-dimensional structures (crystallites) of AEM oxides activated by barium are formed on the DC surface, both clean and covered with the Os-Ir-Al film. Just those structures make the main contribution to the cathode emission. The emergence of crystallites and their existence at working temperatures are a result of an appreciable amount of barium oxide in DCs, which is formed owing to the thermal dissociation of Ba-Ca aluminate during the cathode fabrication, and its diffusion to the working surface. The high thermal stability of AEM oxide formations in bulk is provided by a high binding energy of calcium oxide with the sponge material. The sponge grains are used by CaO microcrystals to form nucleation centers for crystallites of the active medium.
- 2. The enhancement of the DC emission after an Os–Ir–Al film has been deposited on the DC working surface is associated with an increase of the active medium content on this surface in the form of

- AEM oxide crystallites. The Os–Ir–Al film was found to change the rate of evaporation of the Ba component in a complicated way. The character of evaporation is driven by the sponge porosity: the sputtering of the Os–Ir–Al film 0.3 μ m in thickness on cathodes with a high porosity diminishes the flux of the active medium, increases it in the case of cathodes with a moderate porosity, and remains almost invariable if the cathode porosity is low.
- 3. The presence of barium carbonate BaCO₃ in the DCs before their thermal vacuum treatment in EVDs, the dependence of the cathode emission on the partial pressure of CO₂ over the specimens at their degassing, the correlation between the DC emission threshold and the momentum of the practically complete barium carbonate decomposition, and the coincidence of general and some specific regularities in physicochemical processes running at the hydrogen interaction with DCs and OCs allows us to assert that, in essence, the dispenser cathode, at least at the beginning of its service, is a high-temperature, but more complicated, modification of the oxide cathode.
- 4. At the degassing of DCs, free barium, which is responsible for the emission of AEM-based thermionic cathodes, is formed as early as at the initial stages of this process. The preservation of metallic barium till the end of the degassing allows the cathodes to obtain a high activity without additional high-temperature heating. If the durability of DCs, similarly to OCs, is determined by the evaporation of several percent of the Ba component, the exclusion of the high-temperature heating, which gives rise to an unreasonable waste of the active medium, can promote the lifetime prolongation and the reliability of EVDs.
- 5. Dispenser cathodes with the Re-W sponge have a higher emission in comparison with tungsten-based DCs, which is connected with both a larger area of the working surface occupied by the active medium in the form of AEM oxide crystallites and a higher emission of the monolayer film of the Ba component on grains of the rhenium sponge.
- 6. The sponge porosity substantially affects the emission of only those DCs, whose sponge contains rhenium. There are such sponge parameters, at which the ratio between the evaporating amount of the Ba component and that arriving at the cathode surface provides the maximum of the area occupied by the activator. In this connection, the cathode activity is also maximum and corresponds to the best DC spec-

imens covered with the Os–Ir–Al film. Hence, there is a possibility to fabricate highly emissive dispenser cathodes without sputtering films on the basis of osmium or iridium, which are expensive.

For DCs with tungsten sponge, the porosity and the dimension of grains, provided that other conditions are the same, substantially affect the emission current only at the initial stage of the cathode activation. Ultimately, the activity of specimens does not depend on those parameters. If the particle diameter and the sponge porosity decrease, only the time interval required to achieve the maximum DC emission increases, so that several activation cycles have to be done.

7. The geometrical microrelief of the DC surface is responsible for the rate of evaporation of the active medium and the ratio between free and oxidized barium in evaporation products. For cathodes, whose working surface was corrected with the use of the ion etching, the total flux of the Ba component is larger than that for DCs with mechanically treated surface. For ion-etched cathodes, the barium flux considerably exceeds the barium oxide one in the whole interval of working temperatures. The lower rate of BaO evaporation in those specimens can favor the lifetime increase for the crystallites of AEM oxides, which are responsible for the high emission of dispenser cathodes.

