Improving the material properties of vacuum devices electrodes by technology rational improvement

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Abstract. The material of the electrodes of high-current vacuum and plasma electronics is traditionally obtained by powder metallurgy methods (mixing components, pressing blanks, hydrogen sintering in a given mode). However, the material of the cathodes produced according to the adopted technology, has a number of significant limitations. They are caused by the impossibility of a uniform distribution and grinding of the initial powder components by the adopted grinding in globe mills, as well as by abundant gas emission during the sintering time. The nonuniformity of the distribution of the composition in the structure, low density, high porosity, low mechanical strength of the emitting material with a metal matrix give a decrease in the operating properties of the cathodes, which leads to a decrease in the lifetime of electronic tubes. This problem is proposed to be solved by directional changes in the physical and mechanical properties of the electrode material by selecting the gravimetric consist of the base material components and improving the existing production process. The article presents the analysis of research results, changes in the structure of the material by optical and scanning microscopy methods, and also describes a complex of acquired physical and mechanical properties of experimental samples obtained by modernized technology. Thus, the developed innovative techniques allowed to increase the hardness by 36%; density by 19%, and to reduce porosity by 25% in relation to traditional cathodes. Such changes in the physical and mechanical properties make it possible to predict an increase in the service life of produced and developed vacuum tubes operating in current flow regimes up to 100 kA and in highly stressed electromagnetic fields up to 500 kV.

Introduction

High-vacuum tubes are used as key elements in plasma installations, in medical equipment, in oil production and in other fields of the national economy. They serve for transformation of high frequency and high power electromagnetic signals [1]. The operation of such devices is based on the phenomenon of electron emission from the electrodes surface[2, 3]. The cathode serves as the electrode, the main purpose of which is to produce electrons (Fig. 1).

The lifetime of high-vacuum tubes depends on the life of the cathodes. The main operating characteristics of the devices determine the cathodes emissivity. Init’s turn, the stability and high level of cathodes emissivity largely depend on the structure and physical and mechanical properties of the...
materials from which they are made of. Thus, the task of finding ways to increase the emissivity and the lifetime of the electrodes of high-current vacuum and plasma electronics is relevant.

The oxide low-temperature cathodes are most widely used according to the monitoring data on the use of high-current high-vacuum tubes cathodes. Their level of effective efficiency is 3...5 W/cm², and the efficiency of use—100...200 mA/cm² [3].

The cathode material consists of a refractory base and an emission component representing a mixture of oxides of elements of II group. The most common are alkaline earth metals barium, calcium, strontium [4–6].

There are various methods for producing oxide cathodes. One of the common methods is to obtain dispenser cathodes by impregnating a metal sponge of a refractory metal with an emission material [4, 5]. The limitations of such cathodes are low mechanical strength and low stability, strong response of the emissivity to the gravimetric consist of the original powders, to the shape and number of pores of the metal sponge [7–9], the complexity of the technical process [10] and others.

High-emission electrodes obtained by powder metallurgy methods are more durable and stable during operation in high voltage fields of vacuum tubes. Micron and submicron powders of the materials which are electrode components are mixed, compacted and sintered in inert gases environment. The authors of [11, 12] receive electrodes for plasma tubes using a similar technology.

Traditionally, the cathode material composition is a high-melting base of tungsten, a nickel (preferably) metal bond, and an emission material — strontium carbonate. An abundant gassing occurs in the material due to the evaporation of gases on the surface of the initial powders and the primary change in the carbonates structure during the component sintering as the temperature rises. The carbonate synthesis to oxide occurs together with the sintering process, since the oxides of earth metals are unstable in the air — about 1 Pa m³ of gas from 1 cm² of coating is released during the carbonates decomposing.

The technology does not allow to obtain a uniform structure of electrode materials, which leads to its final high porosity, and consequently, low density, which in its turn leads to a decrease in

Fig.1. Scheme of an electrons flow formation: 1— cathode; 2— electron flow; 3— anode
the mechanical resistance. Some cavities are formed in which the component of the emission material freely “lies”. The weak mechanical connection of the electrode base with the component of the emission material contributes to its “tearing” out of the electrode body on exposure to strong current flows — up to 100 kA and high voltages of electromagnetic fields — up to 500 kV.

