An Investigation of the Electrophysical Properties of Composite Ceramic Materials Containing Nickel Nanoparticles

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The regularities in the behavior of the electrophysical properties of composite ceramic materials containing nickel micro- and nanoparticles in the region of the percolation threshold have been studied. Studies have shown regularities in the dependences of electrical conductivity, dielectric constant, thermal conductivity, and thermo-emf of composite ceramic materials on the volume content of nickel particles. When the percolation threshold was approached in these materials, the experimentally obtained dependences of the conductivity and static dielectric constant on the fractional content of nickel differed from the dependences calculated within the framework of the percolation theory while the dependence curve for the dielectric constant was similar to the curve for electrical conductivity. The origin of this discrepancy can be attributed to the formation of a continuous spatial structure from tunnel-connected conductors.

Keywords: Nanoparticles, Microparticles, Electrophysical properties, Ceramic materials, Nickel, Percolation threshold, Conductivity, Temperature dependence

INTRODUCTION

Currently, all over the world, there has been a significant increase in the number of experimental and theoretical studies aimed at creating materials with special and practically important electrophysical properties on the basis of heterogeneous materials containing metal nanoparticles, mainly due to their physical properties that are found to be unique and significantly different from those of the corresponding compact materials. Inhomogeneous systems, among which the electroconductive ceramic materials containing micro- and nanoparticles of metals are very promising, have great potential applications. In such systems, at a certain critical concentration of metal particles called percolation threshold, the electrical, thermophysical, magnetic, and other properties change dramatically.

Today, despite the considerable progress made in the study of ceramic materials containing micro- and nanoparticles of metals, their practical application has been limited due to some reasons. One reason for their limited application is that until now many of the physical phenomena occurring in them remains unexplained. The electrical conductivity and dielectric permeability of inhomogeneous materials containing microparticles of metals can be well explained by the classical percolation theory. However, the application of the classical percolation theory to describe the electrical properties of materials containing metal nanoparticles randomly distributed in a dielectric matrix below the percolation threshold encounters some problems, *i.e.*, their conductivities differ from those calculated within the framework of this classical theory. Explaining this discrepancy is one of the main tasks of researchers in this field.

Currently, particular attention is paid to the creation of a new generation of materials. The energy model of the

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structure explaining the behavior of the conductivity of charge carriers is not clear, and the topology of an infinite cluster in such systems has not been studied yet. The answer to these issues will not only provide a clearer picture of the structure and mechanism of charge transfer of heterogeneous systems containing micro- and nanoparticles of metals but also facilitate their practical use.

Recently, much attention has been focused on creating new generations of materials. Among these materials, new varieties of ceramics have attracted the most attention. The nanocrystal formation in the matrix of such materials makes it possible to manufacture various products that would be useful in power engineering and mechanical engineering. In light of such a promising outlook, it is expected that more fundamental studies focus on such new ceramics around the world. Studying the electrophysical properties of ceramic composite materials containing nickel nanoparticles can lead to fundamental results, which, in turn, can promote the scientific development and application of these composite materials.

Statement of the Problem

In recent years, a number of studies have shown that below the percolation threshold, the conductivity behavior of heterogeneous materials, including ceramic, polymer, and glass matrix ceramics, containing metal nanoparticles (*i.e.*, Fe, Ni) cannot be explained within the framework of the percolation theory. This issue is discussed in detail in a review paper by Balberg *et al.* [1]. In this review paper, the results of studies done on the conductivity of heterogeneous materials containing conductive micro- and nanoparticles for a period of 30 years were analyzed, and the conductivity behavior of composites containing metal nanoparticles was discussed in terms of a spatial-structural hierarchical model. Numerous experimental and theoretical studies have been conducted on the electrophysical properties of heterogeneous materials containing metal nanoparticles [1]. However, there are no studies confirming Balberg *et al.'s* assumption for the samples of the same composition but with different sizes of metal particles. Neither is there any study suggesting that the behavior of the static dielectric permeability depends on the particle size in the region of the percolation threshold in such systems. It has not been established yet that the behavior of electrophysical

properties in composites containing metal nanoparticles is dependent on the content of disperse nanofillers.