8. The active medium is mainly evaporated from DCs in the form of Ba, BaO, and Ba(OH)₂. The presence of barium hydroxide among the products evaporated from dispenser cathodes, analogously to the case of M-cathodes, can make the relevant contribution to a reduction of the DC durability. However, unlike M-cathodes, the loss of the Ba component in DCs owing to the evaporation of Ba(OH)₂ is relatively small and does not change the DC lifetime considerably.

Those conclusions together with the literature data on this issue allowed the authors of works [67, 68] to describe the major stages in the formation of a DC regarded as an effective source of electrons as follows. After the fabrication of a cathode, its active medium, except for Ba-Ca aluminate, contains an appreciable amount of free barium oxide. Owing to the absorption of water vapor from the atmosphere, BaO is hydrated. Later, owing to the presence of carbon dioxide in air, it partially transforms into barium carbonate, BaCO₃. At the thermal vacuum treatment,

when the temperature is elevated, the cathode frees itself from gas contaminations and harmful additives, barium carbonate decomposes, and the reactions, in which free barium (it is responsible for the emission of thermionic cathodes on the basis of AEM oxides) is formed, take place. The main of them is the chemical reaction between the sponge material (tungsten) and Ba-Ca aluminate. If the CO₂ pressure over the DCs is lower than 10^{-7} Pa within this period, the barium content in the specimen becomes appreciable at the end of the degassing. BaO and Ba diffuse to the sponge surface and activate it: three-dimensional structures of AEM oxides activated by barium emerge in pore openings and on sponge grains. Crystals of calcium oxide are nucleation centers for those structures. It is the bulk formations of AEM oxides that make the main contribution to the cathode emission. The monolayer film of the Ba component mainly serves within this period as a channel for the active medium to reach the crystallites. If the DC sponge contains rhenium, this film located on rhenium grains can also be an additional source of electrons.

The worsening of the cathode emission in the course of work is connected with the depletion of the active medium, mainly, the Ba component, at the cathode emitting surface. As a result of this process, there arise conditions that interfere the support of crystallites. The lifetime of those three-dimensional structures is determined by the amount of barium oxide that was formed in the course of cathode fabrication and in the course of cathode exploitation. It also depends on the technological parameters of the cathode sponge (the geometrical microrelief of the emitting surface, the sponge porosity, and the dimensions of sponge particles) and the DC working temperature, i.e. the parameters that affect the rate of BaO evaporation.

6. DCs with Sc_2O_3 Additive

At present, DCs with the scandium oxide additive have the highest emission among thermionic cathodes. They are very stable with respect to the poisoning with the atmospheric air, and they have even be recommended for applications in accelerators of charged particles, plasmatrons, and electrojet engines of space crafts [69]. However, such shortcomings as the non-uniform distribution of the emission over the surface, the abnormal dependence of the emission

current density on the electric field strength, a low resistance to the ionic bombardment, and a bad reproducibility of operational parameters do not allow them to be widely used in various branches of instrument engineering, despite that plenty of works published in recent years were devoted to those problems [70–106].

The author of work [96] is sure that all the mentioned shortcomings are closely connected with the imperfect sponge structure: sponge grains, different by dimensions, make it impossible to create a working surface that would be homogeneous by both the dimensions of pores, from which the active medium diffuses on the surface, and the dimensions of spongegrain conglomerates, where the main physicochemical processes providing the high emission of DCs take place. In addition, the author of the cited work also pays attention to the design of a cathode heater, a factor that the temperature gradient on the surface and, hence, the emission uniformity depend on.

The authors of works [97–99] also consider that the physicotechnical parameters of sponges in the Sc-Ba DCs are one of the major factors governing the inhomogeneity of the cathode surface with respect to the work function. In addition, the non-uniform emission can result from the non-uniform distribution of scandium on the sponge grains, which plays a considerable role in the cathode emission enhancement. In order to appreciably eliminate the shortcomings indicated above, it was suggested in works [79, 100] to add scandium oxide and rhenium taken in certain proportions to a tungsten powder with the use of the so-called solid-liquid method combined with the twostage reduction one. Later, such a modified technology of cathode sponge fabrication allowed the authors of work [100] to obtain the emission current density equal to 31 A/cm² at a brightness temperature of 850 °C with a substantially improved distribution of scandium over the sponge grains [101]. It turned out that, for the optimal emission, the ratio Ba:Sc:O on the cathode surface should be equal to 1.6:1:2.25.

