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Theoretical description of pores in the simulation of composite materials

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The influence of porosity on the electric conductivity and the dielectric constants of composite materials was studied using computer simulation (the Monte Carlo method). A new approach to the simulation of porous systems that treats pores as a component equivalent to the solid phase components was proposed. Within the framework of this approach, an analysis of the influence of the micro- and macroporosity on the electric conductivity was carried out. It was established that the concept of a barrier-disordered system is also valid for pores. It was shown for the first time that pores can serve as one of the factors that forms the contact barrier distribution function. The proposed theoretical models were in good agreement with the experimental data.

Key words: Monte Carlo simulation, electric conductivity; dielectric constant, porosity; barrier-disordered systems.

Pores are the one of most important structure-forming components of solid-phase polycrystalline systems. However, a quantitative and universal model describing the influence of pores on different physico-chemical properties of materials has not been yet created. The goal of this work is to develop such a model on the basis of the statistic (lattice) approach.

The statistic approach allows one to describe systems with an unlimited number of components in an unlimited range of their concentrations and to consider simultaneously several characteristics of a material. The main drawback in the application of this approach to real objects is connected with the search for an adequate correlation between the lattice and physical parameters, and to date the model predictions have been, as a rule, of a qualitative character. For example, the classic lattice models explain well the existence of a percolation phase transition[1] or the phenomenon of dielectric anomaly[2] in metals and the mixtures of dielectrics. Through the improvement of the lattice models,[3] the mathematical model that describes quantitatively the properties of real materials has been found.

We used a model of the bonds at the three-dimensional dense packed lattice. In this case, the lattice bonds are physical space areas that may be occupied with one of the phases or they are hollows that correspond to pores. To simulate the homogeneous distribution, the occupation of the lattice with phases was

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carried out by a random and independent method. The probability of the occupation of a bond with a phase corresponds to its relative volume concentration. To simulate heterogeneous distributions, aggregation and disaggregation procedures, *i.e.*, the directed migration of phases along the lattice, have been involved.

Two characteristics of composite materials, the electric conductivity and dielectric constant, are considered in this work. They both can be calculated using the Laplace equation presented for the lattice

$$\mathrm{div}(\varepsilon \cdot \mathrm{grad}\phi) = \mathrm{div}D = 0$$

or

$$\mathrm{div}(\sigma \cdot \mathrm{grad}\phi) = \mathrm{div}j = 0.$$

where ε is the local dielectric constant, ϕ is the electric potential, s is the local conductivity, D is the electric field induction, and j is the current density. These equations can be solved by the standard method of equilibrating the electric potential.[4]

Pores as an element of volume

Pores have a zero conductivity and a low dielectric constant that results in a decrease in the values of these constants for a material as a whole. The degree of this influence depends not only on pore volume but also on their form and orientation. The dielectric constant (ε) of the TiO_2 ceramic samples[5] obtained by different methods can serve as an example. The usual annealing results in the formation of pores that are approximately spherical in form with sizes from 2 to 100 mm. In some series of samples the porosity was artificially controlled by the preliminary introduction of round paper layers into a pressed mixture.

Figure 1 shows the dependence of ε on the volume concentration of pores for different sample sets. Different slopes of the curves have an easy qualitative explanation. Thin and long pores directed along the field axes bring insignificant distortions to these axes and therefore have a weak effect on the effective dielectric constant of a material. At the same time, pores located across the field lines cause their complete reorganization. It is of interest to estimate quantitatively the correlation between the pore length and their thickness.

To simulate the extended objects by the restricted lattice, we used the method of artificial "stretching" of horizontal bonds of the lattice (we consider that the electric field is applied vertically). Without changing the total number of bonds, we assumed that horizontal bonds are longer than vertical bonds; hence, the former have a higher resistance and lower dielectric constant. A satisfactory description of the experimental data (see Fig. 1, curves *2* and *3*) can be obtained when the ratio of bond length to their thickness is equal to ~100. Such model estimations are in agreement with the real size of paper layers (5×400 mm)

