Conductivity and Permittivity of Nickel-Nanoparticle-Containing Ceramic Materials in the Vicinity of Percolation Threshold

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Conductivity and static permittivity of ceramic materials containing nanoparticles of Ni were measured in the vicinity of percolation threshold. It is found that, below this threshold, the experimentally obtained dependences of conductivity and static permittivity on the fractional Ni content in these materials are different from those calculated in the frame of the percolation theory. The origin of this discrepancy is discussed in terms of the network hierarchy model proposed recently by Balberg *et al.* for composite materials.

I. Introduction

N recent years, interest in nanoparticle-containing materials L has grown explosively owing to their unique physical properties, which are substantially different from the properties of corresponding compact materials. Among these materials, there are various composites containing metal nanoparticles randomly distributed in a dielectric matrix. The application of the classical percolation theory for description of the electrical properties of these composites has problems. For example, below the percolation threshold, the behavior of the conductivity of composites containing the nickel grains embedded in the matrix of SiO₂ is inexplicable in the frame of this theory. This problem has been discussed by Balberg *et al.*¹ in detail. There, it has been shown that the conductivity behavior of the Ni–SiO₂ composites can be explained assuming that it is dictated not only by the nearest-neighbor tunneling as it is suggested by the classical percolation theory, but by the non-nearest-neighbor tunneling as well. In our previous paper,² we obtained that, for composites containing the nickel particles of sizes ≤ 30 nm embedded in a polymer matrix, below the percolation threshold, the measured conductivity differs from that calculated in the frame of the percolation theory. In this paper, we present results of the study of the behavior the conductivity and static permittivity of composites containing nickel nanoparticles embedded in a ceramic matrix.

II. Experimental Procedure

Two types of composites were used for the investigation. One was a ceramic material containing nanoscale nickel particles. The other was a ceramic material containing the high-dispersed nickel particles. The ceramic material with nickel nanoparticles was prepared by thermal decomposition of the nickel formiate mixed preliminary with a ceramic. The mixing was performed in an agate ball mill for 7 h. Thermal decomposition was performed under vacuum at a temperature of 400°C for 5 h.

Previously, we used the same method to create nickel particles of sizes ≤ 30 nm in a polymer matrix.² The ceramic material with high-dispersed nickel particles was prepared by mixing the nickel powder with a ceramic in an agate ball mill for 7 h. The nickel powder used was prepared by thermal decomposition of the nickel formiate under vacuum at a temperature of 400°C for 5 h. In both cases, the ceramic had the following identified components: SiO₂ 61.72 wt%, Fe₂O₃ 3.87 wt%, Al₂O₃ 12.52 wt%, CaO 13.48 wt%, MgO 0.94 wt%, Na₂O 1.78 wt%, K₂O 0.72 wt%, and MnO 0.07 wt%. The remaining 4.9% of composition of the ceramic had various inclusions that are unidentified because of their small quantity. The desirable values of the fractional Ni content V in the ceramic materials were obtained by the calculation of the source materials used.

To determine the sizes of the high-dispersed particles of the nickel powder, an electron microscope (BS242E, Tesla, Prague, Czech Republic) was used. It was found that the sizes of these particles fell in the range from 1 to 3 μ m. The sizes of the nickel nanoparticles were not determined as the method (X-ray diffraction at a glancing angle of incidence), which was used by us for other composite materials (e.g., for composites with nanoparticles in a polymer matrix²), was not applicable because of the fact that the densities of Si, Fe, Al, and other components of the ceramic and the density of nickel nanoparticles are closely spaced.

Electric measurements were performed on samples in the form of tablets 15 mm in diameter and 2 mm in thickness. The tablets were prepared by pressing the ceramic material powder under pressure of 200 MPa and by sintering under vacuum at a temperature of 1000° C.

The conductivity σ was determined by measuring the resistance of the samples. To do this, metal electrodes with a diameter of 13 mm were prepared by vacuum evaporation of aluminum on the flat surfaces of the samples under study. Two meters were used: an ohmmeter for the resistance measurements in the range of 10^{1} – $10^{13} \Omega$ (E6-13A-POB, P8603, St. Petersburg, Russia), and an ohmmeter for the resistance measurements in the range of 10^{9} – $10^{17} \Omega$ (B7-30-POB, B752, St. Petersburg, Russia). The values of conductivity obtained exhibited an error of 1%–7%.

