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Research of Current-Conducting Electrodes of Elements from Piezoelectric Ceramics Modified by the Low-Energy Ribbon-Shaped Electron Stream

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In the article, the regularities of the influence of structural transformations that occur when modifying current-conducting electrodes of elements from piezoelectric ceramics by the low-energy ribbon-shaped electron stream on the performance characteristics (wear resistance and corrosion resistance) of these electrodes. The technological experiment of obtaining modified electrodes on piezoceramic elements is based on a combined process of thermal deposition of a thin silver coating on piezoelectric ceramics in a vacuum. For two groups of samples (formed by the technology proposed by the authors, silver coatings on piezoelectric elements and coatings obtained in an industrial way), the surface state (microrelief, element composition) and the wear rate were studied.

Keywords: Piezoelectric ceramics, Electron stream, Conductive electrode, Atomic force microscopy, Wear resistance, Corrosion resistance.

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1. INTRODUCTION

The development of innovative production technologies has recently been widely spread in various spheres of human activity around the world. This is primarily due to the popularization of such areas as nanotechnology, alternative energy, bionics, functional medicine, nanoelectronics, nanooptoelectronics, and others, as well as with significant investments by the world's leading research and development companies in these sectors. In this regard, the technologies and devices that use the direct and / or reverse piezoelectric effect in the principles of their work are promising [1]. Thus, according to the results of the analysis of the world market of micro-devices based on the piezoelectric effect (piezoactuators, jet nozzles, microphones, pressure, vibration sensors, etc.), the consulting company "Yole Développement" (France) found that, for today, this market has almost reached the mark of $ 85 million, and by 2023 it will be about $ 310 million (while the Compound Annual Growth Rate will be 30.3 %) [2]. It should be noted that the main accent that is being made by this company in the analysis of the piezoelectric device market is the research of devices with piezoelectric ceramics PZT (lead zirconate titanate). The unconditional advantages of using PZT piezoelectric ceramics are: low cost of raw materials and technology for the manufacture of piezoceramic elements, a relatively simple manufacturing technology, the majority of technological operations are unified with operations of microelectronics technologies, high inertness to the influence of climatic factors of the environment (including for aggressive and dangerous environments temperature, pressure, acidity, radioactivity, etc.), highly stable indicators of electromechanical coefficient, electrical and mechanical strength, ultra-high sensitivity to external mechanical influences (up to 10^{-9} N) and others [1].

A significant scientific contribution to the development of the theoretical, mathematical and methodological and experimental basis for the development of new devices with piezoelectric ceramics was made by many domestic and foreign scientists [3, 4].

For solving problems related to the improvement of manufacturing technologies for piezoceramic elements have been devoted the works [5, 6].

However, for items from PZT piezoelectric ceramics, there remain unresolved issues of improving the mechanical strength of silver (less often – nickel) electrodes, which are applied chemically to the surface of the ceramic and have little durability (wear intensity $I_w = 4 \times 10^{-7}$ g/m at the load 0.38 mN, which grows exponentially with increasing load) [7]. Another problem, also related to the material of the piezoelement electrodes, is the low corrosion resistance of these materials to the ammonia and sulfur compounds that are present in the external atmosphere (especially at a high concentration of these compounds in the conditions of large industrial enterprises, thermal power plants, cities with an extensive motor transport system).

Therefore, promising and relevant in this area of research is the improvement of the technology of forming current-conducting electrodes of elements from piezoelectric ceramics, which will increase their wear and corrosion resistance.

The team of authors developed a combined method of depositing metal coatings on the surface of dielectric materials followed by its low-energy electron-beam modification. The essence of this method lies in the thermal (resistive or electron-beam) deposition of the coating material (for example, Ag) in a vacuum on a piezoceramic surface prepared in a special way [8] and the subsequent action (in one technological cycle) of an electron flux of a fixed power on the surface of a piezoelectric material. This action results in the heating and compacting of the coating material while simultaneously increasing the depth of its diffusion penetration into the piezoelement material.

The purpose of the article is to establish the regularities of the influence of structural transformations that occur, when modifying current-conducting electrodes of

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piezoelectric ceramics elements by low-energy ribbon-shaped electron stream, on the operational characteristics (wear resistance and corrosion resistance) of these electrodes.

2. THE TECHNOLOGICAL EXPERIMENT CONDUCTING PROCEDURE

The technological process for obtaining modified electrodes on piezoceramic elements is based on a combined process of thermal deposition of a thin silver coating (80-120 μm thick) on a base of piezoelectric ceramics of a PZT-5 in a vacuum of the order of (5... 6) × 10^{-3} Pa.

