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TOPOLOGY OF INFINITE CLUSTER IN CERAMIC MATERIALS CONTAINING MICRO- AND NANOPARTICLES OF NICKEL

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Перколяция назарияси доирасида никелнинг микро- ва нанозаррачаларини ўз ичига олган керамик материалларда чексиз кластер топологияси ўрганилди. Бундай тизимларда никель заррачалари ҳажмига қараб, чексиз кластернинг скелетлари ва ўлик учлари ҳажмий улуши, зичлиги, эгрилиги аниқланди.

В рамках теории перколяции изучена бесконечная кластерная топология в керамических материалах, содержащих микро- и наночастицы никеля. Определены плотность, объемная доля, извилистость, объемная доля скелета и мертвого конца бесконечного кластера в зависимости от размера частиц никеля в таких системах.

An infinite cluster topology in ceramic materials containing micro- and nanoparticles of nickel has been studied within the percolation theory. The density, volume fraction, tortuosity, volume fraction of skeleton and dead ends of the infinite cluster have been defined depending on the size of nickel particles in such systems.

I. INTRODUCTION

According to the percolation theory [1], conductivity σ of the systems containing metallic particles randomly distributed in a dielectric matrix is described by the following formulas

$$\sigma(V_1) = \sigma(V_1 - V_c)^t, \qquad V_1 > V_c \tag{1}$$

$$\sigma(V_1) = \sigma_2(V_c - V_1)^{-q}, \qquad V_1 < V_c \tag{2}$$

where σ_1 is the conductivity of metallic particles, σ_2 is the dielectric matrix conductivity, V_1 is the volume fraction of metallic particles, V_c is the critical concentration (percolation threshold), when an infinite cluster is formed from the filler particles, t and q are the parameters called critical indexes having the values for the three-dimensional systems 1.6–1.8 and 1, respectively.

It is known [2] that the percolation theory methods make it possible to define a topology of the resistance grating (infinite cluster topology). One of the characteristics of the heterogeneous systems is the infinite cluster density $P(V_1)$. Its value characterizes a share of the infinite cluster nodes and is defined by the formula

$$P(V_1) = V_1' / V_1, \tag{3}$$

where V_1' is the volume fraction of the infinite cluster (IC). For $V_1 < V_c$ the value of $P(V_1)$ is equal to 0 because there is no infinite cluster. With the raise in V_1 the $P(V_1)$ value verges towards unity. The IC density near the percolation threshold is described by the power dependence [2]

$$P(V_1) = D(V_1 - V_c)^{\beta}, \tag{4}$$

where D is the numerical coefficient of about unity, β is the critical index equal to 0.4 for three-dimensional systems.

For the skeleton length to be defined, an IC model proposed for the first time by B.I. Shklovskii [2] is usually used. For the plane problem this model is something like a very large fishing net (Fig. 1). A characteristic linear size of this net R is called the radius of IC correlation and expressed by the formula $R = L / (V_1 - V_c)^{\nu}$ where L is the length equal in order of magnitude to the lattice period, ν is the critical index of the correlation radius (for the three-dimensional case ν=0.8–0.9).

On the basis of this model it was shown that if wire forming a skeleton is tortuous (Fig. 2, the distance between the points of their crossing is equal to R as before) the critical index t of electroconductivity will be more than 1.7 t being defined as a sum of the index ξ considering tortuosity and the index of the correlation radius ν, i.e.

$$t = \xi + \nu. \tag{5}$$

The wire length Z between two points of crossing (Fig. 2) is expressed by the formula $Z = L / (V_1 - V_c)^{\xi\,\xi}$ and the ratio of Z to R

$$Z / R = (V_1 - V_c)^{(\nu - \xi)} \tag{6}$$

shows how longer is the skeleton length as compared to R owing to tortuosity.

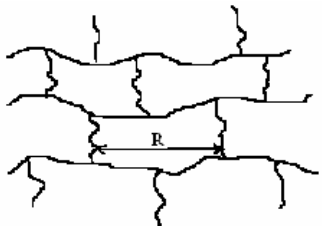


Fig. 1. Infinite cluster skeleton.

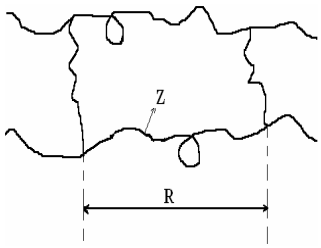


Fig. 2. Infinite cluster skeleton with taking into account tortuosity.

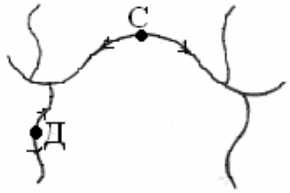


Fig. 3. Infinite cluster fragment with the dead ends.

