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PERSPECTIVE NICKEL-OXIDE CATHODES TECHNOLOGIES FOR CENTIMETRIC RANGE MICROWAVE DEVICES*

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Three technologies of nickel-oxide cathodes on the basis of powder of nickel and powder of a threefold carbonate of barium-calcium-strontium for the microwave oven of devices of centimetric range of lengths of waves are offered. Optimum fraction of powder of nickel at production of cathodes are fractions 45–71 microns, the optimum maintenance of a threefold carbonate – 10% weight, the optimum pressure of pressing – 7 t/cm^2, the optimum temperature of agglomeration – 1100°C within 10 min. Improvement of quality and an exit of suitable cathodes is provided with the use of agglomerates of nickel and threefold carbonates. Agglomerates represent the particles of nickel of fraction of 10–25 microns covered with a threefold carbonate with the maintenance of a carbonate of 50% and baked in the atmosphere of the drained hydrogen at a temperature of 1000°C within 10 min. Formation of the cathode is carried out by mixing and agglomeration of agglomerates of fraction of 45–63 microns and nickel of fraction of 45–71 microns with concentration of carbonates of 10% weight. For improvement of cathodes quality, it is expedient to anneal agglomerates after their production in the environment of carbon dioxide at a temperature of 200–30 °C with a final purge nitrogen at a temperature of 1000°C within 10 minutes. Using agglomerates on the basis of nickel and a threefold carbonate at production of oxide-nickel cathodes provides more uniform distribution of emission active agent in volume and on a surface of cathodes.

Keywords: *thermionic issue, oxide cathodes, oxide-nickel cathodes, technologies of cathode materials, powder technologies, microwave ovens cathodes of devices.*

Introduction

Oxide cathodes, the cheapest and economically viable, operating at rather low temperatures (600–950 °C for different types of cathodes) are still efficiently used in klystrons and traveling-wave tubes providing pulse current take-off up to 5 A/cm^2 and durability up to 10,000 h, as well as in traveling-wave tubes (TWTs) for satellite communication equipment providing current take-off up to 0.15 A/cm^2 and durability up to 100,000 h [1–3]. Oxide-nickel cathodes are one of kinds of oxide cathodes. They are obtained either on the basis of pressed (nickel – mixture of barium-calcium-strontium carbonates) compositions or by plasma sputtering of the above compositions on the cathode core [4]. They are applied in magnetron type devices, where considerable electron bombardment of the cathode surface takes place. Besides, oxide-nickel cathodes found use in the injectors of waveguide accelerators providing current take-off in the continuous mode up to 2 A/cm^2 and pulse current take-off up to 50 A/cm^2 [5].

It is conventionally thought that disperse introduction of nickel into the carbonate phase increases the heat conductivity of the cathode material and reduces its resistance preventing

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warming up of the oxide layer and its peeling, as well as sparking of the cathode [4, 5]. However, the studies performed by us with the use of optical and electronic spectroscopy showed [6, 7] that dispersing nickel in the bulk of the oxide phase of the cathode is followed by:

– changes in the electronic structure of barium oxide, which is the main emission component of the oxide-nickel cathode;

– catalytic impact of nickel on phase transformations in cathode materials.

This study is based on results obtained previously [6, 7] and aims at developing new technologies of oxide-nickel cathodes for electrovacuum microwave devices operating in the centimetric wavelength range.

Physico-chemical fundamentals of the technologies

Previously the authors of [8, 9] succeeded in calculating dependences of the work function of barium oxide on temperature and on the concentration of oxygen vacancies. Combined analysis of these data and of data presented in [6, 7] allowed concluding that the emission properties of an oxide cathode on a nickel core alloyed by various additional elements are determined by two factors:

1) the optimal concentration of oxygen vacancies, which is attained by using various core options in various time periods;

2) the effect of nickel on the electron structure of barium oxide, first of all, on the structure of the valence-band edge, which affects in many respects the value of the work function of barium oxide.