Since scandium is rather an expensive substance, the authors of work [102] made an attempt to partially replace scandium oxide Sc_2O_3 by europium oxide Eu_2O_3 . However, the attempt turned out not so successful: the emission of specimens with the Eu_2O_3 additive was lower than that of Sc-Ba DCs.

The Sc-Ba DC is a complicated multicomponent multiphase system. Therefore, the direct study of

its physicochemical and emission properties did not brought desirable results. No common viewpoint concerning the mechanism of emission in such cathodes was formed among the researchers. In particular, the majority of foreign authors defend the film model of the emission mechanism. They mark that, in the case of scandate DCs, the emission-active complex consists of barium, scandium, and oxygen, with scandium being at the lowest level. At the same time, the results of the works carried out at the Taras Shevchenko National University of Kyiv testify in favor of the three-dimensional structures of an active medium on the surface of scandate specimens. To resolve this dilemma, it was suggested to simulate the emitting surface of cathodes and compare the obtained results with the results of experimental researches of real highly active DCs [81–94].

It was proved that there is a tight interrelation between the emission level from a scandate dispenser cathode and the presence of the scandium component on its working surface. The interrelation consists in that the high emission of specimens is observed, when the Auger spectra of their working surface demonstrate the presence of the Auger line of the scandium component. Moreover, there exists a certain optimum for the amount of scandium oxide on the sponge grains [75].

The complex analysis of works [65–67, 70, 78, 81, 82, 87, 95] and their comparison with the results obtained by other authors dealing with the problems of scandate cathodes make it possible to assert that the introduction of scandium oxide into any part of a dispenser cathode transforms the latter from a thermionic into a thermal-field one. The thermal-field character of the emission from DCs with scandium is discussed by the authors of works [103, 104].

The role of the scandium component in the enhancement of the emission current consists in the creation of conditions for a considerable growth of just the field-emission component in the total current. This is done by promoting a growth of the number of emitting centers, the crystallites of alkaline-earth metal oxides, and a change of their shape. In this case, the chemical composition of the alkaline-earth metal oxide crystallites on the scandate dispenser emitter is such that it substantially promotes the electric field to penetrate deeper into their bulk. As a result, we also obtain the growth of the field-emission component in the total anode current [95].

Despite the significant progress in the fabrication technology of Sc–Ba DCs, the developers of electrovacuum devices in the UHF range are not satisfied with the achieved emission parameters of cathodes, especially what concerns the uniformity of the working surface with respect to the work function. Therefore, the researches aimed at improving the physicotechnical characteristics of such cathodes are intensively continued [105, 106].