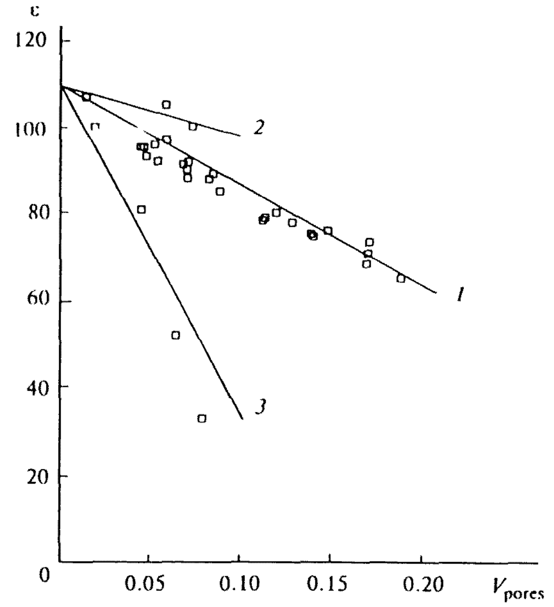

Fig. 1. Plot of dielectric constant ε *vs* concentration for the TiO_2 ceramic samples with different orientation of anisotropic pores: isotropic pores (*1*), plane disk-shaped pores directed along the electric field lines (*2*), the same pores directed across the lines (*3*); the points are the experimental values.

Another example demonstrates the behavior of solid-phase mixtures of metals and dielectrics. Taking into account the porosity, such systems can be treated as three-component. For the simulation, the existence of pores was taken into account by the assignment of the parameters of the air medium ($\sigma_{\mathrm{pores}} = 0$, $\varepsilon_{\mathrm{pores}} = 1$) to the corresponding bonds. In such systems, the dependence of the dielectric constant ε on the relative metal concentration is characterized by the so-called dielectric anomaly, *i.e.* a sharp increase in the effective dielectric constant as the percolation threshold is approached (in theory, at infinity percolation point). In this case, both the location of the threshold and the character of the $\varepsilon(X)$ concentration dependence reflect the structural peculiarities of a material, *i.e.*, its homogeneity, porosity, geometrical form, arrangement of conducting particles, *etc.* At 40 % porosity typical of the majority of natural materials, the volume fraction of a metal $X_c \approx 0.2$ corresponds to the percolation threshold.

This value agrees with the previously published experimental data[6] (Fig. 2) that were the first to follow the behavior of the dielectric constant of composites below the percolation threshold. The measurements were carried out for two sets of the Ag+KCl mechanical mixtures prepared by multiple grinding and pressing. New portions of Ag were consequently added to the previously prepared mixtures. It was noted by the authors[6] that the position of the percolation threshold obtained ($X_c \approx 0.2$) is overestimated as compared with the predictions on the basis of the bond models

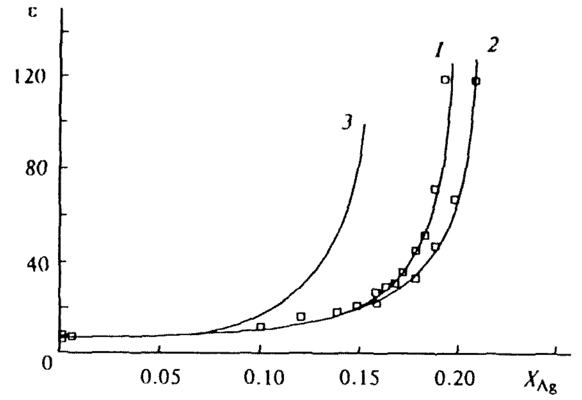

Fig. 2. Effect of heterogeneity of the components' distribution on the dependence of ε of an Ag+KCl mechanical mixture on the metal concentration at 35 % porosity: the initial statistically homogeneous distribution (*1*); the distribution obtained from *1* using the disaggregation procedure (*2*); the distribution obtained from *1* using the aggregation procedure; the points are the experimental values.[6]

(X_c ≈ 0.15 for cubic and X_c ≈ 0.1 for dense-packed lattice). The disagreement of the theoretical and experimental data results from the absence of models adequately considering the porosity of real systems.