EXPERIMENTAL

In what follows, the following topics are briefly discussed: development of composite ceramic materials containing nickel micro- and nanoparticles of nickel, the concentration dependence of electrical conductivity, dielectric permeability, thermal conductivity, and thermo-emf of the developed composites on the content of nickel micro- and nanoparticles, the concentration-temperature dependence of the conductivity of composite ceramic materials containing nickel nanoparticles, the topology of an infinite cluster based on metal particle size and energy diagrams, and identification of a possible area for the practical application for the developed composites.

This study focused on the local ceramics with the following composition in percentage: SiO_2 (61.72), Fe_2O_3 (3.87), Al_2O_3 (12.52), CaO (13.48), MgO (0.94), Na_2O (1.78), K_2O (0.72), MnO (0.07), and impurities (4.9).

Two types of composites were prepared for research. One included ceramic composite materials containing nickel nanoparticles. The other one included ceramic composite materials containing nickel microparticles. Ceramic materials containing nickel nanoparticles were obtained by thermal decomposition of nickel formate pre-mixed with ceramics. Mixing was carried out in an agate ball mill for 7 h. Thermal decomposition was carried out in vacuum at a temperature of 400 °C for 5 h.

As is known, small-angle X-ray scattering can be used to study inhomogeneities of a substance, the sizes of which exceed interatomic distances and range from 5-10 to 104 Å. The size of the nickel nanoparticles was not determined because the above-mentioned method (*i.e.*, small-angle X-ray scattering), which we used for other composite materials, was inapplicable due to the fact that the densities of Si, Fe, Al, and other ceramic components were close to the nickel nanoparticles were close. Therefore, polymer composites containing nickel formate were obtained in a similar way. After the decomposition of nickel formate salts in a heat-resistant polymer based on phenylone and using a KRM-1 small-angle X-ray camera, the radius of nickel particles in composites was calculated. The results showed

that their diameter did not exceed ~ 20 nm.

Ceramic materials containing microdispersed nickel particles were obtained by mixing nickel powder with ceramics in an agate ball mill for 7 h. In the samples used, the nickel particle size was in the range of 1-3 μm. This was established using transmission electron microscopy on a BS242E microscope (Tesla). The volume fraction of nickel in the composition varied from 0.02 to 0.6. The electrical properties were measured on samples in the form of tablets, which were 15 mm in diameter and 2 mm thick. The samples were prepared by pressing a ceramic powder at a pressure of 2×10^2 MPa and sintering the resulting pellets in a vacuum at a temperature of 1000 °C. In both cases, the volume fraction of metals (V_1) was calculated based on the concentration of the metal in the original metal-containing compound.

Electrical and Thermophysical Properties of Composite Ceramic Materials Containing Nickel Micro and Nanoparticles

Figure 1 shows the experimental dependences of the conductivity (σ) on the concentration of nickel particles for both investigated ceramic materials as well as those calculated within the framework of the percolation theory using the equations below.

According to the percolation theory, the conductivity (σ) of systems containing metal particles that are distributed randomly in a dielectric matrix ($V_1 = 0$ and $V_1 = 1$) is described by the boundary conditions and the following equations:

$$\sigma (V_1) = \sigma_2 (V_c - V_1/V_c)^{-q}, \text{ at } V_1 < V_c \qquad (1)$$

$$\sigma (V_1) = \sigma_1 (V_1 - V_c)/(1 - V_c)^t, \text{ at } V_1 \geq V_c. \qquad (2)$$

where σ_1 is the conductivity of metal particles, σ_2 is the conductivity of the dielectric matrix, V_c is the critical concentration (percolation threshold) at which an infinite cluster (IC) of filler particles is first formed, and t and q are parameters called critical indices.