These negative technology aspects reduce the electrode performance characteristics and the service life of high-current vacuum and plasma electronics devices in general.

In this paper, the possibility of changing the fractional composition of the components initial mixture and the sintering medium replacement are considered.

1. The methodology
A well-proven alloy system W-SrO-Ni, which has the tungsten is the base, and the mass fraction of its components corresponds to the following values, %: Ni — 2...3.6; SrO — 3...4.5, is chosen as the object of research.

According to traditional sintering technology, micron powders of components are used. This project proposes a transition to nanoparticles of nickel and strontium oxide powders in the range from 10 to 100 nm. The authors of a number of papers [13–16] showed the positive effect of the nanoscale components introduction on the physical and mechanical properties of various materials. Fractional composition of the developed technology is presented in Table 1.

| Powder                  | Particle size     |
|-------------------------|-------------------|
| Tungsten                | 0.4…0.6µm        |
| Nickel                  | 10…100nm         |
| Strontium carbonate     | 10…100 nm        |

The results of the study of the powders composition by x-ray microanalysis are presented in Table 2. X-ray microanalysis was performed by a Jeol JSM-6490 electron microscope with an INCA 350 energy-dispersive microanalyzer.

| Powder                  | Ni  | Sr  | O   | W   |
|-------------------------|-----|-----|-----|-----|
| Tungsten                | –   | –   | 13.27 | 86.73 |
| Nickel                  | 100.00 | – | – | – |
| Strontium carbonate     | –   | 51.91 | 51.91 | – |

The obtained results show that a significant amount of oxygen is observed in the composition of the tungsten powder. Any other impurities were not detected.

Photomicrographs of the initial loose powders are shown in Fig. 2–4. The photographs were taken in the laboratory of thin physical methods for studying the structure of materials at the Moscow Bauman State Technical University on a scanning electron microscope REM VEGA II LMH.
Fig. 2. The tungsten powder (scaled-up 1000)

Fig. 3. The nickel powder (scaled-up 1000)
Fig. 4. The strontium carbonate powder (scaled-up 1000)

According to the traditional technology of producing electrode blanks, the initial powders are mixed with a plasticizer, which is polyvinyl alcohol, compacted and sintered in a hydrogen medium. The sintering mode is shown in fig. five

Fig. 5. The sintering mode according to traditional technology
The following consecutive processes take place during sintering:
- at $T < 100^\circ C$—evaporation of moisture from the powders surface;
- at $T = 100 \ldots 300^\circ C$—plasticizer burnout;
- at $T = 700 \ldots 900^\circ C$—strontium carbonate structure change with active gas emission;
- at $T = 1300^\circ C$—strontium carbonate decompounding into strontium oxide; the chemical reaction of strontium carbonate decompounding into strontium oxide is described by the equation
  \[
  \text{SrCO}_3 = \text{SrO} + \text{CO}_2 \uparrow,
  \]
  this produces $\text{CO}_2$ gas that promotes pore formation;
- at $T = 1400^\circ C$—sintering with a liquid nickel phase formation.

The analysis shows that all processes are accompanied by abundant gas emission, which causes the final high porosity of the electrode, and hence its low density and low mechanical strength.

The stages of the technological process of traditional and improved technology are presented in Table 3.

**Table 3. Stages of obtaining electrodes**

| Technologic operation | I | II | III | IV | V | VI | VII |
|-----------------------|---|----|-----|----|---|----|-----|
| Traditional technology |  |  |       |  |  |   |     |
| Preparation of powders, weighing |  | Mixing + adding plasticizer | Dehydration | Separation | Molding | Placing samples on a pallet | Hydrogen sintering |
| Improved technology |  | Mechanical activation | Dehydration | Separation | Molding | Placing samples on a pallet | Vacuum sintering |

Differential characteristics of the proposed technology are the following:
- transition to nanoparticles of the initial binder powders and emission material;
- mechanical activation adding;
- sintering in vacuum.

