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Research Article

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Design of Grain Composition of Conductive Cluster of Multicomponent Composite and Mechanism for Monitoring Morphology of its Microstructure

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Abstract

Modern technology requires miniaturization of the main equipment, and puts high demands on their reliability. When creating resistive materials for absorbers or heaters, technical powders are used, which have in their composition crystallites that differ in size from a fraction of micrometers to tens of microns. The purpose of this work was to investigate the relationship between the surface temperature under the influence of current flow on layered multicomponent materials. Laminated multicomponent composites with silicon nitride base and size-calibrated tantalum nitride powders were used as samples. The resistance was measured on direct current by bridge and voltmeter-ammeter method under control of the surface temperature by a contact thermocouple placed at the same thickness from the heating cluster. The electric field strength, and the current density which that promotes the heating of the material, both are also a nonlinear function of the grain composition of the conductive cluster. If the square of current density through the sample is a structure-sensitive parameter for a fine-grained structure, the square of electric field strength shows greater sensitivity in the case of predominance of the coarse microstructure. An empirical formula is proposed that relates the concentration of the coarse fraction (>30 μm) in percent with the electric current density j (in A/mm2), or the electric field strength E (in V/cm), at which the surface temperature of 800K is reached (the beginning of the visible dark red glow of incandescent bodies). It was established that the critical change in the concentration of the coarse fraction, at which the specified color temperature is observed, is 30% .

Keywords: Multicomponent Composite, Conductive Cluster, Grain Composition Microstructure Morphology, Monitoring Mechanism

Introduction

Modern technology necessitates the miniaturization of main equipment and places high demands on the reliability of both the equipment and its constituent materials. According to a global world report, the market is dominated by the electronics and electrical industry and is expected to grow over the forecast period due to the wide range of electrical properties of advanced ceramics, including insulating, semiconducting, superconducting, piezoelectric, and magnetic properties. Silicon nitride, along with silicon carbides and aluminum nitride, is a key material for electronic and electrical devices. It is expected to exceed US$190 million by 2029, up from US$125 million in 2022 [ ]. The market segment associated with electrical and electronic applications is developing intensively against the background of the traditional segment for silicon nitride, such as balls for bearings. Applications include batteries for cars, memory devices in microelectronics, and more.

The beginning of the new century was marked by the widespread appearance of layered heating elements with high radiation intensity in the far infrared region [ ]. Heaters with particularly high luminescence intensity also exhibited a positive temperature coefficient of resistance. Additionally, some of these heaters generated thermoelectric voltage when heated by an external heat source, a phenomenon that is currently under study.

Electrical resistance is a physical quantity that characterizes how strongly a material prevents electric current from passing through it. When creating resistive materials for absorbers or heaters, technical powders are used, which contain crystallites varying in size from a fraction of a micrometer to tens of micrometers. In our work, it was shown that polydisperse ZrC powder contained fractions of 3, 7, 14, 28, 40, and 60 micrometers [3]. The resistance value of the composite at the same additive concentration differs by 5-8 times. Our study on the absorption of microwave electromagnetic waves by conducting particles of basic powders of refractory compounds was published in It is known that the properties of materials obtained from powders are determined by the particle sizes of these powders, which can vary due to technological operations and temperature effects during consolidation, such as recrystallization and aggregation [3]. These variations often complicate the achievement of a functional product with high properties.

The purpose of this work was to investigate the relationship between the surface temperature under the influence of current flow on layered multicomponent materials with different geometric dimensions of the functional area. Additionally, we aimed to develop a technique for controlling the properties of the composite by influencing its grain size and, conversely, to determine the degree of recrystallization of the conductive layer through the magnitude of direct current.