The values (σ) of composites were calculated using Eqs. (1) and (2). The calculated values ($V_c = 0.15$, t = 1.6, q = 1) and the determined values ($\sigma_d = 1.2 \times 10^{-12} \, \Omega^{-1} \, m^{-1}$ and $\sigma_1 = 2.4 \times 10^{-1} \, \Omega^{-1} \, cm^{-1}$; σ value of Ni powder at
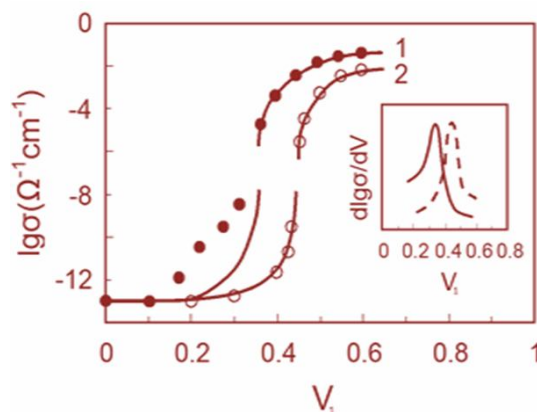

Fig. 1. A comparison of the experimental (points) *vs.* calculated (solid curves) values of conductivity as a function of the volume content (V_1) of nickel particles for ceramic materials containing nanoparticles (filled points, curve 1) and microdispersed particles (empty points, curve 2). The inset shows the curve of dLgσ/dV *vs.* V_1 (solid and dashed lines represent materials containing nanoparticles and microdispersed particles, respectively).

$P = 1.5 \times 10^2$ MPa) did not match the experimental results. Therefore, the values of V_c, t, q, and σ_1 were determined as follows. For the studied ceramic materials, V_c was determined by differentiating logσ with respect to V_1. The critical indices t and q were obtained from the experimental data and presented as a graph in the coordinates logσ-log $[(V_1 - V_c)/(1 - V_c)]$ and logσ-log$[(V_c - V_1) - V_c]$. The angles of the inclination of these graphs were t and q. The σ_1 value was obtained by extrapolating this graph to $V_1 = 1$.

For a ceramic material with nickel nanoparticles, it was found that $V_c = 0.355$; t = 2.21 and $\sigma_1 = 4.3 \times 10^2 \, \Omega^{-1} \, m^{-1}$, and for a ceramic material with microdispersed nickel particles, it was found that $V_c = 0.443$; t = 1.81; q = 1.02 and $\sigma_1 = 3.2 \times 10^2 \, \Omega^{-1} \, m^{-1}$. The value of σ_1 determined by extrapolating the graph in the coordinates logσ-log$[(V_1 - V_c)/(1 - V_c)]$ was an order of magnitude lower than the value of 1 determined at a pressure of 1.5×10^2 MPa. These results show that σ_1 determined by extrapolation was not the conductivity of Ni metal particles, but the conductivity of an infinite cluster of nickel particles in the composite in the

region ($V_c \leq V_1 \leq 0.5$).

As can be seen in Fig. 1, for both types of the studied composite materials, the correspondence between the calculated and experimental data was observed at $V_1 > V_c$. In the case of $V_1 < V_c$, the correspondence between theoretical and experimental dependences was observed only in composite materials with microdispersed nickel particles.

For a composite material with nickel nanoparticles, there was an additional contribution to the electrical conductivity in the region below V_c. These results can be explained on the basis of the model of electrical conductivity in composites proposed by Balberg *et al.* [1]. According to this model, all metal particles in composites, in which metal particles are randomly distributed in a dielectric matrix, are electrically coupled, and the conductivity of these composites is determined both by the tunneling of charge carriers between neighboring particles and the tunneling between particles located at a distance. Percolation behavior is observed when the contribution of tunneling between particles located at a distance from each other to the macroscopic conductivity is negligible. This occurs when the particle radius (b) is much larger than the tunneling region parameter (or the tunneling decay parameter) (d). In cases when b ~ d, the tunneling of charge carriers between non-neighboring particles contributes to the macroscopic conductivity, along with the tunneling between neighboring particles, and the dependence of the macroscopic conductivity on the concentration of metal-containing particles differs from that dictated by the classical percolation theory.

In Balberg *et al.'s* study [1], the manifestation of these two types of conductance behavior in composite materials was demonstrated by carbon nanotubes localized in polymer composites and Ni-SiO$_2$ cermets. A noteworthy result obtained in the present study was that these two types of behavior of conductivity were observed in composites of the same composition, suggesting the dependence of these types of conductivity on the size of metal-containing particles in the composites studied.