The static permittivity ε was obtained from data on the frequency dependence of permittivity in the range from 20 to 200 Hz by means of extrapolation of this dependence to zero frequency. To determine the frequency dependence of permittivity, the measurements of the capacitance were performed on the samples under study in the specified frequency range. Values of permittivity were calculated using the formula

$$\varepsilon(\omega) = \frac{c(\omega)h}{\varepsilon_0 S} \tag{1}$$

where $\varepsilon(\omega)$ is the permittivity at a given frequency ω , *c* is the capacitance of sample, *h* is the thickness of sample, *S* is the area of the above-mentioned electrodes placed on the flat surfaces of the samples, and ε_0 is the permittivity constant. The capacitance of the samples was measured by means of a bridge of capacitors (E8-2, Moscow, Russia) using a sine-wave generator (G3-33-POB

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A1333, Moscow, Russia) and a balance indicator (F510, Mashpribor, Moscow, Russia). The values of the static permittivity obtained exhibited an error of 2%.

III. Results and Discussion

Figure 1 shows the experimental dependences of conductivity σ on the fractional Ni content V for both ceramic materials under study. In this figure, the dependences σ on V calculated in the frame of the percolation theory using the formulas cited below are also shown.

According to the percolation theory,³ the conductivity σ of systems containing metal particles randomly distributed in a dielectric matrix is described by the following formulas:

$$\sigma(V) = \sigma_{\rm m} (V - V_{\rm c})^{\prime} \quad \text{for } V > V_{\rm c} \tag{2}$$

and

$$\sigma(V) = \sigma_{\rm d} (V_{\rm c} - V)^{-q} \quad \text{for } V < V_{\rm c} \tag{3}$$

where σ_m is the conductivity of the metal particles, σ_d is the conductivity of the dielectric matrix, V_c is the critical fractional volume of the metal particles that initiated a first infinite metallic cluster; the parameters *t* and *q* are named as critical indexes. Using boundary conditions (V = 0 and V = 1), formulas 2 and 3 can be written in the following form:

$$\sigma(V) = \sigma_{\rm m} \left(\frac{V - V_{\rm c}}{1 - V_{\rm c}}\right)^t \quad \text{for } V > V_{\rm c} \tag{4}$$

and

$$\sigma(V) = \sigma_{\rm d} \left(\frac{V_{\rm c} - V}{V_{\rm c}} \right)^{-q} \quad \text{for } V < V_{\rm c} \tag{5}$$

For the ceramic materials under study, the critical fractional volume V_c of the Ni particles was derived by differentiation of lg σ with respect to V (see the inset in Fig. 1). To determine the critical index t, the experimental data were presented as an lg σ -lg[$(V-V_c)/(1-V_c)$] plot. The value of t is the degree of inclination of this plot. The values of σ_m and σ_d were obtained by extrapolation of this plot to V = 1 and V = 0, respectively. It was found that $V_c = 0.355$ and t = 2.21 for the ceramic material with the nanoscale nickel particles, and $V_c = 0.443$ and t = 1.81 for the ceramic material with the high-dispersed nickel particles. The critical index q was taken to be equal to 1.0, which is true for three-dimensional systems.³

As can be seen from Fig. 1, for both types of ceramic materials under study, the agreement between the theoretical and experimental dependences was observed when $V > V_c$. In the



Fig. 1. Comparison of the measured (points) and calculated (solid curves) dependences of the macroscopic conductivity (σ) on the fractional Ni content (V) for the ceramic material containing nanoscale Ni particles (full points, curve 1) and high-dispersed Ni particles (empty points, curve 2). In the inset, plots of the dependence of dlg σ/dV on V are shown (the solid line is for the material containing nanoparticles).

case of $V < V_c$, the agreement between the theoretical and experimental dependences was observed for the ceramic materials with the high-dispersed nickel particles only. For the ceramic materials with the nanoscale nickel particles, there was an additional contribution to σ in the range below V_c . These results can be understood in terms of the recently proposed model (Balberg *et al.*¹) of electrical conductivity in composites.

According to this model, all metal particles in composites, in which the metal particles randomly distributed in a dielectric matrix, are electrically connected, and the conductivity of these composites is dictated both by the nearest-neighbor tunneling and by the non-nearest-neighbor tunneling. The percolation-like behavior is observed when the contribution of the tunneling between non-nearest neighbors to the macroscopic conductivity is negligible. It takes place when the radius b of the particles is greatly superior to the tunneling range (or tunneling decay) parameter d. In the case where $b \approx d$, the tunneling between nonnearest neighbors makes a contribution to the macroscopic conductivity along with the nearest-neighbor tunneling, and the dependence of the macroscopic conductivity on the fractional content of metal particles is different from that dictated by the classical percolation theory. One can see that the above-described behavior of the conductivity of the ceramic materials under study is consistent with these model predictions. In Ba-lberg *et al.*,¹ the manifestation of these two types of behavior of the conductivity in composite materials was demonstrated by studying the Carbon Black-Polymer composites and Ni-SiO2 cermets. A peculiarity of our results is that these two types of conductivity behavior were observed in composites of the same composition, demonstrating the dependence of the manifestation of these conductivity behavior types on the size of the metal particles in these composites.