The starting material for obtaining a coating on piezoceramics was Ag powder, which calibrated on particales sizes ("chp" (chemically pure), particle size 1.2 ... 1.6 μm). Powder manufacturer – "Powder nanotechnology, Ltd." (Cherkasy).

Previously, the powder was weighed on an electronic scales VLA-200g-M. Further, the resulting material for spraying was loaded into a special developing tray that was placed in a tungsten evaporator, the temperature of which was maintained at 2300 ... 2800 K.

Technological experiment was carried out in the educational and scientific center "Micronanotechnologies and equipment" (ESC MNE) of the Cherkasy State Technological University on the modified technological vacuum unit UVN-71 on the following modes [9]: evaporation current – $I = 45 \ldots 60$ A; vacuum deposition time – $t = 90 \ldots 110$ s; weight of material for spraying – $m = 40$ mg; specific power of the electron stream $P_{sp} = 35$ watts/mm^2; speed of surface electron-beam processing $v = 10$ sm/s.

The thickness of the coatings obtained was measured by two methods. In the process of precipitation - by the quartz resonator method, which made it possible to select the necessary deposition rate (~ 9 … 11 nm/s). Further, the thickness of the obtained coating was measured by Linnik's optical interferometry on a MII-4 instrument.

The microstructure of the electrode surface of the samples before and after operation and long-term storage, as well as the elemental composition of the coatings, was carried out with a scanning electron microscope "ZEISS EVO 50 XVP" (manufacturer of "Carl Zeiss", Germany) in the Center for the collective use of V.N. Bakul Institute for Superhard Materials NAS of Ukraine (Kyiv), and the nanorelief and wear resistance of the coatings obtained were measured with an atomic force microscope NT-206 (manufacturer: "Microtest-machines", Belarus) in ESC MNE. The measurements of microrelief of the surface of the samples were carried out in a static mode on the surface areas, with a maximum size of 13 × 13 μm, according to the developed methods and recommendations [10].

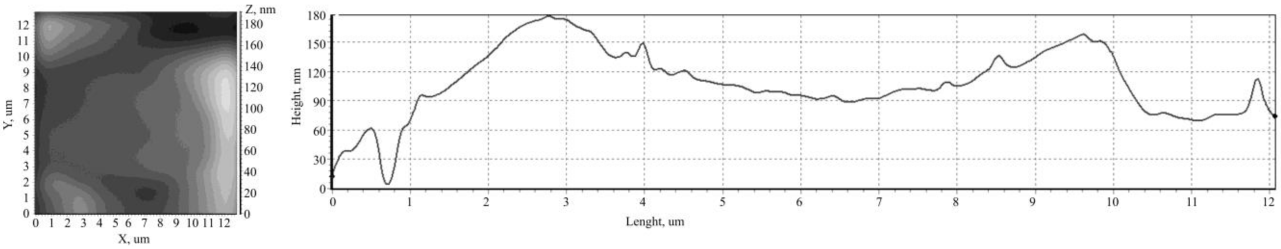
3. RESULTS OF RESEARCH OF WEAR-RESISTANCE AND CORROSION RESISTANCE OF ELECTRODE OF PIEZOCERAMIC ELEMENTS

As a result of the technological experiment, samples (group I) were obtained from the piezoelectric ceramics of PZT-5. To compare the results of the experiment, samples (group II) from the same material obtained in the industrial method were taken ("UkrPiezo", Cherkasy). For both groups of samples, conducted research the state of the surface (microrelief, elemental composition) and the wear rate.

Research of the microrelief of silver coatings on piezoelectric ceramics. The mechanism of nucleation and the formation of a uniform continuous coating of the Ag polycrystalline structure was investigated by scanning electron microscopy, and the microrelief of the coating surface itself was determined by atomic force microscopy.

The obtained experimental results made it possible to elucidate the following. The temperature above which irreversible structural transformations occur in the coating with its electron-beam modification was of the order of 830-900 K.

Herewith, the silver coating on the piezoceramic basis becomes more compacted and less developed, Fig. 1, (the average ratio of the actual coverage area to the area of the investigated area is 1.5:1, in contrast to the samples of coatings obtained in vacuum without electron beam treatment (the original surface) – 2.8:1) and has a relative porosity of the order of 0.06-0.08 (the relative porosity of the surface of coatings without electron-beam processing is 0.1-0.14).



a b

Fig. 1 – External view (a) and microprofile of the surface of the silver electrode (b). Device NT-206

Herewith, as can be seen from Fig. 1, the average arithmetic mean of the microroughnesses of the surface of such a coating is 178.7 nm, which is much less than the microroughness of the initial surface (~ 680 nm).