In composites in which the tunneling of charge carriers between neighboring particles contributed to the electrical conductivity, there were two percolation thresholds. One of these percolation thresholds was observed at high values of
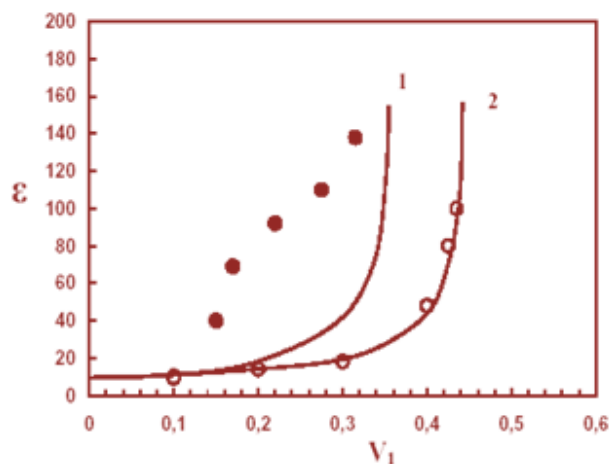

Fig. 2. A comparison of the experimental *vs*. calculated (solid curves) values of the dielectric constant (ε) as a function of the volume content (V_1) of nickel particles for ceramic materials containing nanoparticles (filled points, curve 1) and microdispersed particles (empty points, curve 2).

V_1, which is the percolation threshold V_c determined above, and the other one (additional percolation threshold V_{cd}) was observed at low values of V_1, which was the critical fractional volume of metal particles that initiated the first infinite cluster of tunnel-coupled conductors. By fitting the $V_1 < V_c$ section of the experimental curve 1 (Fig. 1) for a ceramic material with nickel nanoparticles into the functional dependence determined by Eq. (1), in which V_{cd} is the percolation threshold and t is the critical index as t, it was found that $V_{cd} = 0.145$ and t = 3.2.

The study of the frequency dependence of the dielectric constant (ε) of composites showed that there were two regions on the dependence of ε on frequency (f) in the frequency range of $20\text{-}10^8$ Hz of the alternating field. At low frequencies ($20 \div 1000$ Hz), the dielectric constant (ε) of composites decreased significantly. In such systems, a further increase in frequency to 10^8 Hz led to a weak dependence of their ε on f. The decrease in the dielectric constant (ε) of composites at low frequencies can be explained by the Maxwell-Wagner capacitor model [8].

Figure 2 shows the experimental and calculated dependences of the static dielectric constant ε on V_1 for the studied composites. The experimental dependences of ε on

V_1 were obtained by extrapolating the frequency dependences of ε in the range of 20-200 Hz to zero frequency. Theoretical dependencies were calculated by the Eq. (3):

$$\varepsilon(V) = \varepsilon_d \, (V_c - V_1/V_c)^{-q}, \text{ at } V_1 < V_c \qquad (3)$$

where ε_d is the dielectric constant of the ceramic.

In the above calculations, the same V_c values obtained from the experimental dependences of σ on V_1 were used.

As can be seen in Fig. 2, for a composite with microdispersed nickel particles, the experimental dependence of ε on V_1 could be well described by Eq. (3). For a composite with nickel nanoparticles, the experimental dependence of ε on V_1 did not agree with the calculated dependence and showed an additional contribution to ε at V_1, which lay below the percolation threshold.

Based on a qualitative interpretation of the sharp increase near the percolation threshold and the physical concept of the "hierarchy" of electrically coupled spatial structures in composites, for the first time, an interpretation of the behavior of ε composites containing nickel nanoparticles was proposed. In this interpretation, it was taken into account that the V-dependence curves for σ and ε were similar for the studied corresponding composite materials.

The thermal conductivity of composite ceramic materials containing nickel micro- and nanoparticles was investigated. It was found that the thermal conductivity of composite ceramic materials can be described by almost any formula derived within the framework of the effective medium theory. Moreover, the dependence of the thermo-emf (α) of the composites on the concentration of nickel micro and nanoparticles was studied. The concentration dependence of the thermo-emf of the studied compositions exhibited a clearly pronounced critical character (Fig. 3).