The above generalizations of the role of nickel in oxide-nickel cathode materials allow formulating physical and physical and chemical bases for developing technologies of oxide-nickel cathode materials. First of all, the technologies should provide uniform alloying of barium oxide crystallites with nickel atoms in the whole bulk of the oxide phase of the cathode material, which will increase the uniformity of the emission properties of the cathodes and the reproducibility of technologies for their production. Besides, the technologies should provide uniform catalytic impact of nickel on the oxide phase in the bulk of the oxide phase of the cathode material. This will provide uniform decomposition of barium-calcium-strontium triple carbonate with the formation of an oxide phase and prevent the formation of the corresponding hydroxides.

When choosing technological workflows for the production of pressed oxide-nickel cathodes, the following requirements should be taken into account:

– The process of producing the cathodes should be high-efficiency, reliable and economically sound for the serial production of magnetrons.

– The process of producing the cathodes should be hi-tech and controllable.

– The developed cathodes should provide high stability and reproducibility of operational parameters of magnetrons operating in the centimetric wavelength range.

We chose the following options of techniques of producing oxide-nickel cathodes for microwave devices:

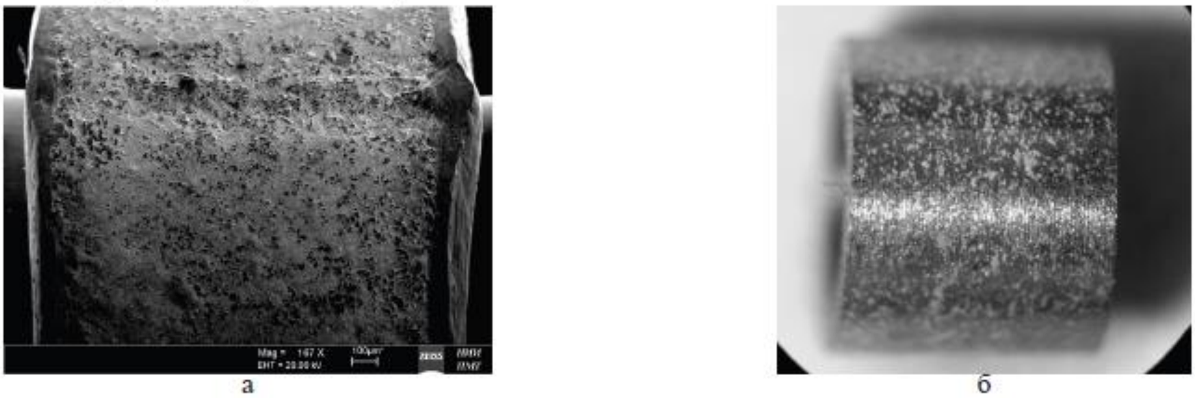
option A – a mechanical mixture of carbonyl nickel (fractional compositions 5–7 μm, 10–25 μm, 45–71 μm and 71–100 μm) and triple barium-strontium-calcium carbonate of KTA-1-6 brand with its content varied in the range 2.5–15% mass.;

option B – a mechanical mixture of carbonyl nickel (a basis with fractional composition 45–71 μm) and synthesized agglomerate (nickel of 5–7 μm or 10–25 μm fractions + triple barium-calcium-strontium carbonate of KTA-1-6 brand with the content of the carbonate 30 or 50% mass.);

option C – a mechanical mixture of carbonyl nickel (a basis with fractional composition 45–71 μm) and agglomerate reduced in a flow of CO_2 (nickel of 5–7 μm or 10–25 μm fractions + triple barium-calcium-strontium carbonate of KTA-1-6 brand with the content of the carbonate of 30 or 50% mass.)