- 1. N.D. Morgulis, Usp. Fiz. Nauk 53, 501 (1954).
- 2. G. Hermann and S. Wagner, *The Oxide Coated Cathode* (Chapman and Hall, London, 1951).
- 3. E.S. Rittner, Philips Res. Rep. 8, 184 (1953).
- G.A. Kudintseva, A.I. Melnikov, A.V. Morozov, and B.P. Nikonov, *Thermionic Cathodes* (Energiya, Moscow, 1966) (in Russian).
- B.Ya. Moizhes, Physical Processes in Oxide Cathode (Nauka, Moscow, 1968) (in Russian).
- P. Zalm, Adv. Electron. Electron Phys. 25, 211 (1968).
- B.P. Nikonov, Oxide Cathode (Energiya, Moscow, 1979) (in Russian).
- 8. V.T. Cherepin and M.A. Vasil'ev, *Methods and Devices* for Surface Analysis of Materials. A Handbook (Naukova Dumka, Kyiv, 1982) (in Russian).
- B.P. Nikonov and K.S. Beinar, Radiotekhn. Elektron. 15, 1272 (1970).
- B.P. Nikonov, Izv. Akad. Nauk SSSR Ser. Fiz. 35, 270 (1971).
- K.S. Beinar and B.P. Nikonov, Izv. Akad. Nauk SSSR Ser. Fiz. 35, 286 (1971).
- 12. B.P. Nikonov, Fiz. Tverd. Tela 15, 1481 (1973).
- A.M. Sokolov and B.P. Nikonov, Izv. Akad. Nauk SSSR Ser. Fiz. 40, 2472-2477 (1976).
- G.Ya. Pikus, G.E. Chaika, and V.F. Shnyukov, Ukr. Fiz. Zh. 37, 1021 (1992).
- V.F. Shnyukov, G.E. Chaika, and G.Ya. Pikus, Prog. Surf. Sci. 51, 175 (1996).
- G. Ya. Pikus, S.P. Rakitin, V.I. Samiilenko, and V.F. Shnyukov, Izv. Ross. Akad. Nauk Ser. Fiz. 62, 2051 (1998).
- M. Saito, R. Suzuki, K. Fukuyama, K. Watanabe, K. Sano, and H. Nakanishi, IEEE Trans 37, 2605 (1990).
- Y. Hayashida, N. Ozawa, and H. Sakutai, Appl. Surf. Sci. 146, 7 (1999).
- A.V. Druzhinin and Yu.A. Kondrashenkov, Radiotekhn. Elektron. 18, 1531 (1973).
- Yu.A. Kondrashenkov, Z.N. Galanina, and A.V. Druzhinin, Elektron. Tekhn. Ser. 1 Elektron. SVCh, Iss. 6, 55 (1974).
- L.A. Ashkinazi and V.A. Zlobin, Elektron. Tekhn. Ser. 4 Elektovak. Prib., Iss. 3, 10 (1982).
- Yu.A. Kondrashenkov, Z.N. Galanina, and A.V. Druzhinin, Elektron. Tekhn. Ser. 1 Elektron. SVCh, Iss. 7, 35 (1974).