The position of the percolation threshold and the form of the ε(X) concentration dependence are effected not only by the value of porosity but also by the degree of heterogeneity in phase distribution. The result of the application of the aggregation and disaggregation procedures to a system homogeneous in the initial state is also shown in Fig. 2. The difference between the experimental curves results equally from the different porosities of the two sample sets and from the existence of weak heterogeneities in the phase distribution that are due to the peculiarities of the preparation procedure. However, a good quantitative description of the experimental data within the framework of this theory is achieved at different combinations of porosity and heterogeneity. For example, curve *1* given in Fig. 2 was obtained on the assumption of 35 % porosity and a statistically homogeneous phase distribution. Curve *2* corresponds to a more disaggregated state of the conducting phase. If the porosity of the system is considered to be 40 %, curve *1* corresponds to the homogeneous distribution and curve *2* to the weakly aggregated one. As can be seen from Fig. 2, the application of the special aggregation and disaggregation procedures can change substantially the position of the percolation threshold. However, the advantage of our model is precisely that it can correctly predict the position of the percolation threshold at a given porosity of a real material and does not need the application of additional procedures.

Pores as an element of a barrier-disordered system

Since the porous structure of real polycrystalline materials is extremely complex and conductivity of crystallites themselves varies over a wide range, the experimental and theoretical analysis of such objects presents difficulties.

Quasi-isotropic polycrystalline carbon materials, whose skeleton is homogeneously shrunk upon thermal treatment,[7] appeared to be convenient objects for the experimental study of the separate influence of micro- and macroporosity on the electroconductivity. Their relative macropore volume, V_{mac}, remains virtually constant after thermal treatment at 1200—2800 °C whereas the micropore volume, V_{mic}, decreases with an increase in temperature. Figure 3 presents the plots of electro-

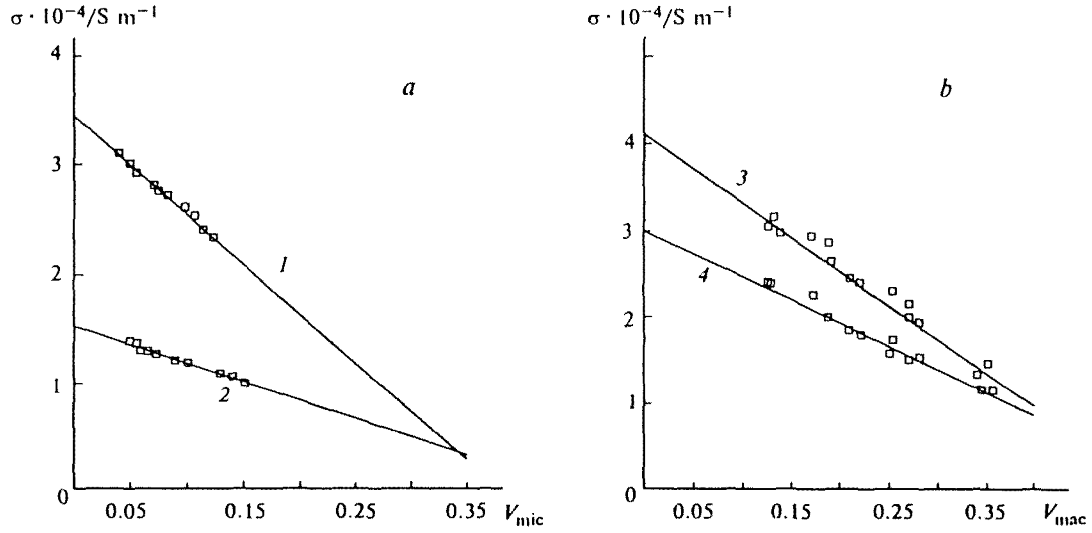

Fig. 3. Dependencies of the conductivity of the carbon materials on micro- (*a*) and macroporosity (*b*). The initial relative macroporosity was 0.125 (*1*) and 0.345 (*2*); the initial microporosity was 0.05 (*3*) and 0.12 (*4*); the points are the experimental values.[7]

conductivities of these materials *vs* their micro- (*a*) and macroporosity (*b*).*

An important feature of the experimental data presented in Fig. 3, *a* is that the slopes of the linear parts of plots *1* and *2*, corresponding to the different macroporosities, differ substantially. The effect of the increase in the microporosity of the sample on the decrease in the conductivity is much weaker under conditions of large macroporosity as compared with small microporosity, although one might expect the same effect for both cases. The straight lines on both plots might have similar slopes, as was particularly true in the case of lattice models in the approximation of zero conductivity of pores.