Options A of technologies for producing the cathodes

Preliminary studies of the microstructure of the cathode materials showed that the best uniformity of the mixtures is attained when using nickel powder of 5–7 μm and 45–71 μm fractions. The nickel powders were subjected to washing, annealing and sifting. Triple barium-calcium-strontium carbonate was calcinated and sifted. Then the nickel and triple carbonate powders were mixed in a planetary type "Turbula" installation for 3 hours and more. After this samples were taken and pressed in a laboratory press in special industrial equipment. The samples of pressed cathodes were agglomerated in dry hydrogen with a dew-point not above –60°C. Then the semi-products were subjected to lathe treatment to attain the preset constructional sizes; chemical degreasing; cleaning by annealing in vacuum; and assembly as a part of cathode preheating blocks. Figure 1 shows (a) the appearance of a conventional oxide cathode after final reduction by pressing in three-section equipment and (b) the appearance of a pressed oxide-nickel cathode. Note that finish pressing of the conventional oxide cathode results in the screens deformation.



а б

Figure 1. The appearance of cathodes: *a* – a conventional spongy oxide cathode; *b* – a pressed cathode based on nickel and triple oxides (Ba, Ca, Sr). [а, б means *a*, *b*]

At the stage of optimization of the fractional composition of the nickel powder press powders were prepared. They consisted of nickel of 45–71 μm fraction and triple carbonate (Ba, Ca, Sr) of KTA-1-6 brand with the content of the latter 2.5, 5.0, 7.5 and 10% mass. Then cylindrical test-pieces of cathodes with diameter d = 6.85 mm and height h = 2.47 – 2.55 mm were pressed at five values of specific compressing force. After agglomerating the semi-products in dry hydrogen at 1100 °C and calculating porosity according to formula

$$\Pi = (1 - \rho_{\text{загот}}/\rho_{\text{комп}}) * 100\%, \qquad (1)$$

where $\rho_{comp} = 8.9$ g/cm^3 (nickel density) [$\rho_{\text{комп}}$ means ρ_{comp}],

$\rho_{semi} = m/V$ (cathode semi-product density) [$\rho_{\text{загот}}$ means ρ_{semi}],

m – mass, V – semi-product volume,

we obtained dependences (Figure 2) of porosity on specific compressing force at various concentrations of triple carbonate. As the content of triple carbonate in the mold powders increases, the cathodes porosity increases. However, when lathing such cathodes, the samples start crumbling.

In contrast to large-fraction nickel, "swelling" of the geometrical sizes occurred in emitters with nickel powder of 5–7 μm fraction after agglomeration, which is due to the existence of particles of other sizes in the initial powders, as well as to the morphology of the powders caused, for example, by their lump formation.

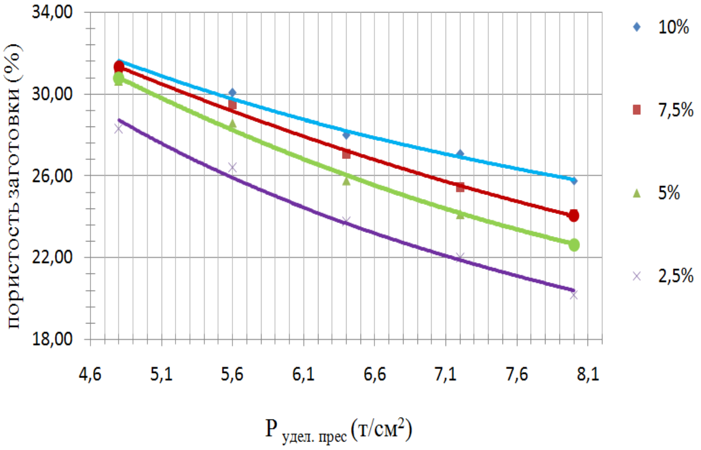


Figure 2. Dependence of porosity of oxide-nickel semi-products for cathodes on specific compressing force. [пористость заготовки (%) means Semi-product porosity (%); $P_{\text{удел. прес}}$ (т/см^2) means Specific compressing force (t/cm^2)]

One more cause of the reduction of density of the semi-products after agglomeration are the closed pores formed in the course of sintering, because elevated pressure is created in them due to evolution of sorbed gases from the powder material. This can be accounted for by the high sorption capacity of fine carbonyl nickel mixed with triple carbonate (Ba, Ca, Sr).