Materials and Methods

The researched resistive Si_3N_4-ZrC composites were used as the glow body of all-ceramic heaters (Fig. 1), representing a dispersed dense structure dielectric-conductor. The dielectric layers of the heater were made from a mixture of Si_3N_4 powders, 93 vol.% (Powder Metallurgy Plant, Baku, Azerbaijan), obtained by furnace synthesis with an average grain diameter of 5 µm, and powder from self-propagating synthesis (SHS, Makiiv experimental production) with a dispersion of 8 µm. Al_2O_3, 7 vol.% (Mykolaiv Alumina Plant, Ukraine) was used as a compaction activator in the hot pressing process. To create an active resistive layer, ZrC powder, 13.5% by volume, was added to the resulting dielectric charge.

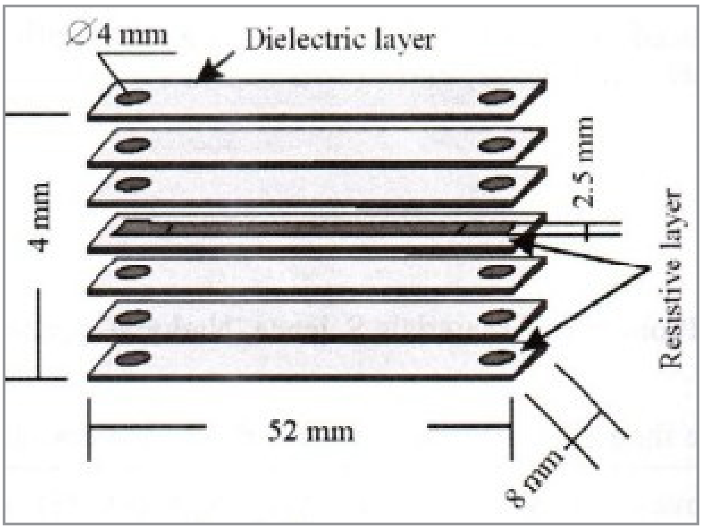


Figure 1: The experimental item outside.

We investigated:

1. Changes in the characteristic parameters of powder particles as a result of technological mixing of shell powders (Si_3N_4-Al_2O_3).
2. Changes in the characteristic sizes of particles during sintering when the functional layer has size limitations (b/t, Fig. 3).
3. Changes in the resistance of the functional layer with a dosed loading of fine and coarse fractions of zirconium carbide: 0% fraction of 3 micrometers (fine) and 100% fraction of 40/28 micrometers (coarse); 30% fine: 70% coarse; 50% fine: 50% coarse; 70% fine: 30% coarse; 100% fine: 0% coarse, at a total concentration of zirconium carbide of 15 vol.%.

The studied ZrC powders were obtained by direct interaction of zirconium with carbon in an inert atmosphere. The resulting synthesis product was ground and separated into four fractions using the air separation method: 3/0, 7/3, 40/28, 60/40, where the numbers represent the ultimate particle size in the powder, in µm.

Homogenization and grinding of the Si_3N_4-Al_2O_3 charge were carried out in a planetary mill with polyethylene-lined drums and Al_2O_3 balls in a controlled humidity environment. The conductive additive was introduced into the finished dried batch in the dry mixing mode using hooks. The technological layers were formed by the method of wet rolling using carboxymethyl cellulose as a binder, 3.8 vol.% [ ]. The samples were obtained by programmed hot pressing (PHP) with isothermal exposure for 20-40 minutes at 1680ºC and 200 atm pressure in the environment of graphite combustion products. The hot pressing mode recorded the flow of chemical processes: oxidation of surface particles of silicon nitride (at 800-1000ºC), oxidation-reduction reaction of carbon oxide and carbon deposition in the pores (1000-1500ºC), and sample consolidation at a controlled speed, isothermal exposure, and controlled cooling. The resulting samples had dimensions of 4 mm × 8 mm × 52 mm.

Laminated multicomponent composites with a silicon nitride base and size-calibrated ZrC powders were used as samples (Fig.1). The resistance was measured on direct current using the P-577 bridge and voltmeter-ammeter method under surface temperature control by a contact thermocouple placed at the same thickness from the heating cluster. Temperature, considered a local macroscopic variable, was measured in ºC using an IR thermometer. A temperature of 527ºC was used as the critical temperature of solid-state glow.

