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THE INFLUENCE OF ORGANIC BINDERS AND THEIR DECOMPOSITION PRODUCTS ON THE MICROSTRUCTURE AND THERMOELECTRIC PROPERTIES OF CONDUCTIVE MATERIALS BASED ON Si_3N_4 WITH TRANSITIONAL METAL CARBIDES ADDITIVES

Об'єктом дослідження є формування функціональної зони багатокомпонентного керамічного композиту на основі тугоплавких безкисневих сполук. Одним з найбільш проблемних місць є встановлення впливу типу біндера на формування функціональної зони приладу.

У ході дослідження використовували промислові порошки нітриду кремнію $\beta - Si_3N_4$ *Бакинського заводу порошкової металургії (Азербайджан) та карбіди гафнію та цирконію Донецького заводу хімічних реактивів (Україна). Гомогенізація та подрібнення шихти здійснювалися в планетарному млині типу Fritsch (барабан і кулі* Si_3N_4*) протягом 40 хв. в етиловому спирті. Концентрація провідника фази включення в композиційних термоелектродах становила 5–40 %. У якості біндеру для цього методу використано сполуку карбоксиметилцелюлоза (КМЦ) в поєднанні з пластифікатором – гліцерином чи каучуком. Зразки виготовлялись у вигляді пластин 100×7×6 мм. Досліджувані зразки нітридокремнієвих композиційних матеріалів отримані методом гарячого пресування підготовлених керамічних стрічок із застосуванням індукційного методу нагрівання прес-форми.*

Встановлено, що для зразків із резистивною добавкою HfC, виготовлених із використанням каучуку, втрати маси зростають пропорційно концентрації HfC до концентрації домішки 27 %, а при подальшому збільшенні концентрації HfC втрати маси знижуються. При використанні КМЦ, як біндера, втрати маси системи менші приблизно в 1,3–1,6 рази, при тих же практично закономірностях змін втрат маси у залежності від концентрації HfC. Термоелектрорушійна сила (термоЕРС) дрібнодисперсного композиту по модулю була вищою за термоЕРС грубодисперсного композиту для всіх концентрацій. Максимальне значення термоЕРС досягало величини 120 мкВ/град у допороговій зоні, 60 мкВ/град для дрібнозернистого композита та 30 мкВ/град для грубозернистого композита у запороговій зоні, відповідно. Доведено, що композити, отримані без біндера, відрізняються нетиповим перебігом концентраційної залежності опору, а термоЕРС цих композитів дорівнює нулю з точністю до похибки експерименту.

Ключові слова: *органічний біндер, карбід гафнію, карбід цирконію, високотемпературні функціональні елементи, каучук, карбометилцелюлоза, мікроструктура функціонального елементу.*

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1. Introduction

The development of layered functional elements based on a matrix of silicon nitride and a resistive functional layer of a fine-grained composite of silicon nitride-titanium nitride [1] led to the establishment of a number of facts. Under certain conditions of high-temperature compaction, a percolation cluster is formed, capable of generating thermoelectric voltage and causing the processes of charge movement under the influence of a local temperature gradient, which can form the phenomenon of a positive temperature coefficient of resistance (TCR) of the resistive layer. Therefore, it is relevant to study the effect of organic binders and their decomposition products on the microstructure and thermoelectric properties of nitride-silicon conductive materials with the addition of transitional metal carbides.

2. The object of research and its technological audit

The object of research is the formation of the functional zone of a multicomponent ceramic composite based on refractory oxygen-free compounds.

To study this phenomenon, a technological audit is conducted, the purpose of which is to determine how such a technological factor as the type of binder affects the formation of the functional area of the device.

The studies are conducted on the basis of the Institute of Materials Science of the National Academy of Sciences of Ukraine (Kyiv) using:

- industrial powders of silicon nitride β – Si_3N_4 (Baku Powder Metallurgy Plant, Azerbaijan) and α – Si_3N_4 (H.C. Starck Inc., Germany);
- Transitional metal carbide powder: HfC and ZrC (Donetsk Chemical Reagents Plant, Ukraine).

Homogenization and grinding of the charge is carried out in a Fritsch planetary mill (drum and Si_3N_4 balls) for 40 min in ethanol. The ratio of the mass of the balls to the mass of the powder is 5:1.

The method of plastic molding of the tape on a spindle machine is used. As a binder for this method, a carboxymethyl cellulose (CMC) compound is used in combination with a plasticizer – glycerin or rubber. For experiments, samples are made in the form of plates of 100×7×6 mm.

The studied samples of nitride-silicon composite materials based on SIALON are obtained by hot pressing of prepared ceramic tapes using the induction method of heating the mold.

The disadvantages of the object of research in the existing operating conditions include a large inertia, which manifests itself in the fact that the manufactured functional devices do not experience sharp peak temperature changes.