The researches with using the methods of electron microscopy of sample surfaces, both Group I and Group II, changes in coatings at temperatures above 900 K have shown the formation of silver conglomerates on it, Fig. 2.

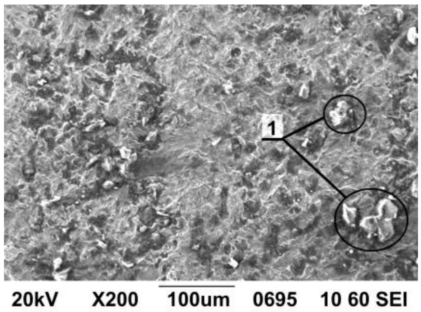
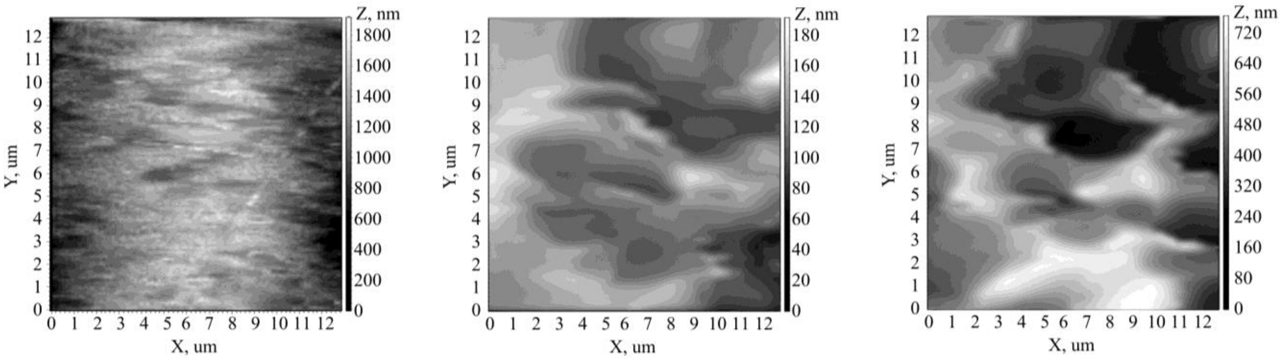


Fig. 2 – The surface of the silver electrode of the sample from the piezoelectric ceramics PZT-5 with formed on it, due to electron-beam modification, at temperatures above 900 K, silver conglomerates (1). Device ZEISS EVO 50 XVP

The formation and growth of such conglomerates are disordered. This is confirmed by the fact that temperature is not the main factor in the formation and growth of these structures, but only acts as a condition for their appearance on the silver coating.

At the same time, changing the coating at a temperature of less than 830 K leads to the formation of an amorphous coating, has a low adhesion strength (~ 6 ... 8 MPa), and wear resistance (the formation of micro- and nanodefectives of surfaces from the action of external force loads and vibrations is characteristic). Therefore, silver electrodes formed at low temperatures are non-continuous and inhomogeneous in thickness, Fig. 3. This significantly worsens the operating life of piezoceramic elements and the main technical and operational characteristics of the devices created on their basis.



a b c

Fig. 3 – The surface of the silver coating on piezoelectric ceramics PZT-5 of group II (a) and group I: with electron-beam modification at a temperature of 880 K (b) and with electron-beam modification at a temperature of 780 K (c). Device NT-206

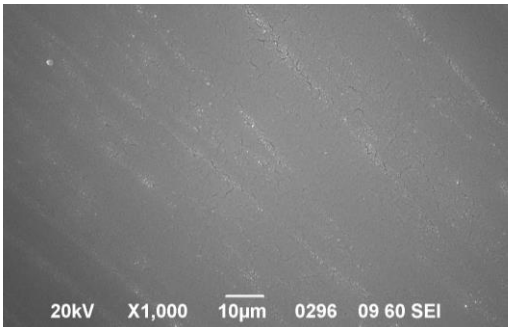
At the same time, the study of the samples showed that the quality of the electrodes is also affected by the method of their deposition. Thus, the electrodes on samples of group I, which were obtained by thermal deposition in vacuum from Ag powder, had a chemical purity of about 99.63 % by weight and a porosity of less than 0.08, while the chemical purity of the electrodes produced in the industrial process (samples of Group II), was 96.98 % by weight with a minimum thickness of about 160 μm and a porosity of 0.24 ... 0.26 (Fig. 4).