For heaters, a high surface temperature with minimal power consumption is essential. Heat transfer equations (5) and (6) from Table 1 express this requirement.

Table 1: Laws of Heat Release, Heat Radiation, and Load Characteristics of a Conventional Heater.

Laws of heat release at courent	Laws of heat radiation from surface	Loading hsaracteristic
Q*Δt=i2R*Δt=U2*Δt/R (3)	Qk=α*S*(Tt-T0) (5)	ΔT=1/α*(I2RΔt)/S (7)
Q*t=i2R*Δt*cosφ=U2/R*Δt*cosφ (4)	QIR=ε*σ*S* (Tt4-T04) (6)	ΔT=1/(ε*σ)*(I2RΔt)/S (8)

Were is: Q-heat: Δt times interval, I2 or U2- current current in square, current voltage voltage in square, α-heat transfer coefficient, ε- spectral emissivity, (I2RΔt)/S- surface power density.

Aur work presents load curves for Si_3N_4-TaN composites, showing that with the same technology and mixture composition, heaters with fundamentally different properties (negative and positive temperature coefficients of resistance) can be obtained [4]. The morphology and particle size composition of ZrC powders were studied by scanning electron microscopy and sedimentation analysis. Microstructure images of the sintered samples were obtained using a Neofot microscope and an Epiquant contamination analyzer. Parameters such as volume fraction of conductive inclusions, their specific surface area, and average distance between them were determined by computer analysis using the SIAMS-340 analyzer

Results and Discussion

Microstructure and Technological Factors

Furnace synthesis powders have significant contamination with process impurities. SHS powders are cleaner but contain a significant amount of β-sialon.

Table 2: Chemical and Phase Composition of Basic Components of Composite

Si3N4	Chemical composition macc %				Phase composition macc %				
	Sicв	N	O	C	Fe	α- Si3N4	β- Si3N4	Si2ON2	SiC
ПC	0.7	36	3.5	1.35	0.75-3.5	0	85	15	4.5
CBC	0.4	37.4	1.6	0.5	0.7	7	93	0	1.8

Binders, such as carboxymethyl cellulose (CMC) and rubber, were used after preliminary studies on their effect on the rheological characteristics of the batch mass. The raw blanks of the layers after forming had a density of 50-54% of the theoretical density.

To study the thermal decomposition of binders under conditions close to those of hot pressing (CO environment, sharp rise in temperature at the initial stage of heating), binder samples in closed boats were placed in a graphite shell. The results of determining the amount of carbon residue during decomposition at 900 °C for 0.5 hours in a CO environment are given in Table 3.

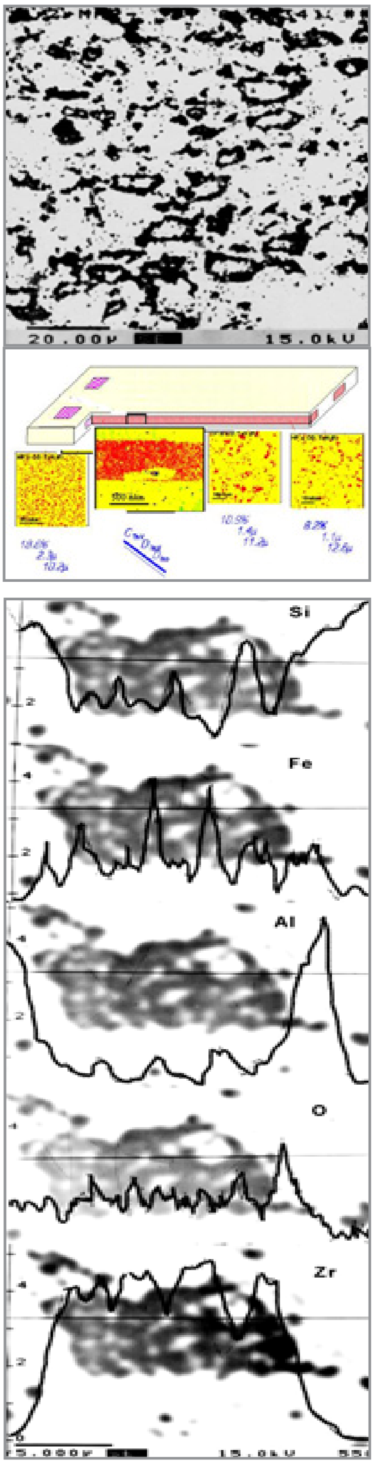
Table 3: Amount of Solid Residue during Pyrolysis of Various Bindersrs