3. The aim and objectives of research

The aim of research is to determine the effect of the thermal decomposition products of binders on the phase composition of the conductive and semiconductor phases formed in situ during high-temperature densification.

To achieve this aim it is necessary to:

1. Produce a binary composite system in the form of a plate 100×7×6 mm using HfC, ZrC.
2. Determine the effect of binder and their decomposition products on the microstructure and thermoelectric properties of silicon nitride conductive materials with the addition of transitional metal carbides.
3. Establish a correlation between mass loss, porosity and concentration of HfC, as well as thermoEMF, resistance of materials HfC, ZrC and concentration.
4. Investigate the range of composite concentrations in which non-linearity of resistance is manifested, depending on the type of binder used.

4. Research of existing solutions of the problem

High temperatures are a favorable factor for the thermoelectric conversion of thermal energy into electrical energy [2]. At present, thermoelectric materials for operating in the temperature range from room temperature to 400 °C are widely known. Solid solutions based on Bi_2Te_3 are most widely used.

For the prospect of using thermoelectric generators in high-temperature installations of aircraft and spacecraft, this is not enough. It is known that the effectiveness of thermoelectric conversion depends on two factors:

1) the maximum possible temperature difference between hot and cold surfaces;

2) the values of thermoelectric figure of merit of materials of thermoelectrodes [3].

It is in this direction that research and innovation in the field of thermoelectric materials are concentrated [4, 5]. Nanostructured is considered an effective way to reduce lattice thermal conductivity by reducing the average mean free path of phonons, which can lead to an increase in thermoelectric figure of merit by a factor of at least 2 [6, 7].

In a number of publications, it is shown that the generation of thermoelectromotive force (thermoEMF) is observed in leading materials based on oxygen-free compounds, which depends on the concentration of the additive in the resistive material and its microstructure, as well as the geometric dimensions of the active region [8].

In this regard, it is promising to develop new multicomponent high-temperature composite materials for thermoelectric electrodes of machineless converters of thermal energy into electrical energy, and to study the effect of new phases. The consolidation of materials based on oxygen-free compounds (sintering processes) is carried out in a graphite inductor under the simultaneous action of high temperature (up to 2000 °C) and pressure (up to 300 k/cm^2). Specimens are made from a fine mixture using organic compounds – binders, which is a heterogeneous chemical-technological process, which is characterized by the occurrence of chemical reactions [1]. In specimen specimens during heat treatment by hot pressing (HP), in situ chemical reactions are possible in the bulk of the specimen between the components of the initial charge [9]. It is possible to change the phase composition of the mixture as a result of decomposition of materials of solid-phase components of the composite, leading to the production of not only the main, but also by-products [10]. This can lead to a change in the concentration and composition of the dispersed composite, an increase in the level of imperfection of crystalline structures, and, consequently, to a deviation of the real values of thermal power, electrical or thermal conductivity of the composite from the calculated ones. However, the influence of organic binders and their decomposition products on the microstructure and, especially, the thermoelectric properties of silicon nitride conductive materials with the addition of transitional metal carbides are insufficiently covered in the literature, and therefore will be considered in more detail in this work.

5. Methods of research

The industrial powders of silicon nitride β – Si_3N_4 of the Baku Powder Metallurgy Plant (Azerbaijan) and hafnium and zirconium carbide of the Donetsk Chemical Reagents Plant (Ukraine) are used.

Homogenization and grinding of the charge was carried out in a Fritsch planetary mill (drum and Si_3N_4 balls) for 40 minutes in ethanol. The concentration of the conductor of the inclusion phase in the composite thermoelectrode is 5–40 %.

Specimens of samples for synthesis are collected according to the method described in [1]. An original method is developed for organizing the macrostructure of a gradient composite. In elastic thick ceramic letters (thickness 0.9–1.8 mm), holes (cavities) are cut from the charge to obtain heat-resistant insulating material by stamping (Fig. 1). They then fit the pre-manufactured parts of the thermal converter tightly. Carboxymethyl cellulose and rubber are used as a binder. Such a ceramic assembly is a specimen of a functional gradient composite, which after heat treatment (sintering) turns into a completely ceramic functional element.

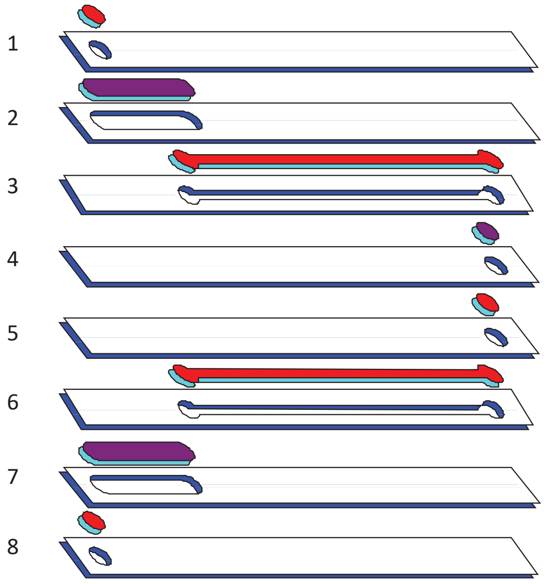


Fig. 1. The structural diagram of the gradient composite: 1, 8 – contacts; 2, 4, 5, 7 – current lead zones; 3, 6 – resistive materials of the core

Raw specimens of layers after molding have a density of 54–74 % of the theoretical dependence on the method of producing tapes (Table 1).