- A.Ya. Knyazev, in Abstracts of the 18-th All-Union Conference on Emission Electronics (Nauka, Moscow, 1981), p. 143.
- V.F. Shnyukov, B.I. Mikhailovskii, A.E. Lushkin, and A.I. Zuev, Elektron. Tekhn. Ser. 1 Elektron. SVCh, Iss. 4, 42 (1981).
- V.F. Shnyukov and A.E. Lushkin, Elektron. Tekhn. Ser. 1 Elektron. SVCh, Iss. 1, 58 (1978).
- V.F. Shnyukov and A.E. Lushkin, Vestnik Kiev. Univ. Fiz. 19, 61 (1973).
- V.F. Shnyukov, B.I. Mikhailovskii, and A.E. Lushkin, Vestnik Kiev. Univ. Fiz. 20, 88 (1979).
- V.F. Shnyukov, B.I. Mikhailovskii, and A.E. Lushkin, Vestnik Kiev. Univ. Fiz. 26, 62 (1985).
- Yu.F. Klement'ev, A.Ya.Knyazev, and E.N. Lifantsev, Elektron. Tekhn. Ser. 1 Elektron. SVCh, Iss. 10, 23 (1986).
- A.N. Govyadinov and P.P. Mardilovich, Deposit manuscript N Ts4272 (Inst. of Electronics, Minsk, 1986) (in Russian)
- D.I. Aleinikova and A.N. Govyadinov, Elektron. Tekhn. Ser. 6 Mater., Iss. 6, 22 (1988).
- A.N. Govyadinov, I.L. Grigorishin, P.P. Mardilovich, and P.A. Ananich, Elektron. Tekhn. Ser. 1 Elektron. SVCh, Iss. 6, 36 (1989).
- 33. I.L. Grigorishin, I.F. Kotova, and N.I. Mukhorov, IVESC'96 G16/101.
- V.I. Kozlov, Obzory Elektorn. Tekhn. Ser. 1 Elektron. SVCh, Iss. 6, 1 (1980).
- N.P. Brodnikovskii, L.A. Vermenko, O.I. Konovaljuk et al., Elektron. Tekhn. Ser. 6 Mater., Iss. 4, 20 (1980).
- P. Zalm and A.J.A. Van Stratum, Philips Tech. Rev. 27, 69 (1966).
- A. van Oostrom and L. Augustus, Appl. Surf. Sci. 2, 173 (1979).
- S. Yamamoto, S. Tagushi, T. Aido *et al.*, Appl. Surf. Sci. 17, 504 (1984).
- G. Gartner, P. Geittner, D. Raasch, and D.U. Wiechert, Appl. Surf. Sci. 146, 22 (1999).
- V.M. Skryleva, Obzory Elektorn. Tekhn. Ser. 1 Elektron. SVCh, Iss. 5, 1 (1976).
- E.S. Rittner, W.C. Rutledge, and R.H. Ahlert, J. Appl. Phys. 28, 1468 (1957).
- 42. A. Ahmed, Sci. Progr. Oxi. 57, 259 (1969).
- 43. A.V. Druzhinin, Radiotekhn. Elektron. 10, 498 (1965).
- I. Brodie and R.O. Jenkins, in Effective Thermionic Cathodes, Vol. 2 (Gosenergoizdat, Moscow, 1960), p. 334 (in Russian).
- G.A. Haas, C.R.K. Marrian, and A. Shih, Appl. Surf. Sci. 3/4, 430 (1985).
- A.W. Denier van der Gon, M.F.F.K. Jongen, H.H. Brongersma, U. van Slooten, and A. Manenschijn, Appl. Surf. Sci. 111, 64 (1997).
- R. Cortenraad, A.W. Deiner van der Gon, H.H. Brongersma, G. Gartner, and A. Manenschijn, Appl. Surf. Sci. 191, 153 (2002).