Pyrolysis conditions: average heating rate 15 deg/min	Amount of solid residue, % for binders			
	rubber	KMC+glycerol	KMC	glycerol
20 - 450 ° C,	42,02	11,32	57,75	0,05
20 - 600 ° C	3,15	7,5	48	0
20 - 750 ° C	0	–	29	0
20 - 1000 ° C	–	–	16,5	–

Structural Analysis and XRD Analisis

The microstructure of the sintered samples was analyzed using scanning electron microscopy (SEM). Figure 2 shows SEM images of samples with different ZrC particle size distributions. The images reveal that finer particles lead to a more uniform and dense microstructure, which correlates with the electrical and thermal properties observed.

Contact characteristics Si3N4 - ZrC



Si outside the inclusion in the form of Si3N4. There is no depletion region of silicon near the inclusion, there are traces inside the silicon inclusion.

The concentration of Fe both in the inclusion and at a distance from it is 0%. At the boundary of the inclusion it is maximum.

There is no Al in the inclusion; Outside the inclusions, the maximum of Al coincides with the maximum of Si

The maximum of O coincides with the minimum of Si and does not always coincide with the maximum of Al. O is present at the inclusion boundary

The concentration of Zr in the inclusion is maximum, at a distance of 2 μm from the inclusion the concentration drops to zero; In the immediate vicinity of the inclusion there is a region enriched in Zr

Figure 2: Image of the microstructure of the composite of composition PS Table 1, 20% zirconium carbide polydisperse (a), functional area in the shell body (b, numbers indicate the concentration of particles according to the results of image measurement, particle size and size of interparticle distances), and c) SEM Images of Sintered Samples with Different ZrC Particle Size Distributionsa)

Zirconium particles are not completely carbidized during the synthesis process; zirconium carbonitride ZrCN is formed in the surface layers of the larger ones (> 5 μm). The ZrC_3/0 fraction differs from others in the presence of iron impurities in the forms of Fe and Fe2O3, as well as a small amount of zirconium nitride and oxide. Fractions ZrC_7/3 and ZrC_40/28 have higher intensity of ZrC reflection peaks compared to ZrC_3/0. They do not contain impurities of ZrN and Fe2O3, but ZrCN is present in large quantities (Fig.3). The interaction of silicon nitride with zirconium carbide can be represented as follows: at the points of contact of Si3N4 and ZrC particles, reaction diffusion of silicon and nitrogen into zirconium carbide occurs with the formation of silicide phases of zirconium and silicon carbide and zirconium carbonitride part of the zirconium atoms, about 1%, is replaced by silicon atoms [4].