Table 1

The composition of the samples studied in the work

Sample type	Composition	Binder	Conductor concentration, volume, %	The grain size of the conductor, microns
Volumetric sample (Fig. 1)	Si3N4-ZrC	Without binder	5–40	3.34
	Si3N4-ZrC	CMC, rubber	5–40	3.34
	Si3N4-HfC	CMC	5–40	polydisperse

When studying the pyrolysis of the used binders, an open substrate with the test sample is placed in a laboratory furnace and heated at a speed of about 15 deg/min. The processes of thermal decomposition of binders are controlled visually and photographed. Sintered samples are subjected to finishing machining; for them, the values of experimental density, open and closed porosity, and weight loss are determined.

6. Research results

6.1. Binder pyrolysis process and its contribution to changing the composition of the consolidation environment. The type of binder can also affect the loss of mass of the mixture during sintering, the composition and properties of the resistive composite. The calculations for the above plasticizers, the ratio of carbon, hydrogen and oxygen are given in Table 2. A study is made of the laws of thermal decomposition of the binders used both in a normal atmosphere and in conditions close to the conditions that occur during hot pressing.

Research results of the thermal decomposition of rubber, a mixture of CMC and glycerol, as well as CMC and glycerol separately on an open substrate when heated at a speed of about 15 deg/min are shown in Table 3.

Table 2

Plasticizers and their main characteristics

Plasticizer	Chemical formula	Density, g/cm^3	Pyrolysis temperature, °C	C:O:H ratio (mass %)
natural rubber	$[-CH_2C(CH_3)=$ $=CHCH_{2-}]_n$	0.91	300	88.2–11.8
artificial rubber	$[-CH_2C(CH_3)=$ $=CHCH_{2-}]_n$	1.2	280	88.2–11.8
CMC	$[C_6H_7O_2(OH)_{3-}\times$ $\times(OCH_2COOH)X]_n$	1.59	170	43.6–50.9–5.45
glycerol	$CH_2OHCHOHCH_2OH$	1.26	290	36–48–8

Table 3

The amount of solid residue during the pyrolysis of various binders

Pyrolysis conditions	The amount of solid residue, mass %			
	rubber	CMC+glycerol	CMC	glycerol
Heating from 20 to 450 °C	42.02	11.32	57.75	0.05
Heating from 20 to 600 °C	3.15	7.5	40	0
Heating from 20 to 750 °C	0	–	29	0
Heating from 20 to 1000 °C	–	–	16.5	–

From the results of X-ray spectral analysis of consolidated composites, it is found that the carbon and oxygen content in the finished material was significantly different. Moreover, the material obtained using CMC and glycerol is characterized by a high content of both oxygen and carbon (Table 4).

Table 4

The relative content of elements in the sintered material

Element	Binder type	
	Rubber	CMC+glycerol
C	90	125
O	63	75
N	44	37
Si	3387	3400

Let's associate this phenomenon with the different course of chemical reactions in the gas phase before the beginning of the process of consolidation of the preform (Table 5).

Table 5

Chemical reactions that occur during the temperature treatment of composite specimens

Binder-rubber:

$[-CH_2C(CH_3)=CHCH_{2-}]_n \rightarrow C+H_2.$ (1)

Binder-CMC:

$[C_6O_2H_7(OH)_2+(OCH_2\text{-}COONa)] \rightarrow C+H_2+Na.$ (2)

Glycerol:

$HOCH_2CH(OH)\text{-}CH_2OH \rightarrow CH_2OHCHOHCHO \rightarrow C+H_2;$ (3)

$2H_2+O_2 \rightarrow 2H_2O;\ C+O_2=CO_2;\ CO_2+C=2CO;$ (4)

$9H_2+2N_3 \rightarrow 6NH_3;\ Si_3N_4+6H_2O \rightarrow 3SiO_2+4NH_3$ (5)

For samples containing more than 3 % SiO_2 in the charge, the formation of SiC occurs very weakly (1–1.5 %), even when the optimum temperature of the hot pressing process is exceeded. It is proved that an increase in the temperature of the HP leads to a threshold increase in the SiC concentration, and simultaneously with an increase in the SiC concentration, the SiO_2 content also increases. The interaction occurs in accordance with the reaction:

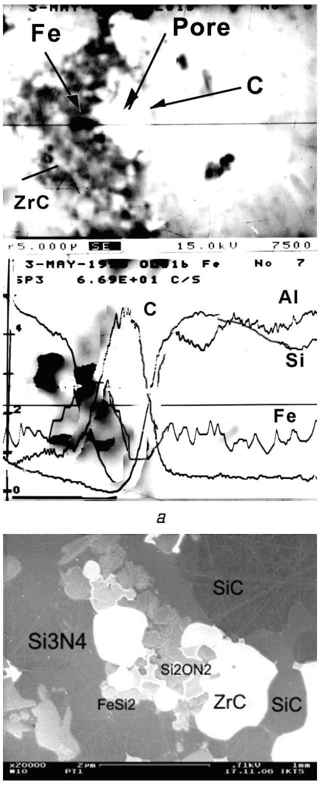
$$2Si_3N_4+4CO\uparrow=4SiC+2SiO_2+4N_2\uparrow, \quad (6)$$

$$2Si_3N_4+2SiO_2=4Si_2ON_2. \quad (7)$$

Carbon release (in situ formation of SiC) occurs on the surface of the pore in the presence of iron, which, apparently, acts as a catalyst for the process [1], (Fig. 3). Silicon nitride, which has not reacted (Fig. 4), reacts with the formed silicon oxide to form silicon oxynitride. Iron present in the starting materials, like contamination by the material of grinding media, melts at a temperature of 1500 °C (before the start of the compaction process) spreads over the surface of the pores, interacting with silicon nitride by the reaction:

$$2Si_3N_4+3Fe=3FeSi_2+4N_2. \quad (8)$$

These processes occur both with a decrease in the amount of silicon nitride in the reaction zone, and with an increase in mass loss through the volatility of nitric oxide, which leaves the reaction zone. This nitrogen can subsequently react with certain carbides (HfC, ZrC), violating their stoichiometry and forming carbonitrides HfC_xN_{1-x}, ZrC_xN_{1-x} or doping SiC formed in situ, fundamentally changing its properties [10].



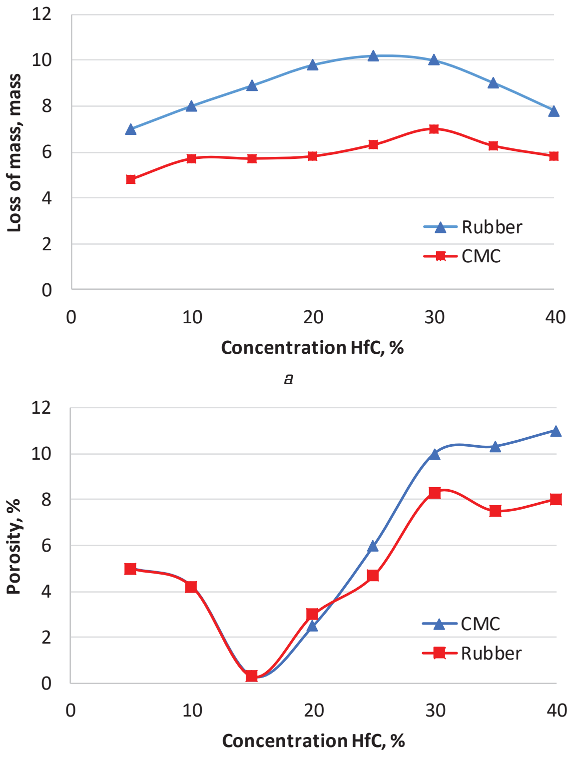
a

b

Fig. 2. The localization of carbon on the surface of the pores of the specimen: *a* – according to local X-ray spectral analysis; *b* – view of the leading cluster of thermoelectric composite

6.2. Mass loss and porosity for manufactured samples of resistive materials. Based on the experimental results (Fig. 3), it is found that for samples with a resistive HfC additive made using rubber, the mass loss increases in proportion to the HfC concentration to the impurity concentration of 27 %. With a further increase in HfC concentration, mass loss decreases. When using CMC as a binder, the mass loss of the system is about 1.3–1.6 times less, with the same practically regular patterns of changes in mass loss depending on the concentration of HfC.