Mechanical activation is carried out in a planetary mill (2SL mechanical activator), where the processes of mixing powders and plasticizers, additional grinding of powders by grinding media and the mixture mechanical activation due to high kinetic energy of grinding bodies [17], resulting from significant overloads, are combined.

Mechanical activation affects the microstructural properties of powders. The significant particle size reduction [18–22] and active mixing powders occur under the influence of this technological stage. That provides a more uniform and crushed structure during sintering.

The proposed transition from sintering the mixture of the initial powder components in a hydrogen medium to sintering one in vacuum allows to increase their density and, consequently, their mechanical strength. In addition, the possibility to eliminate the effect of a "shell" formation around the emission material component appears.

Obtaining a uniform electrode structure as a result of using binder powders and emission material in the range of 10 ... 100 nm, on condition that the powder mixture is mechanically pre-activated, improves the performance characteristics of the electrode material, i.e., increases the emission ability of the electrodes and the operation life of high-current vacuum and plasma electronics devices.
2. Results

Table 4 shows the characteristics of an electrode material for a comparative analysis of the cathodes samples properties obtained by traditional and improved technology.

| Production technology | Density, г/см³ | Pore volume, % | Hardness, HV |
|------------------------|----------------|---------------|--------------|
| Traditional            | 12.84          | 28            | 310          |
| Improved               | 15.34          | 7             | 422          |

The measurement of density and pore volume was carried out by hydrostatic weighing and performed according to State Standard GOST 2409–2014.

Hardness measurement by the Vickers method was carried out on the EMCO-TEST hardness machine according to State Standard GOST 2409–2014.

An illustrative comparative analysis of these properties is presented at Fig. 6.

The studies of the surface of electrodes obtained by scanning electron microscopy are shown at fig. 7, 8.

Fig. 6. The relative improvement in performance characteristics as a result of the technology improvement
Fig. 7. The surface of the electrodes produced by the traditional (a, b) and improved (c, d) technology.
Fig. 8. The microstructure of electrodes produced according to traditional (a, b) and improved (c, d) technology

3. Discussion
The photographs of the surface in the microstructure of the samples microsections, obtained by the improved technology, show a uniform structure, a reduced number and size of pores in the structure alternatively to the traditional implementation — with an uneven distribution of pores and large bright nickel inclusions. In addition, it is possible to determine visually the grinding of grain about 10 times.