As is shown in Balberg *et al.*,¹ in composites for which a contribution to σ from the non-nearest neighbor tunneling takes place, there are two percolation thresholds. One of them is observed at high values of *V*, and it is the above-defined percolation threshold V_c . Another (the additional percolation threshold V_{cd}) was observed at low values of *V*, and it is a critical fractional volume of metal particles, which initiates a first infinite cluster of tunneling-connected conductors. Fitting the part (for $V < V_c$) of the experimental curve 1 (Fig. 1) for the ceramic material with the nickel nanoparticles to the functional dependence of Eq. (4) (denoting, in this equation, the percolation threshold as V_{cd} and the critical index as t'), we found that $V_{cd} = 0.145$ and t' = 3.2.

In Fig. 2, the experimental and theoretical dependences of the static permittivity ε on V for the ceramic materials under study are shown. The experimental dependences are obtained by extrapolation of low-frequency data (for the range between 20 and 200 Hz) to the zero frequency. The theoretical dependences are calculated with the following formula:

$$\varepsilon(V) = \varepsilon_{\rm d} \left(\frac{V_{\rm c} - V}{V_{\rm c}}\right)^{-q}, \quad V < V_{\rm c}, \tag{6}$$



Fig. 2. Comparison of the measured (points) and calculated (solid curves) dependences of the static permittivity (ε) on the fractional Ni content (*V*) for the ceramic material containing nanoscale Ni particles (full points, curve 1) and high-dispersed Ni particles (empty points, curve 2).

where ε_d is the permittivity of the ceramic; the index q is just the same as in Eq. (5). This formula, using the boundary condition V = 0, was derived from the expression for the static dielectric permittivity near the threshold, which has the form³

$$\varepsilon(V) = \frac{\varepsilon_{\rm d}}{|V - V_{\rm c}|^q}, \quad \omega = 0 \tag{7}$$

The calculations were performed with the same values of V_c , which were obtained from the experimental dependences σ on V, as described above.

As can be seen from Fig. 2, for the ceramic material with the high-dispersed particles, the experimental dependence of ε on *V* is well described by the formula Eq. (6). For the ceramic material with nanoparticles, the experimental dependence of ε on *V* does not agree with that calculated from this formula and shows an additional contribution to ε . It is remarkable that, for this ceramic material, the curve of *V*-dependence for ε is similar to that for σ .

Based on the qualitative interpretation of the sharp increase of ε near the percolation threshold³ and the physical view of "hierarchy" of electrically connected networks in composites," taking into account the fact that, for the corresponding composite materials under study, the curves of V-dependence for ε and σ are similar, the following interpretation of the ε behavior can be proposed. In the composite materials under study, as V increases, the nickel particles form metallic clusters, which are separated by dielectric material of the matrix. Each pair of the clusters represents a capacitor. In the case of the composite material with relatively large nickel particles (high-dispersed particles), the contribution of non-nearest-cluster-included capacitors to the macroscopic capacitance is negligible, and V-dependence of ε is percolation like. This form of dependence resulted from the fact that the capacitance of the capacitors increases with V(as a result of the decrease in the clusters' separation and an increase of their effective surface) and tends to infinity near the percolation threshold (as a result of formation in continuous metallic network). In the case of the composite material with relatively small nickel particles (nanoparticles), the presence of the characteristic feature of the V-dependence of ε at the additional percolation threshold $V_{\rm cd}$ considered above allows one to conclude that the non-nearest-cluster-included capacitors contribute to the macroscopic capacitance along with the nearestcluster-included capacitors. The change of run of curve of dependence of ε on V for this composite in the range of $V_{\rm cd}$ may be attributed to the process of formation of the continuous network of tunneling-connected conductors.

IV. Conclusion

By measuring the dependences of the conductivity σ and the static permittivity ε on the fractional Ni content (V), performing the measurements on two types of Ni-particle-containing ceramic materials with the same compositions, but with the different sizes of the Ni particles, the influence of the size of these particles on the form of these V-dependences is demonstrated. It is found that, for the ceramic material with the Ni nanoparticles, in the range below the classical percolation threshold, the dependences of σ and ε on V are different from that predicted by the classical percolation theory in the fact that the curve of this dependence for ε is similar to that for σ . It is concluded that, in the nickelnanoparticle-containing ceramic material under study, the percolation-tunneling process, which is considered (Balberg et al.) as the cause of the low percolation threshold V_{cd} and determines the behavior of σ in the range below the classical percolation threshold, also determines the behavior of ε in this range.

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