The porosity of the samples of the Si_3N_4-HfC system, as follows from the data shown in Fig. 5, *b*, practically does not depend on the type of binder that is used, but has a nonlinear dependence on the content of the conductive additive. At an HfC concentration of up to 15 %, the porosity of the samples decreases with increasing impurity concentration, at an HfC concentration of 15 %, the dependence of porosity on the concentration has a minimum, and with a further increase in the content of the conductor phase, the porosity increases to 9–12 %, and for the MgO activator by 2–4 % more than for Al_2O_3.



a

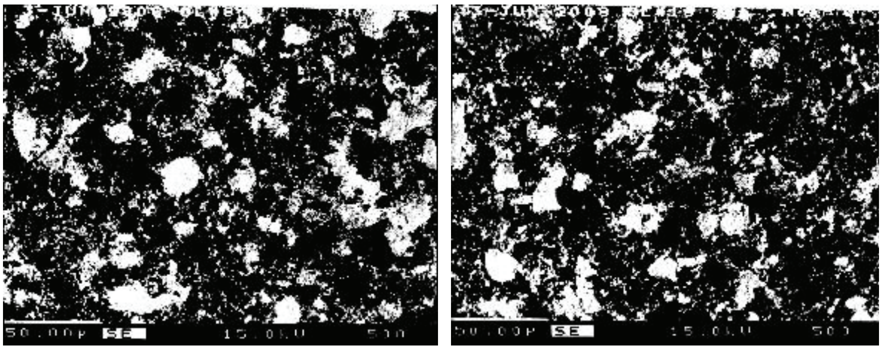
b

Fig. 3. When using various binders of baked samples of the Si_3N_4-HfC-Al_2O_3 system: *a* – mass loss; *b* – porosity

Too high dispersion of the additive, especially in the presence of small amounts of oxygen (for example, as a decomposition product of CMC), on the contrary, reduces the intensity of the interaction. Thus, during the hot pressing process, the total fraction of the liquid phase in the system reacts, becomes small, and the main reaction product is hafnium oxycarbonitride. Silicon carbide is not formed in this case. Only those small particles that are in close proximity to large particles participate in the process of aggregation of additive grains, while the majority of very small particles are statistically distributed in the volume of inter-grain of the insulating phase.

In the presence of pyrolysis products of CMC, the formation of the structure proceeds in the same way as in the presence of rubber pyrolysis products with the difference that the size of the inclusions in the conductor is larger, and in the zone surrounding the particle of inclusions, there is no iron. In addition, the size of the area of hafnium penetration into the matrix is slightly smaller than in the rubber sample.

As a result of electron microscopy studies of the microstructure of samples obtained with ZrC or HfC additives and various binders, it was found that the microstructure for these types of samples is qualitatively similar. Typical electron microscopic images of the microstructure are shown in Fig. 4.



a *b*

Fig. 4. General view of the distribution of inclusions of the conductor phase (dark image) in a Si_3N_4-based dielectric matrix for samples with an admixture of HfC: *a* – binder rubber; *b* – carbomethyl cellulose; image of thin sections in scanning electron microscopy

To construct a model curve describing the concentration dependence of electrical conductivity, the equation of the generalized theory of the effective medium is used, however, it is supplemented by the introduction of the coefficient *M*:

$$(1-f_c)\frac{\sigma_i^{1/s}-\sigma_M^{1/s}}{\sigma_i^{1/s}+\left(\frac{1}{\varphi_c}-1\right)\sigma_M^{1/s}}+f_c\frac{(M\sigma_c)^{1/t}-\sigma_M^{1/t}}{(M\sigma_c)^{1/t}+\left(\frac{1}{\varphi_c}-1\right)\sigma_M^{1/t}}=0, \quad (9)$$

where M_s – conductivity of the (thermo) composite; σ_i and σ_c – conductivity of the insulating and leading phases, respectively; f_c – volume fraction of inclusions of the leading phase; φ_c – critical volume fraction of the leading phase (LP); *s* and *t* – percolation indices characterizing the insulating and leading phases, respectively.

The introduction of this coefficient is justified by the fact that the particles of the leading phase, during the formation of an infinite cluster, can completely arbitrarily create many parallel and series resistance compounds.

6.3. Thermoelectric properties of dispersed materials depending on the type of binder (materials of the Si_3N_4-ZrC, Si_3N_4-HfC system). For all samples obtained using binders, the value of the measured resistivity in the direction parallel to the pressing axis exceeded the resistivity in the direction perpendicular to the pressing axis by more than an order of magnitude (Fig. 5).

The parameters of the percolation equation for the systems under study are calculated (Table 6). It is found that for the composite obtained in the presence of CMC in the direction transverse to the HP direction, two leading clusters are formed. One, two-dimensional, of small particles of a conductor with a threshold resistance of about 1 Ohm·cm at a conductor concentration of 2.5 %. The second cluster is voluminous at a concentration of 12 %. In the presence of rubber, 2 parallel clusters also form in this plane: three-dimensional with a threshold concentration of 2.5 % and 9 % with almost the same threshold support. Along the direction of hot pressing, the resistance at the percolation threshold is 3600–7200 Ohm·cm and 2 three-dimensional clusters are formed with percolation thresholds of 2.5 % and 12 % when using CMC and 2.5 % and 4.5 % when using rubber.