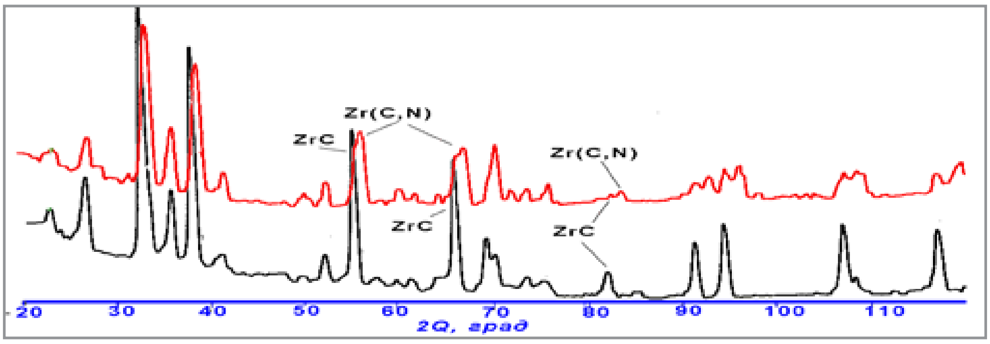


Figure 3: Illustration of the interaction of a zirconium carbide particle with a silicon nitride matrix by XRD analysis.

Electrical Properties

We determined the influence of the distribution of particle sizes on the electrical resistance of the functional layer at room temperature (25ºC). The results are shown in Fig.4.

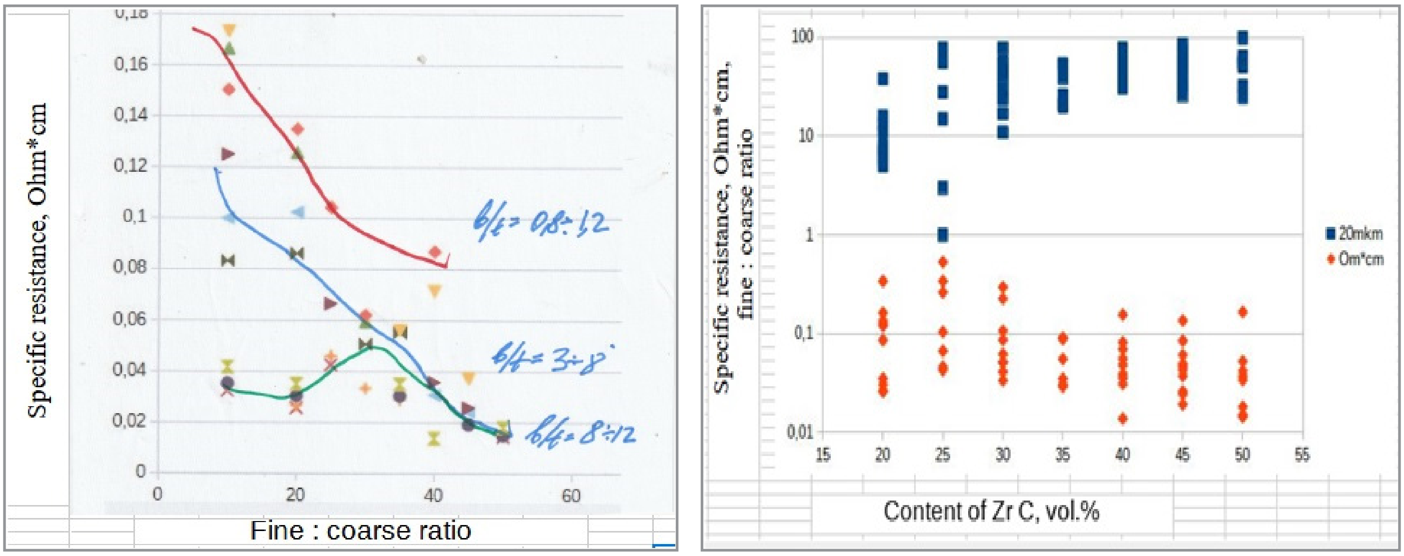


Figure 4: Dependence of electrical resistance of 15 vol.% zirconium carbide composites on the fine:coarse inclusion ratio a) (where fine is 3 µm, coarse is 28 µm) and b) content of ZrC 15-60% for particle 2 and 20 mkm (red – spesific resistance, blue – pa4rticle 20 mkm