Analysis of the samples from group I showed that after 10 years of operation, the surface porosity of the electrodes for 50 % of the samples of this group increased to an average of 0.12 (the chemical purity of such coatings was 83.3 % by weight) and 0.36 for samples with electrodes produced in the industrial process (the chemical purity of such coatings was 56.8 % by weight), which makes it impossible to further exploit the industrially manufactured samples (Fig. 5).

Thus, it is established that the temperature of the piezoceramic sample during the electron-beam modification of silver coatings is a necessary condition for the formation of qualitative electrodes, for which the possibility of the appearance of defects from the action of external force loads and vibrations is minimized. At the same time, a change in the structure and microgeometry of the modified coatings on piezoceramics from the parameters of the ribbon-shaped electron stream has been determined.

Comparing the results of a study of the state of the surface of silver coatings obtained using the proposed combined technology and coatings obtained in an industrial way, it was established that the maximum service life under extreme conditions of 90 % of the samples of Group I exceeded eight years, after, under normal conditions, a decrease in functionality all samples of Group I were not detected during their operation for 10 years. Herewith, for samples from group II (with industrially formed electrodes), the maximum service life in extreme conditions will be limited to six years. Under normal operating conditions, only for 40 % of samples of group II the service life will exceed 10 years.

Research of the element composition of silver coatings by the method of scanning electron microscopy. Investigation of the element composition of coatings of electrodes, resistance, is carried out using a technique for



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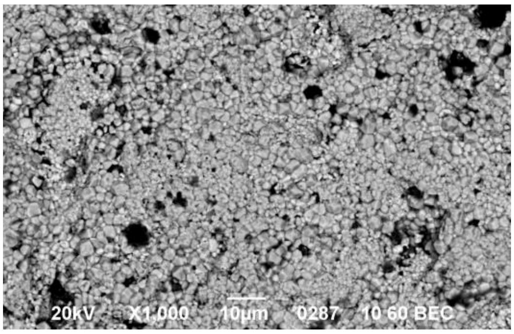
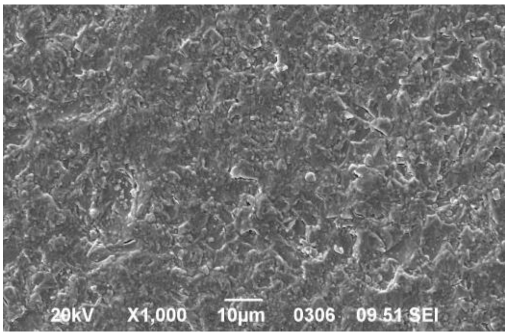


b

Fig. 4 – Fragments of electrode surfaces on samples with piezoceramics PZT-5 (were not in operation): (a) electrodes modified with an electron stream (I group of samples); (b) electrodes produced in the industrial process (II group of samples). Device ZEISS EVO 50 XVP



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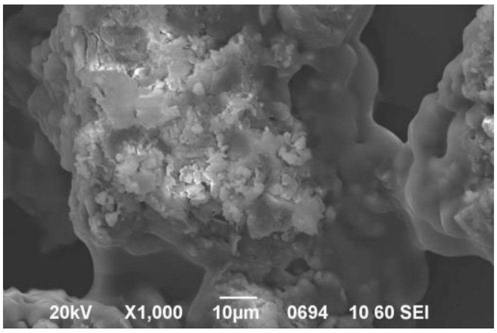

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Fig. 5 – Fragments of electrode surfaces on samples with piezoceramics PZT-5 (were in operation under extreme conditions for 10 years): (a) electrodes modified with an electron stream (I group of samples) (b) electrodes produced by industrial method (II group of samples). Device ZEISS EVO 50 XVP

determining the spectral energy dispersion of elements in the coating, which was realized by means of a scanning electron microscope ZEISS EVO 50 XVP. The results of these studies are presented in Table 1.