4. Conclusion
There is an increase in physical and mechanical properties and the structure uniformity is ensured as the result of innovative techniques in the developed technology for an electrode material production, namely: the use of nickel and strontium carbonate powders in the range of 10...100 nm, the introduction of the operation of micro- and nanopowders mixture mechanical activation, the transition from sintering the mixture of the initial powder components in a hydrogen medium to sintering one in vacuum. The findings demonstrate the effectiveness of the advanced technology in the increasing of the operational life of electrode and device as a whole.
References
[1] Ashkinazi L.A. Materials of electronic emitters. Moscow, Moscow State Institute of Electronics and Mathematics (Technical University), 2007, 150 p.
[2] Bondarenko G.G., Kristya V.I., Savichkin D.O. Modeling of the effect of field electron emission from the cathode with a thin insulating film on its emission efficiency in gas discharge plasma. Vacuum, 2018, vol. 149, p. 114–117.
[3] Popov V.S., Nikolaev S.A. General electrical engineering with the basics of electronics. Moscow: Energy, 1972, 507 p.
[4] Mishra K.C., Garner R., Schmidt P.C. Model of work function of tungsten cathodes with barium oxide coating. J. Appl. Phys., 2004, vol. 95, no. 6, pp. 3069–3074.
[5] Melnikova I.P., Lyaasnikov V.N., Lyaasnikova A.V. Physics of Wave Processes and Radio Engineering Systems, 2012, vol. 15, No. 2, p. 84–90.
[6] Brodie I. A new model for the mechanism of operation of scandate and refractory oxide cathodes. IEEE Trans. Electron Devices, 2011, vol. 58, no. 4, pp. 1247–1254.
[7] Getman O.I., Skorokhod V.V., Krylova N.A. Stabilization of the microstructure of tungsten frames of impregnated metal-porous cathodes. Electrical contacts and electrodes. Ser. Composite, layered and gradient materials and coatings, 2014, p. 102–111.
[8] Smirnov V.A., Akimov P.I., Aleksandrov V.Yu. et al. Study of metal-porous cathodes with a slotted pore structure. Microwave Electronics and Microelectronics, 2016, vol. 2, No. 1, p. 115–119.
[9] Kapustin V.I., Lee I.P., Shumanov A.P. and others. The mechanism of formation and properties of crystallites of barium oxide in a metalloporous cathode. Promising Materials, 2016, vol. 7, p. 5–15.
[10] JiangD., SikongH., ChenfengZ. etal. Preparation of Impregnated Barium Scandate Cathode and Its Application. 1982. P. 206–207.
[11] Ledentsova N.E., Li I.P., Petrov V.S. and other promising technologies of oxide-nickel cathodes of microwave devices of the centimeter wavelength range. Fine Chemical Technologies, 2016, vol. 11, No. 3, p. 74–81.
[12] Kuchina I.Y., Polushin N.I., Zaharova E.S. etal. Experimental Support of Magnetron Nickel Oxide Cathode Fabrication Process. Izv. Vyss. Uchebn. Zaved. Mater. Elektron. Tekhni = Mater. Electron. Eng, 2015, vol. 18, no. 4, pp. 285–290.
[13] Sevost'yanov M.A., Nasakina E.O., Balin A.S. et al. Biocompatibility of new materials based on nano-structured nitinol with titanium and tantalum composite surface layers: experimental analysis in vitro and in vivo. J. Mater. Sci. Mater. Med. Springer US, 2018, vol. 29, no. 3.
[14] Yagodnikov D.A., Ignatov A. V., Gusachenko E.I. Ignition and combustion of pyrotechnic compositions based on micrized and ultra-nanosized aluminum particles in a moist medium in a two-zone gas generator. Combust. Explos. Shock Waves, 2017, vol. 53, no. 1, pp. 15–23.
[15] Kalashnikov I.E., Bolotova L. K., Bykov P. A. et al. Tribological properties of the babbit B83-based composite materials fabricated by powder metallurgy. Russ. Metall, 2016, vol. 2016, no. 7, pp. 669–674.
[16] Silkin A.A., Linnik A.A., Pankratovets A.S. etal. Formation of the structure of the weld metal upon the introduction of nanoparticles into the weld pool. Russ. Metall, 2016, vol. 2016, no. 13, pp. 1253–1256.
[17] Bulgarevich S.B., Boiko M.V., Tarasova E.N. et al. Kinetics of mechanoactivation of tribocutaneous processes. J. Fric. Wear, 2012, vol. 33, no. 5, pp. 345–353.
[18] Gaffet E., Bernard F., NiepeJ-C. et al. Some recent developments in mechanical activation and mechanosynthesis. J. Mater. Chem, 1999, vol. 9, no. 1, pp. 305–314.
[19] Živojinović J., Pavlović V., Kosanović D. et al. The influence of mechanical activation on structural evolution of nanocrystalline SrTiO powders. J. Alloys Compd, 2017, vol. 695, pp. 1–10.
[20] Mostaan H., Mehrizi M.Z., Rafie M. et al. Contribution of mechanical activation and annealing in the formation of nanopowders of Al(Cu)/TiC-Al2O3 hybrid nanocomposite. Ceram. Int, 2017, vol. 43, no. 2, pp. 2680–2685.

[21] Padhan A.M., SathishM., SaravananP.et al. Mechanical activation on aluminothermic reduction and magnetic properties of NiO powders. J. Phys. D. Appl. Phys. IOP Publishing, 2017, vol. 50, no. 21.

[22] Vega L.E.R., LeivaD.R., Leal Neto R.M.et al. Mechanical activation of TiFe for hydrogen storage by cold rolling under inert atmosphere. Int. J. Hydrogen Energy, 2018, vol. 43, no. 5, pp. 2913–2918.