It has been established that in a limited space (Figure 4) the grain composition of the polydisperse composite of silicon nitride - zirconium carbide significantly depends on the concentration of zirconium carbide and the ratio of the width to the thickness of the functional area. The minimum content of the coarse fraction is 5-10% with an additive concentration of 20-25%, if the length-to-thickness ratio was 8-12. And if the specified ratio was 0.8-1.2 at the same concentration of the additive, the content of the coarse fraction increases to 60-80%. It is also obvious that the processes of enlargement of conductive particles depend decisively on the ratio of the width to the thickness of the functional region. An extremely intensive change in the resistance of the composite from the amount of coarse fraction occurs in volumetric functional zones, when the ratio of the width to the thickness8 is close to 1. And the most stable properties from the point of view of the grain structure are laminate functional regions with a ratio of the width of 5 to the thickness of 8-12.

In the presence of carboxymethyl cellulose (CMC) pyrolysis products, the structure formation proceeds similarly to that with rubber pyrolysis products. However, the size of the inclusions in the conductor is larger, and there is no iron in the area surrounding the inclusion particle. Additionally, the size of the area of tantalum penetration into the matrix is somewhat smaller than in the sample with rubber. Therefore, the shell directly surrounding the inclusion particle has fewer stoichiometric violations, and to create a chain of inclusions, the ZrC concentration needs to be increased to 15%.

Figure 5 shows the dependence of the resistivity of the composite on the percentage of coarse fraction at a zirconium carbide concentration of 15 vol.% and various ratios of width to thickness of the functional area.

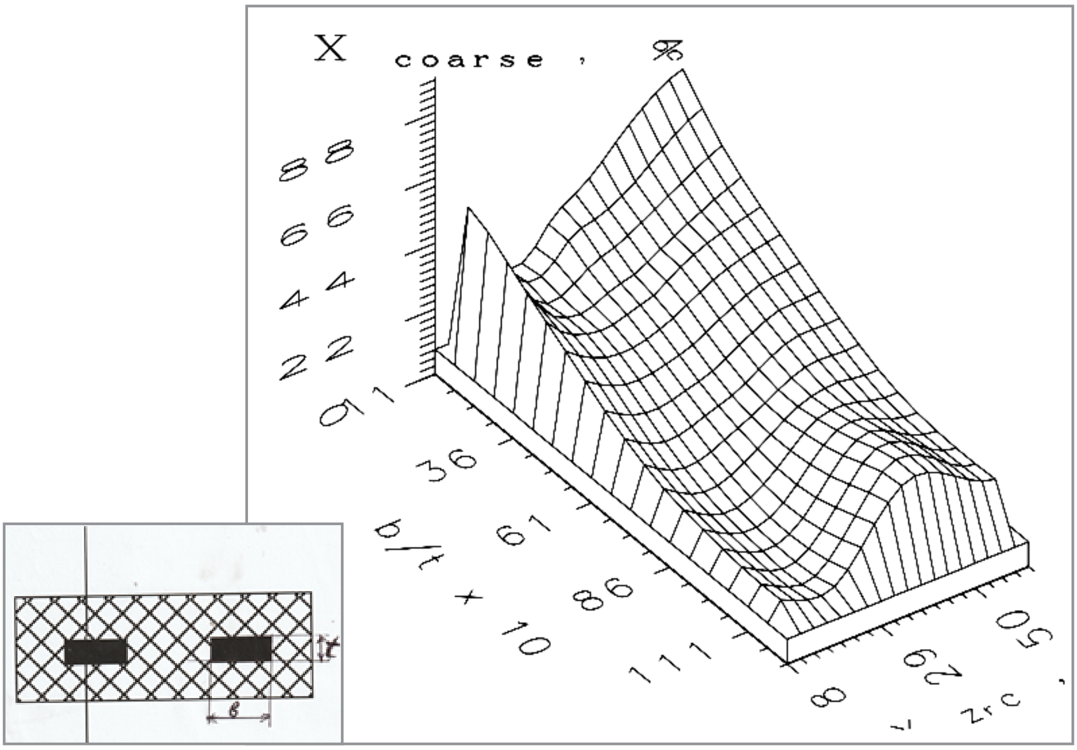


Figure 5: Dependence of the electrical resistance of the silicon nitride-zirconium carbide composite on the concentration and the width-to-thickness ratio of the functional zone

Figure 6 shows the results of measuring the squared current density and the squared voltage density for samples, the granulometric composition of which was shown in Figure 6.