Table 1 – Spectral element analysis of the coating of samples I and II group

Service life, years	Element, mass.%				
	Ag_K	N_K	H_K	S_K	Other
Samples of Group I					
Before operation	1.12	25.21	26.20	46.26	1.21
1	12.04	18.84	13.43	54.88	0.81
3	91.98	3.22	4.48	–	0.32
5	24.27	9.46	2.87	58.14	0.58
7	55.94	–	0.93	22.21	–
10	89.10	–	–	–	–
Samples of Group II					
Before operation	1.78	25.67	26.88	43.64	2.03
1	14.70	16.46	8.31	59.44	1.09
3	87.12	4.23	5.16	32.23	0.26
5	24.97	12.11	3.21	69.63	0.08
7	73.28	0.47	1.78	24.47	–
10	99.89	–	0.11	–	–

The data given in Table 1 allow us to conclude that the Ag component in the coating decreases with the time of operation. The mass fraction of sulfur with operating time varies as follows: in a less dense surface layer, the mass fraction of sulfur grows with time, whereas in denser (at the base of piezoceramics) it decreases by 4 ... 5.5 times. At the same time, the mass fraction of nitrogen and hydrogen (composing of ammonia), as the coating operation time increases, increases from insignificant 0.1 ... 0.5 % to 25 ... 27 % (after 10 years of operation). As for other element impurities, a decrease of their fraction along the depth of the coating is also observed.

From the surface images of the samples obtained by scanning electron microscopy, it is evident that the coatings of both groups are initially uniform – they have a clearly formed surface.

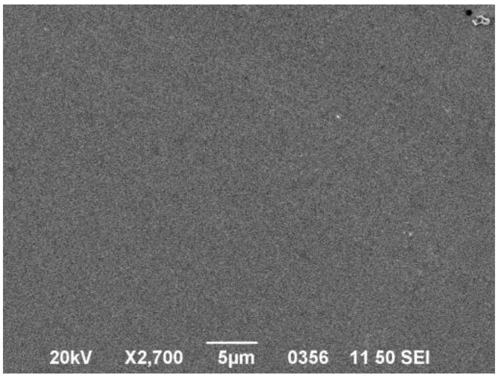
Elemental analysis of Group I samples from the energy spectra of impurity distribution of chemical elements shows a significant decrease in the latter in the coating as compared to samples of Group II. Herewith, the residual mass fraction of lead in the coating indicates a sufficiently high rate with which the lead molecules diffuse into the silver coating, as well as the low density and high porosity of the latter, which is confirmed by the surface images of these samples by the scanning electron microscopy method.

Research of element analysis of Group II samples at energy spectrums of the distribution of chemical elements in the coating indicates that, in terms of quantity, the mass fraction of silver in such a coating exceeds the mass fractions of other elements.

The mass fraction of Ni that forms part of the buffer layer during industrial coating formation on the piezoelement is also quite high, which may indicate the heterogeneity and inaccuracy of the formed silver layer.

Also, it should be noted the high mass fraction of lead in the coating. In our opinion, this is due to the partial sublimation of volatile elements from the surface of the piezoceramic material during the preparation of the sample prior to the formation of a coating on it, and, directly during the formation at temperatures above 900 K, while heavy elements such as lead, diffuse into the less dense structure of the coating created.

At the same time, the elemental analysis of the samples of group I after the electron-beam modification of the coating according to the energy spectra indicates the complete absence of impurities of the chemical elements (Fig. 6b), which confirms the hypothesis of densification of the structure of the coating, a decrease in the size of its crystallites, decrease of porosity of the latter, Fig. 6a.



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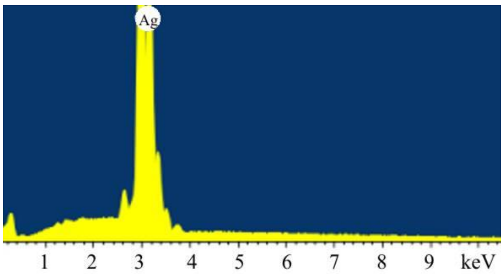


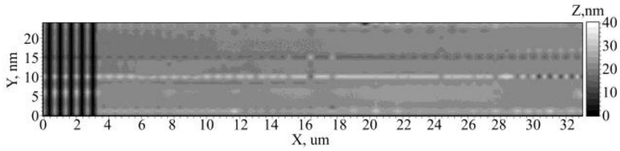
b

Fig. 6 – Image of the surface of the sample of Group I after the electron-beam modification (a) and the energy spectrum of the distribution of chemical elements in the coating (b). Device ZEISS EVO 50 XVP, Increase × 10000

Thus, it is established that the silver coatings formed on the piezoelectric elements formed by the technology proposed by the authors are more uniform in comparison with the coatings obtained in the industrial method. In some cases, after the electron-beam modification of these coatings, a certain ordering of the crystalline micro-formations on their surface can be traced back to the creation of ordered nanostructures on the surfaces of piezoceramic materials.