In cases where the electrical conductivity of the metal (σ_1) was much higher than that of the dielectric (σ_2) with close values of the thermal conductivity λ (*i.e.*, $\sigma_m > \sigma_d$ and $\lambda_m \sim \lambda_d$), the concentration dependence was described by a power law:

$$\alpha(V) = \alpha_m \left(\frac{V - V_c}{1 - V_c} \right)^{-k} \qquad (4)$$
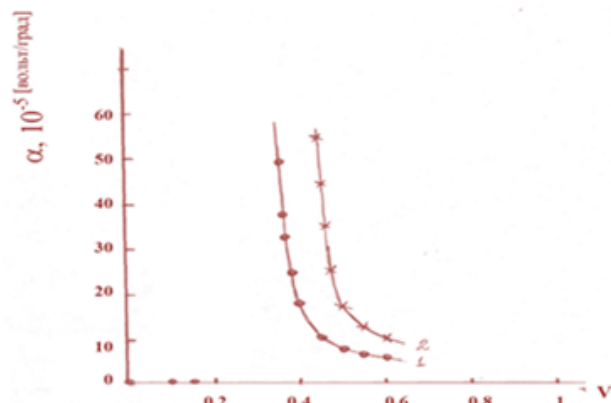

Fig. 3. The dependence of the Seebeck coefficient (a) of compositions on the volumetric content of nickel nano (1) and microdispersed (2) particles.

at $k = 0.8 \pm 0.1$ and at α-thermo-emf, infinite cluster.

To describe the character of the dependence of (α) on V_1 of composites within the framework of percolation theory, the experimental results were plotted in the coordinates loga *versus* the $(V_1 - V_c)/(1 - V_c)$ log. From the slope of the dependence, the critical index (k) was determined; the k values for composites were 0.71 and 0.80, respectively. The obtained index values were in good agreement with those calculated by Eq. (4).

It is known that the percolation theory approach makes it possible to establish the topology of the resistance grid (topology of an infinite cluster). The density of IC, the volume fractions of the skeleton, and dead ends belonging to the IC as well as their dependence on the volumetric content of the filler were determined. It was found that near the percolation threshold, the volume fraction of the skeleton was negligible compared to that of dead ends (Table 3.1) [8].

The Z/R values at t = 1.81 and t = 2.21 are shown in Table 1. As can be seen in Table 1, in composites containing nickel nanoparticles and near the percolation threshold, an infinite cluster is more sinuous compared to IC in composites containing highly dispersed particles. These results show that the higher the dispersion is, the more tortuous is the infinite cluster in such composites. Z/R values show how many times the skeleton was longer than R due to tortuosity.

Table 1. The Dependence of Parameters $P(V_1)$, V_1', Z/R, V_1'', and V_1''' on the Volume Fraction of the Filler for Composites Containing Nickel Nanoparticles

№	V_1	$P(V_1)$	V_1'	Z/R	V_1''	V_1'''
1	0.36	0.143	0.052	11.9	1.3×10^{-5}	5.19×10^{-2}
2	0.362	0.173	0.063	9.4	3.0×10^{-5}	6.27×10^{-2}
3	0.365	0.188	0.069	8.3	5.7×10^{-5}	5.84×10^{-2}
4	0.380	0.272	0.10	5.2	4.0×10^{-4}	1.0×10^{-1}
5	0.40	0.344	0.138	3.9	1.5×10^{-3}	1.4×10^{-1}
6	0.50	0.550	0.275	2.1	2.2×10^{-2}	2.5×10^{-1}
7	0.55	0.619	0.34	1.8	4.4×10^{-2}	3.0×10^{-1}
8	0.60	0.678	0.41	1.6	7.9×10^{-2}	3.3×10^{-1}

As can be seen in Table 1, the value of P (V_1) increased with distance from the percolation threshold toward large V_1. This means that the infinite cluster gradually joined the final clusters formed between the nickel particles and became denser and denser.

The Nature of the Conduction Mechanism in Composite Ceramic Materials Containing Nickel Nanoparticles

The mechanism of the electric transport of charge carriers in composite ceramic materials containing nickel nanoparticles was studied.