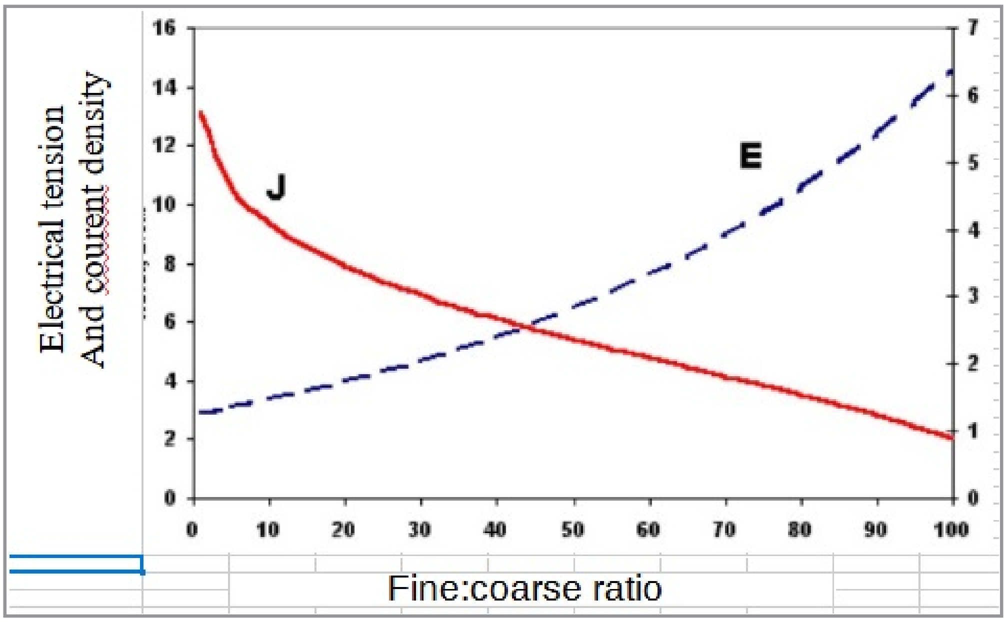


Figure 6: Electric current density and electric field strength for a grain composite of 15% zirconium carbide and a width-to-thickness ratio of 8-12

The light temperature of 527ºC was used as a temperature reference point - the temperature at which a dark cherry glow of the surface appears. As can be seen, both the square of the current density and the square of the electric field intensity density are nonlinear functions of the content of the coarse fraction at a constant ratio of the width to the thickness of the functional region and at a constant concentration of the conductive additive.