However, the problem remains a high mass fraction of lead in the resulting coating, which diffuses from the base of the sample with an increase in the operating time of the latter, which prevents the formation of ordered structures and can worsen the operational (wear resistance, mechanical strength) properties of such coatings.

Research of the wear resistance of silver coatings on piezoelectric ceramics. The wear resistance of silver coatings on piezoelectric ceramics was tested by sclerometry. The tests were carried out on an NT-206 instrument with the impact of the probe on the coating with a load of 0.5 mN. The results of sclerometry of samples from groups I and II are shown in Fig. 7.



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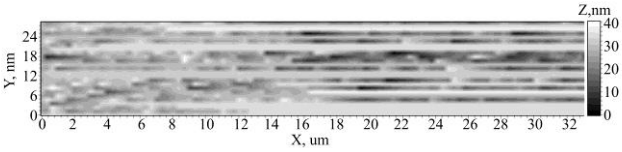

b

Fig. 7 – The result of sclerometry of the silver coating surface obtained by combined precipitation in vacuum after electron beam modification (a) and coating obtained in the industrial process (b)

As can be seen from Fig. 7, the intensity and distribution of the material's bulk (the horizontal bands along the scratching track (X axis) correspond to the uniformity of the bulk, and the vertical distribution along the Y axis is the intensity of the distribution of these bulk) that were obtained by scratching the coating an atomic force microscope probe more irregular and intermittent for the surfaces of the coating obtained in the industrial process (Fig. 7b), whereas for the surface of the sample after the electron-beam modification, the distribution of these bulk is more uniform in intensity (Fig. 7a).

This fact can be interpreted as follows. The horizontal scratches are the result of the reaction of the surface material to the action of the probe, which scratches it. Thus, low density and heterogeneity of the material (actually corresponds to its low wear resistance), when scratching the surface, creates a high uniform of the scratching tracks (the surface of the material along the probe's motion crackles and collapses), whereas the action of the probe on a denser material, as if "skipping" its surface, forming a more even distribution of the bulk along these tracks.

According to the results of the study, it is established that the wear rate of the silver electrode after the electronic modification at a load of 0.5 mN is $I_w = 2.1 \times 10^{-8}$ g/m, whereas, for the surfaces of electrodes produced in the industrial way, the wear rate at the same load is $I_w = 4.82 \times 10^{-7}$ g/m.

4. CONCLUSIONS

It is established that the temperature of the piezoceramic sample during the electron-beam modification of silver coatings is a necessary condition for the formation of qualitative electrodes, for which the possibility of the appearance of defects from the action of external force loads and vibrations is minimized. At the same time, a change in the structure and microgeometry of the modified coatings on piezoceramics from the parameters of the ribbon-shaped electron stream has been determined.

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It is established that the silver coatings formed on the piezoelectric elements formed by the technology proposed by the authors are more uniform in comparison with the coatings obtained in the industrial method. In some cases, after the electron-beam modification of these coatings, a certain ordering of the crystalline micro-formations on their surface can be traced back to the creation of ordered nanostructures on the surfaces of piezoceramic materials.

However, the problem remains a high mass fraction in the resulting coating of lead, which diffuses from the base of the sample with an increase in the operating time of the latter, which prevents the formation of ordered structures and can worsen the operational (wear resistance, mechanical strength) properties of such coatings.

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Дослідження струмопровідних електродів елементів із п‘єзоелектричних керамік, модифікованих стрічковим електронним потоком низької енергії

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В статті встановлені закономірності впливу структурних перетворень, що відбуваються при модифікуванні струмопровідних електродів елементів із п’єзоелектричних керамік стрічковим електронним потоком низької енергії на експлуатаційні характеристики (зносостійкість та корозійну стійкість) цих електродів. В основі технологічного експерименту отримання модифікованих електродів на п’єзокерамічних елементах лежить комбінований процес термічного осадження тонкого срібного покриття на основі з п’єзоелектричної кераміки у вакуумі. Для двох груп зразків (утворені за запропонованою авторами технологією срібні покриття на п’єзоелектричних елементах та покриття, отримані у промисловий спосіб) проводилися дослідження стану поверхні (мікрорельєфу, елементного складу) та інтенсивність зношування.

Ключові слова: П’єзоелектрична кераміка, Електронний потік, Струмопровідний електрод, Атомно-силова мікроскопія, Зносостійкість, Корозійна стійкість.

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