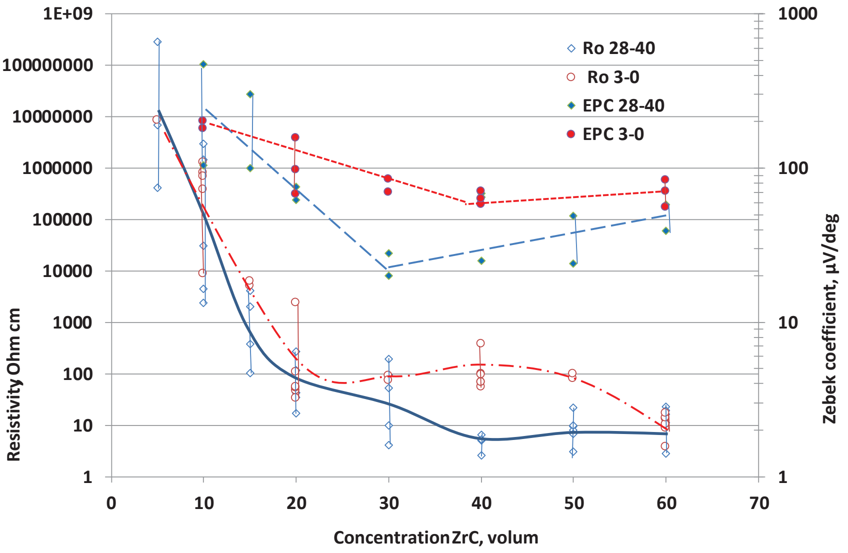


Fig. 5. Results of measuring the resistivity of composite materials of the Si_3N_4-HfC system along (filled up marker) and across (empty marker) directions of hot pressing using carbomethyl cellulose (triangle) and rubber (circle)

Table 6

MacLachlan model parameters for the Si_3N_4-HfC system

Plasticizer	Measuring direction	Model parameters				
		ρ_c^*, Ohm·cm	*Xc*		*t*	
			c=5–15 %	*c*=30–40 %	*c*=5–15 %	*c*=30–40 %
CMC	‖HP	1.01	0.025	0.12	1.4	1.8
	⊥HP	$3.6\cdot10^{-3}$	0.025	0.12	2.15	2.5
Rubber	‖HP	0.9	0.025	0.09	1.75	1.9
	⊥HP	$7.2\cdot10^{-3}$	0.025	0.045	2.45	2.45

As a result, the resistance of the cluster as a whole will differ from the theoretical one, calculated on the basis of only the specific resistance of a particular material and the geometric dimensions of the cluster. Taking this factor into account allows to more accurately describe the experimental data of the model curve.

The thermoEMF of a finely dispersed composite modulo was higher than the thermoEMF of a coarse composite for all concentrations (Fig. 5). The maximum value of thermoEMF reached 120 µV/deg in the subthreshold zone, and 60 µV/deg for a fine-grained composite and 30 µV/deg for a coarse-grained composite in the postthreshold zone. Let's attribute this to the fact that according to structural studies, the intensity of interfacial interaction to create in situ ZrCN in fine-grained zirconium carbide is greater.

Fig. 6 shows the dependences of the resistivity of Si_3N_4-HfC composites on the concentration obtained using rubber and CMC as a binder, as well as without using any binder. As can be seen from Fig. 6, the composites obtained without a binder differ not in the typical course of the concentration dependence of the resistance, and the thermoEMF of these composites is equal to zero accurate to the experimental error. Composites made from rubber have a positive thermoelectric coefficient in the suprathreshold concentration zone of the additive, and a negative value in the subthreshold concentration zone. At the percolation threshold, thermoEMF passes through zero. Composites made from CMC as a binder in the entire concentration range have a positive coefficient of thermoEMF, but less than this value in composites prepared using rubber.

The following fact indicates the in situ reaction of silicon nitride with carbon monoxide. The nonlinearity of the composite resistance, defined as the ratio of the resistances (at currents of 30 mA and 100 mA), is more pronounced for resistance in the direction of hot pressing. In the transverse direction, it is characteristic only for composites with a concentration of up to 20 % for the use of rubber and up to 10 % for the use of carbomethyl cellulose.