As a result of the performed study it was found that the sintering of semi-products for cathodes based on triple oxides should be carried out in the atmosphere of dry hydrogen at 1100 °C for 10 min. It is expedient to perform cleaning annealing in vacuum, but at lower temperatures (600–700 °C) with preliminary rubbing of emitters with petroleum ether. Cleaning annealing of the emitters without degreasing is strongly undesirable, because mechanical impurities remain on them.

The structure of the surface of cathodes based on oxide-nickel cathode materials after lathing has marking of the cutter. The subsequent cleaning annealing of the cathodes in the atmosphere of hydrogen smooths the structure a little. However, a large number of islands of emission-active substance emerge on the surface. When carrying out cleaning annealing in vacuum, the quantity of the formed islands significantly decreases.

After agglomeration of the semi-products for cathodes their porosity can change. The influence of this factor on the porosity of cathodes was studied for two compositions of the cathode materials containing 10% of triple carbonate and nickel powder of 5–7 μm and 45–71 μm fractions. The samples were pressed at compressing force P = 60 atm and sintered in dry hydrogen at temperatures 1000, 1050, 1100, 1150 and 1200 °C for 10 min. After this all the samples were lathed for convenience of porosity calculation, because the samples with nickel of 5–7 μm fraction changed their form in contrast to the samples made of nickel with fractional composition 45–71 μm. The dependence of porosity on sintering temperature for samples with different fractions of nickel is presented in Figure 3.

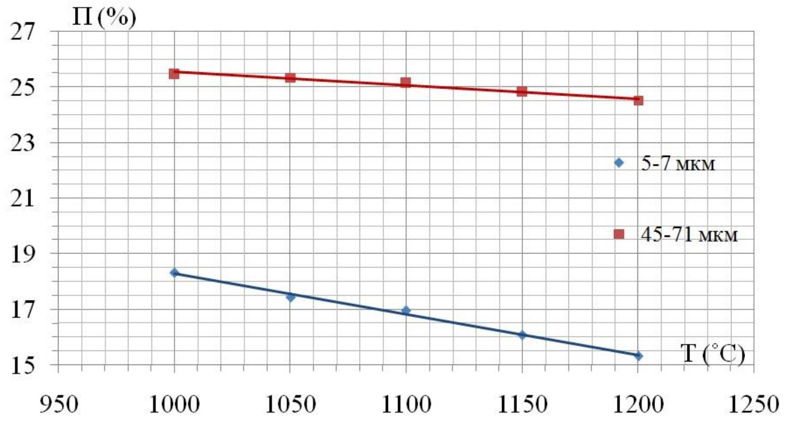


Figure 3. Dependence of porosity of semi-products of oxide-nickel cathode materials on the temperature of sintering in dry hydrogen.

[мкм means μm; П means P]

Similar experiments were carried out with samples containing other amounts of emission-active agent. The optimum compressing force for making semi-products was found to be ~ 7 t/cm^2. Besides, the quantitative ratio of nickel and triple carbonate was determined. The content of the latter in the mixture can vary from 7.5 to 10% mass depending on operating conditions of the cathode. Porosity under the found experimental conditions was 25 – 28% for nickel of 45–71 μm fraction and 15 – 19% for nickel of 5–7 μm fraction. Devices with such cathodes are characterized by steady and trouble-proof operation during dynamic tests.

Considerable decrease in mechanical strength was noted at carbonate concentration 10% mass and higher. This can cause sparking, deterioration of the spectrum and reduction of the power of the generated oscillations in the course of the device training.