- A.P. Makarov, O.K. Kultashev, E.D. Kuranova et al., Radiotekhn. Elektron. 36, 2196 (1991).
- V.F. Shnyukov and A.E. Lushkin, Radiotekh. 100, 267 (1996).
- P. Zalm, in Advances in Electronics and Electron Physics, edited by L. Marton (Academic Press, New York, 1968), p. 221.
- B.B. Shishkin, Izv. Akad. Nauk SSSR Ser. Fiz. 38, 2279 (1974).
- Yu.V. Gurkov, A.V. Druzhinin, A.A. Isaev *et al.*, Izv. Akad. Nauk SSSR Ser. Fiz. 38, 2264 (1974).
- C.E. Melony and N. Richardson, Appl. Surf Sci. 8, 2 (1981).
- V.F. Shnyukov, B.I. Mikhailovskii, A.E. Lushkin et al., Radiotekhn. Elektron. 24, 1184 (1979).
- V.F. Shnyukov, B.I. Mikhailovskii, A.E. Lushkin et al.,
 Elektron. Tekhn. Ser. 1 Elektron. SVCh, Iss. 8, 25 (1980).
- V.F. Shnyukov, B.I. Mikhailovskii, A.E. Lushkin et al.,
 Elektron. Tekhn. Ser. 1 Elektron. SVCh, Iss. 6, 36 (1982).
- V.F. Shnyukov, B.I. Mikhailovskii, A.E. Lushkin et al., Elektron. Tekhn. Ser. 1 Elektron. SVCh, Iss. 9, 40 (1984).
- V.F. Shnyukov, B.I. Mikhailovskii, A.E. Lushkin et al., Elektron. Tekhn. Ser. 4 Elektovak. Gazorazr. Prib., Iss. 1, 8 (1985).
- V.F. Shnyukov, B.I. Mikhailovskii, A.E. Lushkin et al., Elektron. Tekhn. Ser. 1 Elektron. SVCh, Iss. 8, 30 (1986).
- V.F. Shnyukov, B.I. Mikhailovskii, A.E. Lushkin et al.,
 Izv. Akad. Nauk SSSR Ser. Fiz. 52, 1500 (1988).
- V.F. Shnyukov, B.I. Mikhailovskii, A.E. Lushkin et al., Elektron. Tekhn. Ser. 4 Elektovak. Gazorazr. Prib., Iss. 4, 50 (1989).
- V.F. Shnyukov, B.I. Mikhailovskii, A.E. Lushkin, and A.N. Bozhko, Elektron. Tekhn. Ser. 1 Elektron. SVCh, Iss. 5, 24 (1991).
- V.F. Shnyukov, B.I. Mikhailovskii, A.E. Lushkin et al.,
 Izv. Akad. Nauk SSSR Ser. Fiz. 5, 2357 (1991).
- 64. O.I. Get'man, A.E. Lushkin, V.V. Panichkina *et al.*, Izv. Akad. Nauk SSSR Ser. Fiz. **58**, No. 10, 76 (1994).
- V.F. Shnyukov and A.E. Lushkin, Radiotekhn. 100, 267 (1997).
- O.I. Get'man, A.E. Lushkin, S.P. Rakitin, and V.V. Panichkina, Poroshk. Metallurg. N 11/12, 97 (2005).
- A.E. Lushkin, Ph.D. thesis, Kyiv University, Kyiv, 1996 (in Russian).
- V.F. Shnyukov, Dr. Sci. thesis, Kyiv University, Kyiv, 1994 (in Russian).
- S.I. Plankovskii, E.K. Ostrovskii, and E.V. Tsegelnik, Aviats. Kosmich. Tekhn. Tekhnol. 2, 78 (2008).
- V.F. Shnyukov, B.I. Mikhailovskii, A.E. Lushkin, S.P. Rakitin et al., Izv. Akad. Nauk SSSR Ser. Fiz. 58, No. 10, 171 (1994).
- G. Gartner, P. Geittner, H. Lydtin, and A. Ritz, Appl. Surf. Sci. 111, 11 (1997).
- S. Sasaki, I. Amano, T. Yaguchi, N. Matsuzaki, E. Yamada, S. Taguchi, and M. Shibata, Appl. Surf. Sci. 111, 18 (1997).