An infinite cluster has a skeleton and the dead ends [2]. It is considered (Fig. 3) that a point belongs to the IC skeleton, if, at least, two ways outgoing from it to different sides allow going to infinite distance (point C). If only one way outgoing from a point goes to infinite distance then this point (for example, point D) belongs to the dead end. All the IC nodes belonging to both the skeleton and the dead ends make contributions to $P(V_1)$. The density of the IC skeleton, $P_{sk}(V_1)$, characterizes a share of the nodes belonging to the IC skeleton and is defined by the expression

$$P_{sk}(V_1) = V_1'' / V_1', \tag{7}$$

where V_1'' is the volume fraction of the IC skeleton. As shown by the results of the percolation theory, the ratio of $P_{sk}(V_1)$ to $P(V_1)$ can be defined by the following expression

$$P_{sk}(V_1) / P(V_1) = D(V_1 - V_c)^{(2\nu - \beta)}, \tag{8}$$

where D is the numerical coefficient of about unity.

Here, we consider a topology of the infinite cluster in ceramic materials containing micro- and nanoparticles of nickel within the percolation theory.

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 micro-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 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 [3]. The ceramic material with micro-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: 61.72 wt% SiO_2, 3.87 wt% Fe_2O_3, 12.52 wt% Al_2O_3, 13.48 wt% CaO, 0.94 wt% MgO, 1.78 wt% Na_2O, 0.72 wt% K_2O, and 0.07 wt% MnO. 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_1 in the ceramic materials were obtained by the calculation of the source materials used.

To determine the sizes of the micro-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 mm.

The size of the Ni nanoparticles was determined by X-ray diffraction at a glancing angle of incidence using an X-ray camera (KPM-1, Moscow, Russia). It was found that the size of these particles was in the range of 20–30 nm.

Electric measurements were performed on samples in the form of tablets of 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 the temperature of 1000°C.

The conductivity 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} Ω (E6-13A-POB, P8603, St. Petersburg, Russia), and an ohmmeter for the resistance measurements in the range of 10^9–10^{17} Ω (B7-30-POB, B752, St. Petersburg, Russia). The values of conductivity obtained exhibited an error of 1%–7% .

III. RESULTS AND DISCUSSION

The experimental dependencies of conductivity σ on Ni fraction content are presented in Fig. 4 for the both composite materials under study. The dependencies of σ on V_1 calculated within the percolation theory with the following formulas are also given in this figure. With the boundary conditions ($V_1 = 0$ and $V_1 = 1$) the formulas (1) and (2) can be reduced to the following form [4]:

$$\sigma(V_1) = \sigma_1 \left((V_1 - V_c)/(1 - V_c)\right)^t, \qquad V_1 > V_c \tag{9}$$

$$\sigma(V_1) = \sigma_2 \left((V_c - V_1)/V_c\right)^{-q} \qquad V_1 < V_c \tag{10}$$

For the composite materials under study the critical fraction volume V_c of nickel particles was defined by differentiation of lgσ over V_1 (see the inset in Fig. 4). To determine the critical index t the experimental data are presented as a graph in coordinates $\lg\sigma - \lg[(V_1 - V_c)/(1 - V_c)]$.

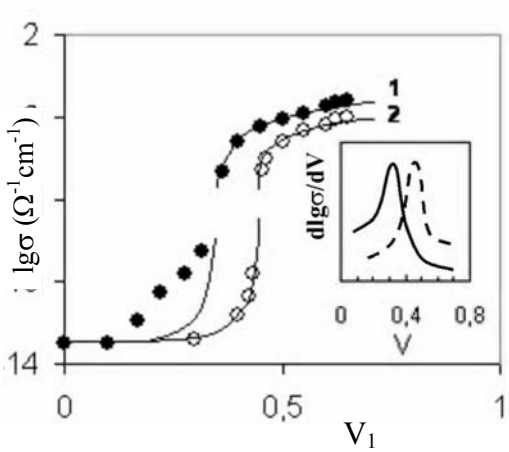


Fig. 4. Comparison of the measured (points) and calculated (solid curves) dependences of the macroscopic conductivity (σ) on the fractional Ni content (V_1) for the material with nanoscale Ni particles (full points, curve *1*) and high-dispersed Ni particles (empty points, curve *2*). In the inset, plots of the dependence of $d\lg\sigma/dV_1$ on V_1 are shown for the material with nanoparticles (solid line) and with micro-dispersed particles (dashed line).

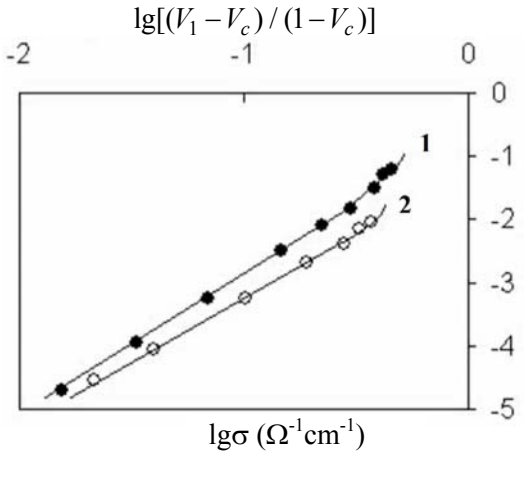


Fig. 5. The dependence of $\lg\sigma$ on $\lg[(V_1 - V_c)/(1 - V_c)]$ for composites containing nano (*1*) and micro (*2*) particles of nickel/