Options B of technologies for producing the cathodes

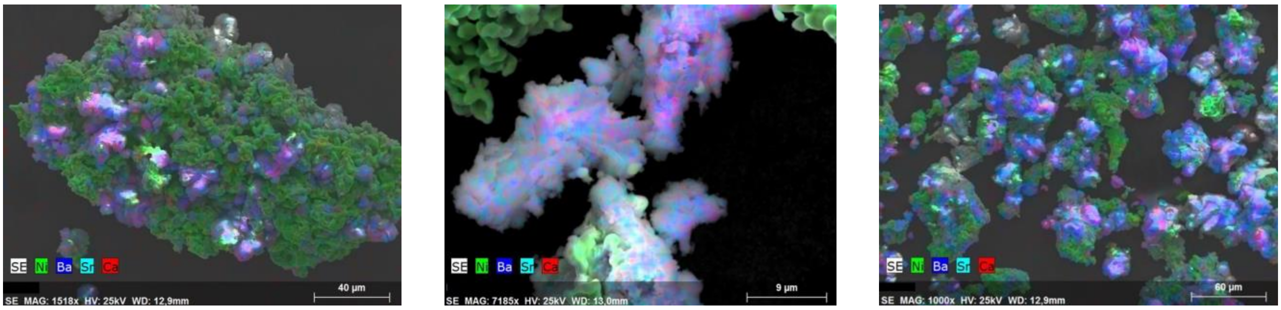
In these options of technologies a material based on a mechanical mixture of nickel (45–71 μm fraction) and agglomerate (Ni of 10–25 μm fraction + 30 or 50% mass KTA-1-6 brand carbonate) was chosen for the studies. Powders for the production of agglomerates were mixed in the planetary type installation and sintered in bulk in the atmosphere of dry hydrogen. After this the sintered mixtures were ground in an agate mortar to obtain a 45–63 μm fraction and mixed with nickel (45–71 μm fraction) to obtain a concentration of the emission-active agent in the mold powder equal to 10% mass. The modes of the agglomerates sintering are presented in Table 1.

Table 1. Modes of components sintering in dry hydrogen for the preparation of agglomerates

Sample No	Composition	Temperature, °C	Time, min
1	Ni of 5–7 μm fraction + 30% mass. of carbonates KTA–1–6	1100	10
2	Ni of 5–7 μm fraction + 30% mass. of carbonates KTA–1–6	900	10
3	Ni of 5–7 μm fraction + 50% mass. of carbonates KTA–1–6	1100	30

The obtained sintered mixtures were ground in agate mortars and studied in a scanning electron microscope EVO 40 produced by Zeiss Company equipped with a SDD silicon drift detector X Flash 1106. The sintered mixtures obtained at 1100 °C formed plate-shaped particles upon powdering. This effect was most clearly shown in samples sintered for 30 min at of 1100 °C. For samples obtained at 900 °C we observed the existence of unbound particles of the oxide phase.

Results of the study of the microstructure of samples **1**, **2** and **3** and agglomerates are presented in Figure 4.



1 **2** **3**

Figure 4. Microstructure of agglomerates **1**, **2** and **3** at different sintering modes.

As a result of the conducted studies it was found that the optimal scheme for the production of agglomerates is:

– fractional composition of nickel powder: 10–25 µm;

– content of emission-active agent in the initial powder: 50% mass;

– synthesis of agglomerates in the atmosphere of dry hydrogen at 1000 °C;

– time of holding at the maximum temperature: 10 min;

– powdering of sintered mixtures in an agate mortar to obtain a 45–63 µm fraction.

Images obtained in a scanning electron microscope for the initial agglomerates and agglomerates after sintering are presented in Figure 5.