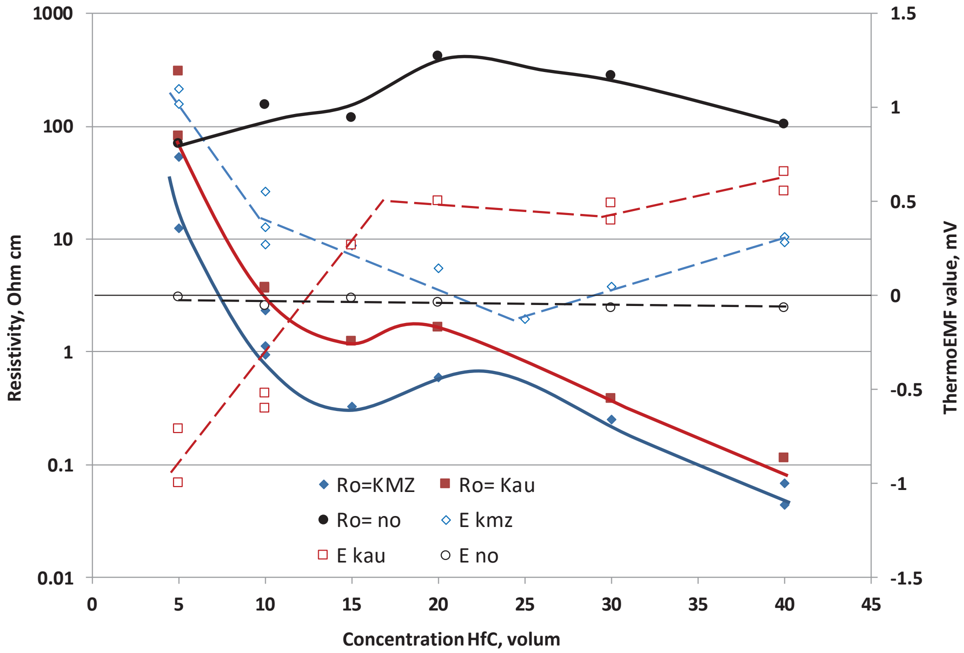
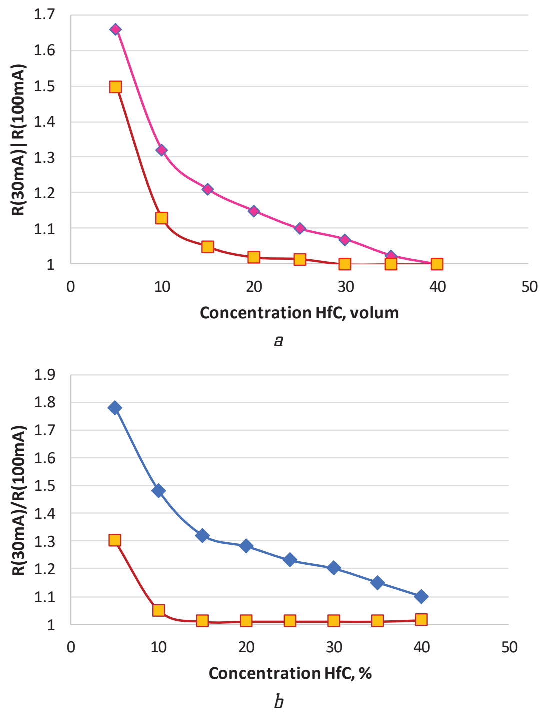


Fig. 6. Dependence of thermoelectromotive force (thermoEMF) and resistance on HfC concentration obtained using rubber, carbomethyl cellulose as binder, and also without using any binder

From this it is possible to conclude that in the direction transverse to the direction of hot pressing, silicon carbide is part of the lead cluster only in the range of indicated concentrations. In the direction along the direction of hot pressing, silicon carbide is included in the structure of the lead cluster for both binders, and its effect on the cluster resistance decreases with increasing additive concentration (Fig. 7).



a

b

Fig. 7. Concentration dependence of the nonlinearity of resistance of resistive composite materials of the Si_3N_4-HfC system: *a* – rubber; *b* – carbomethyl cellulose for resistances along the direction of hot pressing (rhombus) and across (square)

Factors that make an important contribution to the functional characteristics of resistive materials include non-linearity of resistance, additional release or absorption of energy at the metal-pyramid-dielectric barriers, and release or absorption of energy by a metal-dielectric-metal capacitor.

For Si_3N_4-HfC composites obtained with or without a different binder, there is a fundamental difference in the resistance value at currents of various sizes. Fig. 8 shows how the nonlinearity coefficient, calculated as the ratio of the resistances measured at currents of 30 and 100 mA, depends on the concentration of the additive in composites obtained without the use of a binder, or when used as a binder, rubber and CMC.