Figure 4 shows the experimental temperature dependences of conductivity (σ) at temperatures ranging from 100 K to 450 K for composites containing nickel nanoparticles at $V_1 < V_c$. In order to understand the nature of the temperature dependence of electrical conductivity in such systems, one should study their structure. From a physical point of view, the formation of ceramic composites containing metal nanoparticles can be attributed to the doping of the initial dielectric with metal nanoparticles, similar to doped compensated semiconductors. This suggests that electronic states similar to impurity levels appear in the band gap of the initial ceramic.

An increase in the volume content of metal nanoparticles affects not only their concentration but also their size distribution. If this representation is correct, the conduction mechanism in such systems is hopping, and its temperature dependence can be described by the following equation:
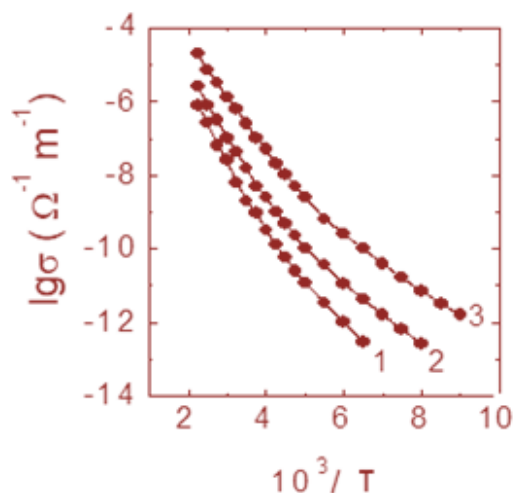

Fig. 4. Temperature dependence of conductivity in composite ceramic materials. Volume fraction of filler 0.220 (1), 0.275 (2), and 0.315 (3).

$$\sigma = \sigma_0/\exp[-(T_0/T)^x] \tag{5}$$

at $x = n + 1/n + d + 1$, $g(\varepsilon) = g_0(\varepsilon - \varepsilon_F)^n$; density of localized states, ε_F (Fermi level), and d-dimension of space.

To check the applicability of law (5), the dependence of σ on T is usually plotted in the coordinates $\log\sigma \sim T^{-x}$. As can be seen in Fig. 4, the dependence of σ on T can be straightened not only in the coordinates $\log\sigma \sim T^{-1/2}$ but also in the coordinates $\log\sigma \sim T^{-1/3}$ and $\log\sigma \sim T^{-1/4}$. To determine x in Eq. (5) in composite materials, the temperature dependence of the reduced activation energy of conduction

was analyzed. In Zabrodsky's [15] study, the following equation is proposed to determine x:

$$\log\omega = B - x\log T, \quad \omega = 1/T\partial\log\sigma/\partial T^{-1} = \partial\log\sigma/\partial T,$$
$$\text{at } B = \text{const} \tag{6}$$

where ω is the reduced activation energy of conduction.

Figure 5 shows the temperature dependence of ω for composites obtained by graphical differentiation of the curves in Fig. 4 in coordinates $\log\sigma$-$\log T$. It can be seen from these data that in the studied temperature range, there were three regions with different temperature dependences, including the high (I) and low (III) temperatures separated by a certain transition region (II).

When the density of localized states near the Fermi level is constant (*i.e.*, g (ϵ) = const), the value of x in Eq. (5) is 0.25 (n = 0, d = 3) and thus Eq. (3) turns into the well-known Mott's law (variable range hopping, VRH).

As can be seen in Fig. 5, in the high-temperature region (T $\geq$ T$_a$, to the right of curve a), there is a region of linear dependence of $\log\sigma$ on $\log T$, corresponding to the exponential law σ (T) with x $\approx$ 1:

$$\sigma = \sigma_0\exp(-\Delta\epsilon/KT) \tag{7}$$

Based on the results obtained, Eq. (7) corresponded to conductivity with the activation energy of conductivity ($\Delta\epsilon$), and its value in the temperature range from T$_a$ (to the right of curve a) to 450 K was constant.