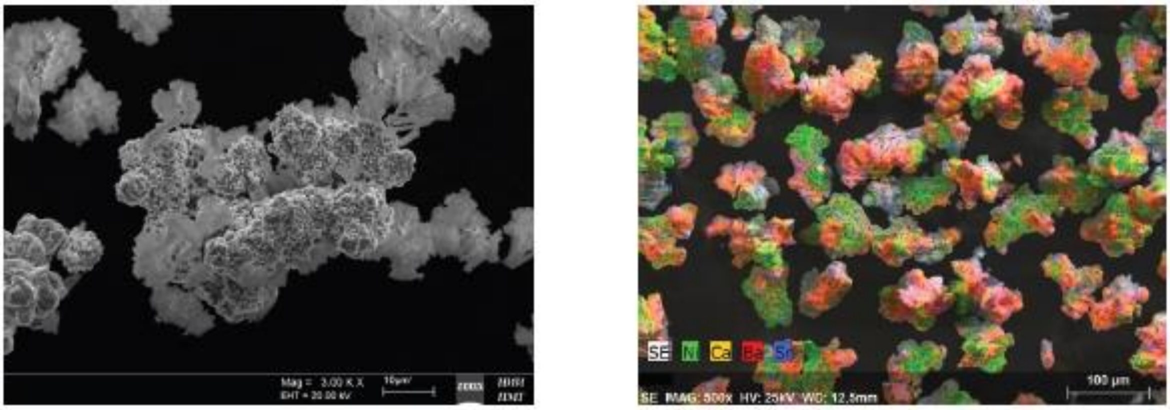


Figure 5. Microstructure of agglomerates before (left) and after (right) sintering.

It can be seen in Figure 5 that there are no particles of free carbonate after the agglomeration, and the nickel particles are completely “wrapped” in the emission-active agent.

The following stage of cathodes production is obtaining a mold powder. For this purpose the synthesized agglomerate was ground in an agate mortar, sifted through sieves to obtain a 45–63 µm fraction, and then mixed with carbonyl nickel of 45–71 µm fraction to obtain the content of the emission-active agent in the mold powder 10% mass. The mixing was carried out in a planetary type "Turbula" mixer for 3 h. The obtained powder was pressed into emitters, the cylindrical surface of which was studied in a scanning electron microscope. The result is shown in Figure 6.

Figure 6. Mapping of the cylindrical surface of an oxide-nickel emitter produced with the use of agglomerates.

Due to the presence of the agglomerates as a part of the cathodes based on the oxide-nickel cathode materials uniform distribution of the emission-active agent in the nickel matrix of the cathode was attained. The magnetic properties of nickel were completely excluded.

Options C of technologies for producing the cathodes

In this case the material based on the mechanical mixture of nickel (45–71 µm fraction) and the agglomerate (Ni of 10–25 µm fraction + 50% mass of KTA-1-6 carbonate reduced in CO_2) was chosen for the study.

It was found by X-ray phase analysis that the oxide compounds obtained by agglomeration are transformed into hydroxides and peroxides after extraction of the agglomerates from the hydrogen furnace according to option **B**, as well as in the course of grinding the agglomerates and pressing the cathodes. The latter cannot be reduced to barium oxide upon activation of the cathodes. Therefore, we studied the effect of the conditions of storing the powdered cathode materials after their agglomeration in the air, in an anhydrous medium (dessicator) and in carbon dioxide on their properties.

The mixtures of the carbonates for obtaining the agglomerates based on carbonate-coated nickel were sintered in bulk in hydrogen atmosphere with a final purge by nitrogen at 1000 °C for 10 min. The obtained agglomerate was divided into three parts, which were placed at once into the air, anhydrous and carbon dioxide environments. Table 2 presents the masses m of the material samples and the mass changes Δm as a result of their storage in various environments during various times. Figures 7 and 8 below present for comparison the results of studying the structure of the agglomerates in a scanning electron microscope.

Figure 9 presents the composition of the surface of a cathode made with the use of nickel powder of 10–25 μm fraction and nickels/carbonate agglomerates reduced in the atmosphere of CO_2.

Table 2. The masses of samples of materials (g) and mass changes upon storage in various media

Air	Anhydrous medium (dessicator with silica gel)	CO_2
Initial mass *m*		
11.0963	11.1189	11.1217
After 1 day		
11.1218 (Δ*m* = 0.23%)	11.1239 (Δ*m* = 0.04%)	11.1488 (Δ*m* = 0.24%)
After 3 days		
11.1271 (Δ*m* = 0.05%)	11.1246 (Δ*m* = 0.006%)	11.1691 (Δ*m* = 0.18%)
Total Δ*m* after 5 days		
Δ*m* = 0.28%	Δ*m* = 0.05%	Δ*m* = 0.42%