- S. Sasaki, T. Yaguchi, N. Mori, S. Taguchi, and M. Shibata, Appl. Surf. Sci. 146, 17 (1999).
- E. Uda, O. Nakamura, S. Matsumoto, and T. Higuchi, Appl. Surf. Sci. 146, 31 (1999).
- S. Sasaki, T. Yaguchi, Y. Nonaka, S. Taguchi, and M. Shibata, Appl. Surf. Sci. 195, 214 (2002).
- P. Geittner, G. Gartner, and D. Raasch, J. Vac. Sci. Tecnol. 18, 997 (2000).
- G. Gaertner, P. Geittner, and D. Raasch, Appl. Surf. Sci. 201, 61 (2002).
- I.I. Bekh, V.V. Il'chenko, O.M. Kostyukevych, and A.E. Lushkin, Visn. Kyiv. Univ. Ser. Fiz. Mat. Nauky 2, 236 (2003).
- J. Wang, Y. Wang, S. Tao, H. Li, J. Yang, and M. Zhou, Appl. Surf. Sci. 215, 38 (2003).
- J. Li, S. Yan, W. Shao, Q. Chen, and M Zhu, Appl. Surf. Sci. 215, 49 (2003).
- V.F. Shnyukov, A.D. Gorchinskii, and A.E. Lushkin, Izv. Akad. Nauk SSSR Ser. Fiz. 582, N 10, 166 (1994).
- 82. V.F. Shnyukov, A.D. Gorchinskii, B.I. Mikhailovskii, A.E. Lushkin, and V.N. Telega, in *Physicochemical, Structural, and Emission Properties of Thin Films and Solid Surface*, edited by M.G. Nakhodkin (Zaporizhzhya, 1995), Vol. 2, p. 158 (in Ukrainian).
- 83. W. Muller, Appl. Surf. Sci. 111, 30 (1992).
- 84. P.M. Zagwijn, J.W.M. Frenken, U. Van Stoolen, and B.A. Duine, Appl. Surf. Sci. 111, 35 (1997).
- S.H. Magnus, D.N. Hill, and W.L. Ohlinger, Appl. Surf. Sci. 111, 42 (1997).
- Shih, J.E. Yater, and R. Abrams, Appl. Surf. Sci. 146, 1 (1999).
- I.I. Bekh, O.Ye. Lushkin, and Yu.A. Len', Visn. Kyiv. Univ. Ser. Radiofiz. Electron. 3, 16 (2001).
- Shih, J.E. Yater, C. Hor, and R. Abrams, Appl. Surf. Sci. 7931, 1 (2002).
- S. Iida, T. Tsujita, T. Nagatomi, and Y. Takai, Surf. Interface Anal. 35, 7 (2003).
- T. Nagatomi, S. Iida, T. Tsujita, and Y. Takai, Surf. Sci. Lett. 523, 37 (2003).
- S. Iida, T. Tsujita, T. Nagatomi, and Y. Takai, Surf. Sci. 543, 1 (2003).
- T. Tsujita, S. Iida, T. Nagatomi, and Y. Takai, Surf. Sci. 547, 99 (2003).
- S-i. Iida, Y. Nakanishi, T. Nagatomi, and Y. Takai, Jpn. J. Appl. Phys. 43A, 6352 (2004).
- A. Shih, J.E. Yater, and C. Hor, Appl. Surf. Sci. 242, 35 (2005).
- 95. I.I. Bekh, Ph. D. thesis, Kyiv, 2007 (in Ukrainian).
- 96. W. Shuguang, Appl. Surf. Sci. 251, 114 (2005).
- H. Yuan, X. Gu, K. Pan, Y. Wang, W. Liu, K. Zhang,
 J. Wang, M. Zhou, and J. Li, Appl. Surf. Sci. 251, 106 (2005).

- 98. W. Jinshu, L. Hong, L. Lili, and Zh. Meiling, J. Rare Earths **25**, 194 (2007).
- J. Wang, L. Li, W. Liu, Y. Wang, and Y. Wang, J. Phys. Chem. Solids 69, 2103 (2008).
- J. Wang, L. Li, W. Liu, Y. Wang, L. Zhao, and Y. Wang,
 J. Phys. Chem. Solids 68, 2209 (2007).
- J. Wang , Y. Wang, W. Liu, L. Li, Y. Wang, and M. Zhou,
 J. Alloys Comp. 459, 302 (2008).
- J. Wang, X. Wang, W. Liu, T. Gao, and Y. Wang, J. Phys. Chem. Solids 72, 1128 (2011).
- 103. B.Ch. Dyubua, A.G. Mihal'chenkov, O.V. Polivnikova, and M.P. Temiryazeva, Elektron. Tekhn. Ser. 1 Elektron. SVCh, Iss. 1, 25 (2010).
- 104. Y. Wang, J. Wang, W. Lin, K. Zhang, and J. Li, IEEE Trans. Electr. Dev. 54, 1061 (2007).
- 105. J. Wang, Ch. Lai, W. Liu, F. Yang, X. Zhang, Y. Cui, and M. Zhou, Mater. Res. Bull. 48, 3594 (2013).

106. X. Zhang, J. Wang, W. Liu, T. Tian, and M. Zhou, Mater. Res. Bull. 48, 5040 (2013).

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Про ефективні термоелектронні катоди

Резюме

Проведено огляд наукових робіт, які присвячені найбільш ефективним сучасним термоелектронним катодам, а саме: оксидним катодам (ОК) та металево-пористим катодам (МПК). Основна увага приділена аналізу механізмів емісії цих джерел електронів. Крім того, розглядається зв'язок емісійної здатності МПК з їх фізико-технічними параметрами. Також обговорюється і вплив технології виготовлення на експлуатаційні характеристики катодів.