As can be seen in Fig. 5, in the samples under study, a linear dependence of $\log\sigma$ on $\log T$ was also observed at relatively low temperatures (T $\leq$ T$_c$, to the left of curve c), which corresponded to the exponential law ω (T) cx $\approx$ 0.5. This corresponds to the special case of Eq. (5) for conductivity with variable activation energy.

$$\sigma = \sigma_0' \cdot \exp[-(\Delta\epsilon/KT)^{1/2}] \tag{8}$$

Figure 6 shows a possible energy model of composite ceramic materials containing metal nanoparticles. Occupied and free states (Fig. 6) near the Fermi level were chaotically distributed and localized due to the disorder of the system.
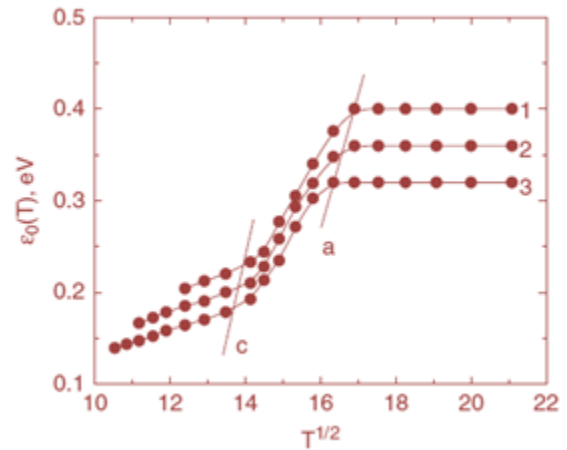

Fig. 5. Temperature dependences of the reduced activation energy of the conductivity (ϵ) of composite ceramic materials. The volume fraction of the filler in the composition is 1- 0.220, 2-0.275, and 3-0.315.
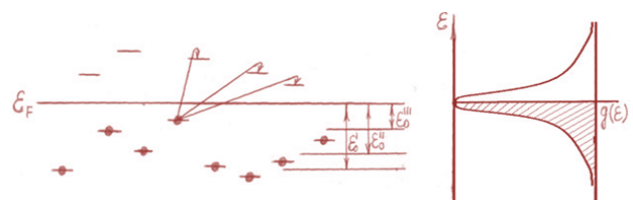

Fig. 6. The energy model of ceramic materials containing nanodispersed metal particles.

Therefore, the tunneling transition between the states of two metal nanoparticles, which affects the value of the hopping conductivity, requires a certain activation energy.

The solid line is the Fermi level at thermodynamic equilibrium. The dashes above and below the Fermi level are the lowest free levels and the highest occupied levels, respectively. $\epsilon_0' > \epsilon_0'' > \epsilon_0'''$ are the strip widths corresponding to $T_1 > T_2 > T_3$. The latter can be determined in two ways: 1) by disordering the system associated with the presence of metal nanoparticles of various sizes, leading to a strong spread of levels and localization of their electronic states, and 2) by calculating the Coulomb interaction of an electron passing into a neighboring metal nanoparticle with a hole arisen in the previous place, which causes the appearance of a Coulomb gap near the Fermi level. With a decrease in temperature, in accordance with

Mott's model, one should expect a transition to the regime of hopping conduction with a variable hopping length, the temperature dependence of which is determined by the Coulomb interaction and its dimension in the system. The indicated parabolic gap in such systems, as in other disordered systems, is the Efros-Shklovskii Coulomb gap [12]. The bandwidth ε0 according to Eq. (8) is expressed by the following equation:

$$\varepsilon_0 = 0,5KT_0^{1/2}T^{1/2} \tag{9}$$

As ε_0 decreases by decreasing the measurement temperature, the average hopping length of charge carriers $\bar{r}$ increases, and its temperature dependence can be described by the following equation:

$$\bar{r} = \frac{a}{4}\left(\frac{T_0}{T}\right)^{1/2} \tag{10}$$

$$T_0 = \frac{\beta}{g_0^{1/3}aK} \tag{11}$$

at β = 2, 8, α (localization radius).

Identification of (8) with VRH and low anisotropy (d = 3) leads to the conclusion that hopping occurs in the region of the parabolic quasigap g (ε) = g0 (ε - εF)² in the density of localized states in the vicinity of the Fermi level.