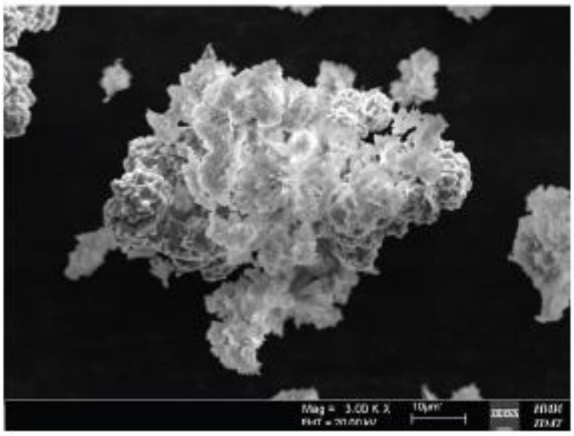


Figure 7. Initial barium-calcium-strontium carbonates before agglomeration.

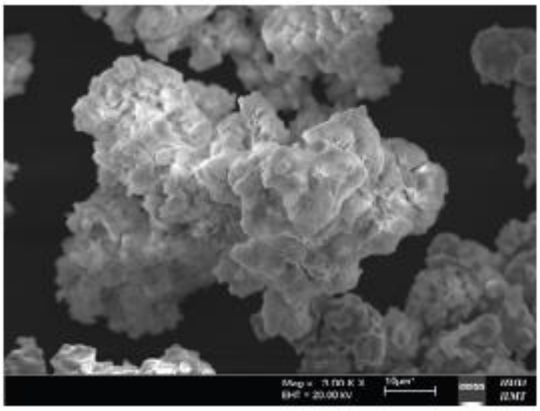


Figure 8. Agglomerates after sintering in hydrogen at 1000 °C for 10 min (with final purge by nitrogen) stored in the anhydrous medium.

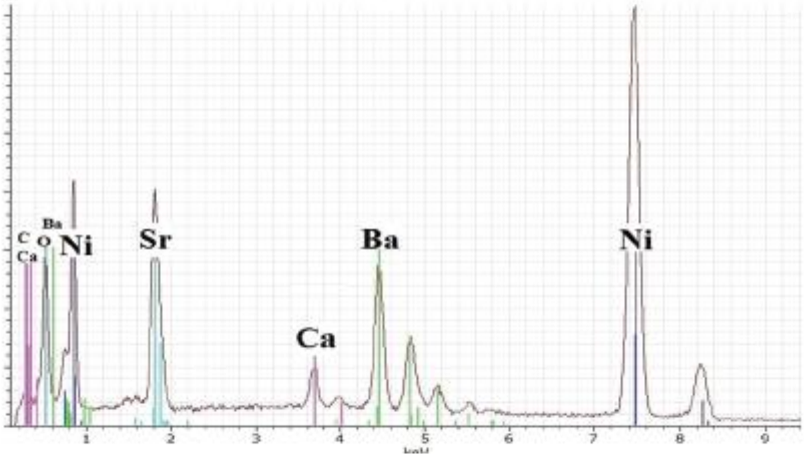


Figure 9. The elemental composition of agglomerates of nickel and triple carbonate (Ba, Ca, Sr) reduced in a flow of CO_2 found by means of a scanning electron microscope.

As a result of the analysis it was found that the triple carbonate that was decomposed into triple oxides upon agglomeration is transformed back into the triple carbonate upon calcination for 1–2 h in a flow of carbon dioxide heated to 180–200 °C, the compact form of the obtained agglomerates being preserved.

Test of cathodes made according to the developed technologies

The design of the cathode-preheating blocks with the pressed emitters based on oxide-nickel cathode materials includes a core and a porous sponge with the emission active substance of a particular porosity and composition distributed in it. Figure 10 gives an example appearance of the cathode-preheating blocks of various small-sized magnetrons, in which oxide-nickel cathode materials are applied.

Figure 10. Cathode-preheating blocks with emitters based on oxide-nickel cathode materials: 1 – M1 type product; 2 – M2 type product; 3 – M3 type product.