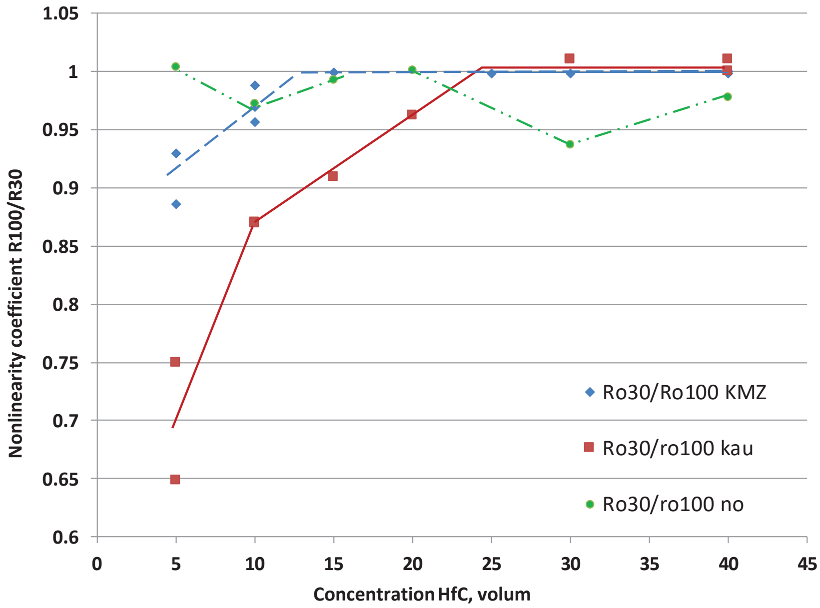


Fig. 8. Concentration dependence of the coefficient of non-linearity of the resistivity of composites obtained without the use of a binder (filled circle), or when used as a binder, rubber (filled square) and carbomethyl cellulose (filled rhombus)

Fig. 8 shows that composites that are formed without the participation of a binder have significant nonlinearity at additive concentrations of 30–35 vol. % and 10 vol. % using binder, CMC, significantly reduces the range of composite concentrations in which non-linearity is manifested, being limited to the range of low additive concentrations (5–10 vol.%) Composites made with rubber are characterized by the highest non-linearity, which are characterized by a higher non-linearity coefficient and a significant range of additive concentrations (5–25 vol.%).

7. SWOT analysis of research results

Strengths. Among the strengths of this research, it is necessary to note the results obtained on the technological factor of the formation of the functional zone of a binder-type device. This statement is supported by the above results of the analysis of world scientific periodicals in which these studies were not conducted. Using the obtained data allows to create thermoelectric converters with specified parameters.

Weaknesses. The weakness of this research is the insufficient study of percolation processes in the formation of the microstructure of the functional zone of the device. There is no explanation of the fact that in materials using rubber as a binder, it is impossible to describe the course of the concentration dependence of thermoEMF, based on the generalized theory of percolation.

Opportunities. Using these studies, it became possible to manufacture thermoelectric systems such as HfC-Si_3N_4, ZrC-Si_3N_4 and determine the main factors affecting the maximum value of the coefficient of thermoEMF.

Threats. Difficulties with further research are connected with the fact that powders for experiments are purchased abroad and their cost is fixed in US dollars. Due to the unstable hryvnia exchange rate to the US dollar, a significant increase in the cost of experiments is possible.

8. Conclusions

1. In the course of the study, it is observed that during the burnout of the binders, rubber enriches the material with carbon black, and CMC – with a concentrated charred residue. An admixture of glycerin in the CMC shifts the decomposition temperature of the CMC to the low-temperature region and sharply accelerates its decomposition. This makes such a binder promising for use in resistive materials manufactured using in situ reactions.

2. It is established that the binder species determines the morphology of the microstructure of the leading cluster, namely:
   - particles of the leading cluster with hafnium carbide, obtained in the presence of CMC, and particles of the leading cluster of zirconium carbide, obtained in the presence of rubber, have the form of flakes arranged in a plane in the direction of application of the HP force;
   - particles of hafnium carbide obtained in the presence of rubber have the form of cylinders elongated in the same direction;
   - particles of the leading cluster of zirconium carbide in the presence of CMC become similar spheres.

3. It is proved that the thermoEMF of a finely dispersed composite was higher in modulus than the thermoEMF of a coarse composite for all concentrations. The maximum value reached 120 μV/deg in the subthreshold zone, and 60 μV/deg for a fine-grained composite and 30 μV/deg for a coarse-grained composite in the suprathreshold zone, respectively. This is due to the fact that according to structural studies, the intensity of interfacial interaction to create in situ ZrCN in fine-grained zirconium carbide is greater.

4. It is established that the composites obtained without a binder differ in an atypical course of the concentration dependence of the resistance, and the thermoEMF of these composites is equal to zero accurate to the experimental error. Composites made from rubber have a positive thermoelectric coefficient in the suprathreshold concentration zone of the additive, and a negative value in the subthreshold concentration zone. At the percolation threshold, thermoEMF passes through zero. Composites made from CMC as a binder in the entire concentration range have a positive coefficient of thermoEMF, but less than this value in composites made using rubber. In this case, it is possible

to use approximations of the percolation theory both for describing the concentration dependence of resistance and for the concentration dependence of thermoEMF.

It is shown that composites that are formed without the participation of a binder have significant non-linearity at additive concentrations of 30–35 vol. % (Rubber application) and 10 vol. % (CMC application). The use of CMC as a binder significantly reduces the concentration range of the composite, where the nonlinearity of resistance is manifested. Composites are the most nonlinear in resistance; they are prepared using rubber.

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