In what follows, some possible areas of practical use of the obtained composites are outlined. In particular, elements with relatively high values of dielectric constant can be used in the field of radio electronics while elements with relatively high values of thermo-emf can be used as converters of thermal energy into electrical energy.

The ever-increasing need of modern technology, in particular microwave technology, to non-conductive (high-resistance) materials with increased and adjustable dielectric constant values necessitates the search for new materials to address this need. At present, researchers are trying to use large amounts of ferroelectric ceramics powders in a matrix as fillers, a practice which significantly impairs the physical and mechanical properties of the compositions. A dielectric anomaly in the region of the percolation threshold was found in a number of composite materials containing

microdispersed (~ 1 ÷ 5 μm) metal powders obtained by mixing the components. This method has a number of disadvantages, one of which is that finely dispersed metal particles accumulate during the mixing of the components; therefore, the electrical properties of the compositions filled with metal powder near the metal-dielectric transition are difficult to reproduce. However, this method can be used to obtain stable materials with not very high dielectric constant values. In this regard, the most acceptable are composite materials containing nanodispersed metal particles.

Figure 2 shows the advantage of composite ceramic materials with nanodispersed metal particles over microdispersed metal particles. As can be seen in Fig. 2, in composite ceramic materials containing nanodispersed metal particles and far from the percolation threshold $V_{cd} < V_c$, the dielectric constant had a sufficiently high value.

The study of the behavior of the thermo-emf of the developed composites showed that the concentration dependence of the thermo-emf value had a clearly pronounced critical character (Fig. 3). These results show that such composites can be used as converters of thermal energy into electrical energy.

CONCLUSIONS

Based on the results obtained, the following conclusions were made:
1. There were regularities in the dependences of electrical conductivity, dielectric constant, thermal conductivity, and thermo-emf of composite ceramic materials on the volume content of nickel particles. When approaching the percolation threshold, the experimentally obtained dependences of the conductivity and static dielectric constant on the fractional content of nickel in composite ceramic materials differed from the dependences calculated within the framework of percolation theory, evidenced by the fact that the dependence curve for the dielectric constant was similar to the curve for electrical conductivity. This discrepancy can be explained by the formation of a continuous spatial structure from tunnel-connected conductors.
2. Two types of percolation thresholds were established in composite ceramic materials of the same composition but

different sizes of metal particles. One of the two percolation thresholds was observed at values of V_c, which was dictated by the classical theory of percolation, and the other one (V_{cd}) was observed at $V_{cd} < V_c$, which initiated the first infinite cluster of tunnel-coupled conductors.

3. It was found that in ceramic materials containing nickel nanoparticles in the region below the classical percolation threshold (*i.e.*, the high-temperature region, $T \geq T_a$) and in electrical conductivity, both the tunneling between the nearest neighboring particles with a constant activation energy of conduction and the carrier tunneling contributed to the charge between non-nearest neighboring particles. At comparatively low temperatures ($T \leq T_c$), electrical transfer in samples was carried out by the tunneling of charge carriers with variable activation energy of conduction in the region of a parabolic quasigap in the density of localized states and in the vicinity of the Fermi level.

4. An energy model of the structure is proposed to explain the physical properties of ceramic materials containing metal nanoparticles.

5. The possibility of applying the percolation theory to study the aforementioned structure (*i.e.*, IC topology in electrically conductive ceramic materials) was examined. The density, volume fraction, tortuosity, volume fraction of the skeleton, and dead ends of an infinite cluster were determined based on the volume content of nickel particles in such systems. Near the percolation threshold, the volume fraction of the skeleton belonging to the BC was found to be an insignificant fraction of its total volume, and the bulk of the IC concentrated in the dead ends. Near the percolation threshold in composites containing nickel nanoparticles, an infinite cluster was more tortuous compared to IC in composites containing microdispersed particles. These results show that the higher the dispersion is, the more tortuous is the infinite cluster in such composites.

6. Finally, the high value of the dielectric constant in the region below the percolation threshold allows nanocomposites to be used as new materials in electrical engineering. In addition, the relatively high value of thermo-emf in nanocomposites allows them to be used as converters of thermal energy into electrical energy.

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