The technological process of producing the pressed oxide-nickel cathodes is hi-tech and controllable. Introducing it in the batch production will allow, on one hand, significantly increasing the efficiency of the production of electrovacuum devices (magnetrons, TWTs, klystrons, etc.) and, on the other hand, considerably increasing their reliability and life cycle. Operations for producing the pressed cathodes based on oxide-nickel cathode materials include:

– annealing and sifting of triple carbonate KTA-1-6;
– washing, annealing and sifting of carbonyl nickel powders;
– production of mold powder consisting of a mixture of nickel and triple carbonate powders;
– pressing and agglomeration of semi-products for cathodes;
– lathing of the semi-products for cathodes;
– degreasing and cleaning annealing of the emitters.

The results of testing the pressed oxide-nickel cathodes made according to option A in devices showed that the cathodes containing carbonyl nickel of 45–71 μm fraction have the best emission characteristics and a higher stability as compared to the cathodes containing nickel of 5–7 μm fraction.

Tests of the oxide-nickel cathodes made according to option B in devices showed that spectrum doubling and decrease in the power characteristics of the devices is observed in some devices as compared to the cathodes made according to the usual technological scheme. This is probably the result of the transformation of the emission-active agent into hydroxides and crystallohydrates upon taking the agglomerates out into the air after their synthesis in hydrogen. Testing of magnetrons with the pressed oxide-nickel emitters made according to option B with the use of the agglomerates reduced in CO_2 (Table 3) was carried out.

Table 3. Results of testing the cathodes made with the use of agglomerates in M1 type product magnetrons

Magnetron No	Thermal emission current in the diode mode (mA)	Results of dynamic test
1	189	Usable
2	205	Usable
3	171	Usable

Conclusion

1. The properties of the oxide-nickel cathode material made according to the conventional technology by mixing, pressing and agglomeration of nickel and barium-calcium-strontium triple carbonate powders considerably depend on the fractional composition of the initial carbonyl nickel powder, the content of triple carbonate in it, compressing force, temperature, gaseous medium and agglomeration time, as well as on the gas medium in which the cathodes are stored.

2. The optimal fractional composition of the nickel powder at the production of the oxide-nickel cathodes according to the conventional technology is the powder of 45–71 μm fraction. The optimal content of triple carbonate of KTA-1-6 brand is 10% mass. The optimal specific force is 7 t/cm^2. The optimal sintering temperature is 1100 °C for 10 min. The optimal medium for the agglomeration is dry hydrogen. The cleaning annealing should be carried out in vacuum at 600–700 °C with preliminary rubbing of the emitters with petroleum ether. The optimum medium for storing the cathodes after their production according to the conventional technological scheme is a dried medium.

3. Increasing the quality and percentage of usable oxide-nickel cathodes is possible by using agglomerates of nickel and triple barium-calcium-strontium carbonates. The agglomerates are nickel particles of 10–25 μm fraction coated with triple carbonate with the content of carbonate 50% mass and sintered in dry hydrogen at 1000 °C for 10 min. It is expedient to carry out the formation of the cathode material by mixing and subsequent sintering of the agglomerates of 45–63 μm fraction and nickel of 45–71 μm fraction with the concentration of carbonates 10% mass. In order to improve the cathodes quality it is expedient to anneal the agglomerates after their production in carbon dioxide at 200–300 °C.

4. The oxide-nickel cathodes made according to the optimized conventional technological scheme allow successfully replacing the conventional oxide cathodes thus increasing the expensive materials use coefficient, increasing the percentage of usable devices and their life cycle. In addition, the process of producing the oxide-nickel cathodes is characterized by high technological effectiveness and a decrease of the share of hand work.

5. Using the agglomerates based on nickel and triple carbonate for the production of oxide-nickel cathodes provides more uniform distribution of the emission-active agent in bulk and on the cathodes surface. However, this technology requires recovery annealing of the cathode materials in carbon dioxide.

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