As seen from Fig. 5, for the samples containing nickel over the range $V_c < V_1 \le V_a \approx 0.6$ the dependence lgσ on $\lg[(V_1 - V_c)/(1 - V_c)]$ has a linear character. The value t is the slope angle of this graph. The value of σ_1 is defined by extrapolation of the linear part of this dependence to $V_1 = 1$. It was found that $V_c = 0.355$, $t = 2.21$ and $\sigma_1 = 2.4 \times 10^{-1}$ $Om^{-1}cm^{-1}$ for a composite material with the nano-dimensional particles of nickel and $V_c = 0.443$, $t = 1.81$ and $\sigma_1 = 4.8 \times 10^{-2}$ $Om^{-1} \cdot cm^{-1}$ for a composite material with the micro-dispersive particles of nickel. Defined in such a way, the value of σ_1 is not conductivity of metallic particles of nickel but is conductivity of IC over the range $V_c < V_1 \le V_a \approx 0.6$. The critical index was taken as equal to 1, which is valid for the three-dimensional systems [2].

As seen from Fig. 4, for the both types of composite materials under study a correspondence between the theoretical data and experimental ones is observed for $V_1 > V_c$. In the case of $V_1 < V_c$ a correspondence between the theoretical and

experimental dependencies is observed only for a composite material with the micro-dispersive nickel particles. The nature of this non-correspondence is discussed in [4] within the terms of a spatially structural model proposed by Balberg et all [5] for composite materials. In [6], it is also shown that for such systems the nature of the conductivity mechanism can be explained by tunneling of charge carriers between the nearest neighboring particles and the non-nearest ones.

For an IC topology to be defined, we use the above-given formulas obtained within the percolation theory. With the boundary conditions $V_1 = 1$ the expressions (4), (6) and (8) are transformed to the following form

$$P(V_1) = D\left((V_1 - V_c)/(1 - V_c)\right)^{\beta}, \tag{11}$$

$$Z / R = \left((V_1 - V_c)/(1 - V_c)\right)^{(\nu - \xi)}, \tag{12}$$

$$P_{sk}(V_1)/P(V_1) = D\left[(V_1 - V_c)/(1 - V_c)\right]^{(2\nu - \beta)}. \tag{13}$$

With the raise in V_1 the values of $P(V_1)$ calculated with the dependence (11) verge to unity (Tables 1 and 2). The increase in $P(V_1)$ with the distance far from the percolation thresholds in the direction of large V_1 means that IC gradually attaching clusters becomes more and more dense.

Table 1. The dependence of the parameters $P(V_1)$, V_1', Z/R, V_1'' and V_1''' on filler volume fraction V_1 for composites containing nano-dispersive particles of nickel.

№	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	0.100	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	0.340	1.8	4.4×10^{-2}	3.0×10^{-1}
8	0.60	0678	0.410	1.6	7.9×10^{-2}	3.3×10^{-1}

Table 2. The dependence of the parameters $P(V_1)$, V_1', Z/R, V_1'' and V_1''' on filler volume fraction V_1 for composites containing micro-dispersive particles of nickel.

№	V_1	$P(V_1)$	V_1'	Z/R	V_1''	V_1'''
1	0.45	0.173	0.078	1.62	4.5×10^{-5}	7.79×10^{-2}
2	0.455	0.215	0.098	1.52	1.4×10^{-4}	9.78×10^{-2}
3	0.465	0.274	0.127	1.42	5.2×10^{-4}	1.26×10^{-1}
4	0.50	0.400	0.200	1.28	4.1×10^{-3}	1.96×10^{-1}
5	0.55	0.516	0.284	1.20	1.7×10^{-2}	2.8×10^{-1}
6	0.60	0.602	0.361	1.15	4.2×10^{-2}	3.2×10^{-1}

As seen from Tables 1 and 2, near the percolation threshold the IC volume fraction V_1' calculated with (3) is negligibly small as compared with V_1. The values of Z/R calculated with the formula (12) near the percolation threshold shows that IC is very

tortuous, the value of ν being taken equal to 0.85 and that of ξ from the expression (5). The volume fraction of the IC skeleton V_1'' and the IC dead ends $V_1''' = V_1'' - V_1'$ was calculated with the expressions (7) and with $P_{sk}(V_1)$ from the formula (13). As seen from Tables 1 and 2, near the percolation threshold the volume fraction of the IC skeleton is negligibly small as compared to that of the dead ends.

IV. CONCLUSION

Thus, on the basis of the above statements one can conclude that near the percolation threshold a volume fraction of the IC skeleton is negligibly small as compared to its total volume and the main mass of IC is concentrated at the dead ends. For composites containing nickel nanoparticles near the percolation threshold an infinite cluster is more tortuous as compared with that in composites containing micro-dispersive particles. These results show that the higher dispersion, the more tortuous the infinite cluster in such composites.

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