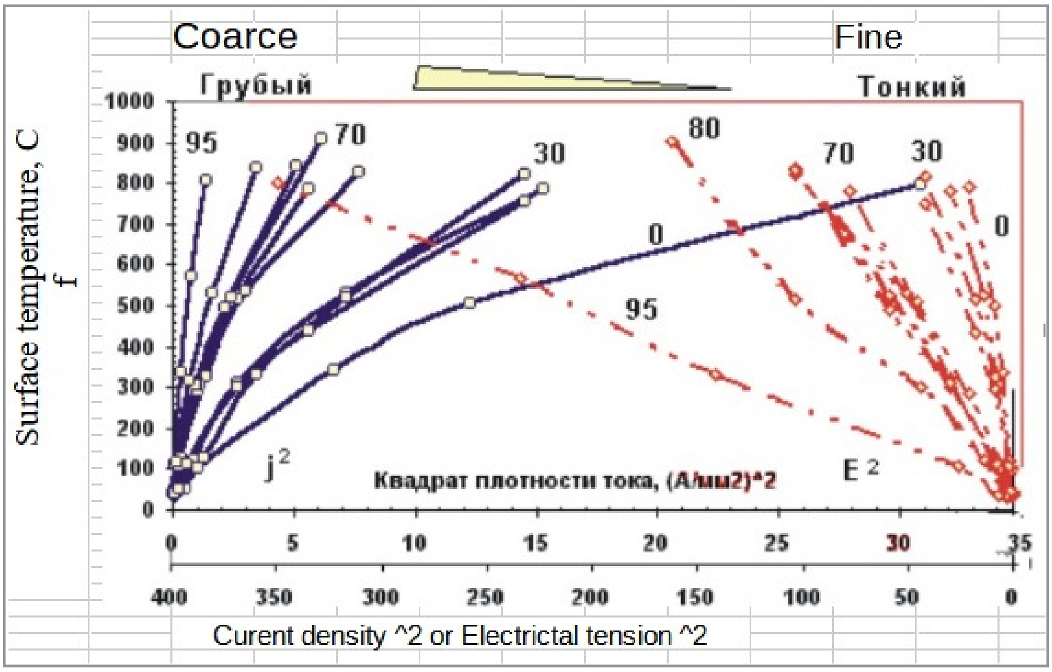


Figure 7: Dependence of current density and electric field strength on the grain composition of the conductive cluster of the resistive composite (numbers near the curves are the percentage content of the coarse fraction (30 µm) in the grain composition of the cluster; solid lines are the dependence on j2, dashed lines are the dependence on E2.

The resistance value of the composite at intermediate conductor concentrations depends weakly on the resistance of the filler material and strongly on the grain size of the conductor inclusions. If a current is passed through the resistive region of the material, which will lead to its heating to a certain temperature (for example, 527C), then depending on the ratio of the sizes of the small and large fractions in the composition of the structural fragments ("ensembles") of the conducting cluster, this temperature will be achieved at a higher density current, the lower the coarse fraction content is observed The electric field strength at which the current density occurs, which contributes to heating the surface of the material to a temperature of 527°C, is also a nonlinear function of the grain composition of the conductive cluster, as follows from Ohm's differential law. However, as can be seen from, if the square of the current density through the sample is a structure-sensitive parameter for a fine-grained structure, then the square of the electric field strength shows greater sensitivity if the coarse fraction predominates in the conductive cluster. If the concentration of the coarse fraction (30 µm) is denoted by XmCoarse and expressed as a percentage, then the empirical relationship expressing the relationship between the grain composition of the cluster is the total electric current j (in A/mm2) and the electric field strength E (in V/cm) at which The surface temperature of the resistive region of the material reached 527°C and looks like this:

$$j = \sqrt{2.05 - \frac{\lg X_m^{Coarse}}{0.0625}} \qquad E = 10^{\frac{X_m^{Coarse}+64}{141}}$$

Thus, empirical relationships are the basis for calculating the coarse fraction content in the morphology of the microstructure of a conductive cluster based on direct measurements of the electric current density through the resistive material or the resistive region of the gradient composite and the magnitude of the electrical voltage drop across the resistive material [5-7].

Conclusion

1. It was established that the formation of the grain structure of a dispersed composite of the "dielectric-conductor" type is determined by many technological factors, most of which were known (Grain composition of the charge, consolidation temperature), but new ones were discovered, first of all, the grain composition of the conductive additive, and the physical dimensions of the functional area, primarily the ratio of width to thickness.

2. It has been proven that if the square of the current density through the sample is a structure-sensitive parameter for a fine-grained structure, then the square of the electric field strength shows greater sensitivity in the case of a predominance of the coarse fraction in the conductive cluster. The linear relationship between current and surface temperature also indicates predictable behavior, essential for practical applications. The developed technique for controlling the properties of the composite by adjusting the grain size can be used to optimize the performance of these materials in various electronic and electrical applications.

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