The concept of barrier-disordered systems[8] can serve as a more satisfactory theoretical ground for the simulation. On the basis of this concept, the conductivity of a dispersed system is determined by contact barriers that appear at the points of contacts of individual grains rather than by specific properties of materials. According to the model lattice approach[3] proposed by us, the conductivity of each element of the lattice depends not only on which substance (or phase) is assigned to this element but also on the phase that is in contact with this element.

To describe the experimental data,[7] we used the following model procedure. Macropores were simulated as clusters of lattice bonds emerging from the common joints. The distribution of the central joints of these complexes over the lattice was random and independent. Some bonds were considered to be micropores; first, they also were distributed over the lattice independently and randomly but then they were additionally dispersed to avoid the random fusion of several "micropores" into one "macropore". The number of micro- and macropores distributed over the lattice corresponded to the chosen porosity values. In this case, the relative volume percent of pores was calculated as a relative percent of bonds belonging to micro- and macropores, respectively.

Each lattice bond was assigned a value of conductivity that was found as follows. One random bond was chosen among the bonds adjacent (*i.e.*, having a common joint) to the bond under consideration. Let us assume that the *i* and *j* phases where *i* and *j* may be carbon (C), micro- (mic), or macropore (mac), correspond to these two joint bonds. Then the conductivity of the bond considered is established by the law adopted for contacts of *ij* type in accordance with their physical interpretation. The CC combination means contact between two carbon crystallites, and this is the case of the best conductivity for this system. The conductivity of the CC-contacts was chosen as a random value uniformly distributed within the interval from σ_{min} to σ_{max} in a logarithm scale. A high dispersion of this value results from the natural disorder of crystallites in a carbon material. The macmac, macmic, and micmic combinations mean that there is no conducting material and the conductivity is equal to zero. The Cmac and Cmic combinations mean that the carbon crystallite is located near a pore and the main function of a pore is that its presence causes a microscopic dislocation violating the contact between the adjacent carbon crystallites. In this case, the conductivity does not disappear but it is substantially weakened as compared with the "undisturbed" carbon mass. The degree of this weakening is one of the model parameters to be adjusted. The quantitative characteristics of the conductivity distributions, σ_{Cmac} and σ_{Cmic}, depending on the type of contact, are the following:

Type of contact	σ_{min}	σ_{max}
CC	$1 \cdot 10^{-6}$	$1 \cdot 10^{3}$
Cmic	$1 \cdot 10^{-6}$	$1.8 \cdot 10^{2}$
Cmac	$1 \cdot 10^{-6}$	$1 \cdot 10^{2}$
macmac, macmic, micmic	0	0

Using the set of constants obtained, we were able to reproduce with equal accuracy the dependence of the conductivity on both micro- and macroporosity (see Fig. 3, *a* and *b*, respectively).

We attempted to explain qualitatively the results obtained. As a rough approximation, the difference between micro- and macropores may be neglected and lines *1* and *2* in Fig. 3, *a* may be treated as parts of the same plot of conductivity *vs* total porosity. A break is observed when passing from part *1* to part *2*. Apparently, in the case when the total number of pores is not large (part *1*) and the conductivity of the system is high, the addition of low-conducting pores results in a noticeable decrease in the conductivity. But if the conductivity of the system itself is close to that of the pores (part *2*), the addition of new pores already has no effect on the conductivity. It is obvious that to explain the behavior of the curves observed one should assume that pores have a conductivity distinct from zero.

The presence of pores with a conductivity distinct from zero changes the total contact barrier distribution function.

Thus, when describing a composite material it is necessary to treat pores as a separate component of the system along with the solid phase components. The similarity between pores and the solid phase components is so perfect that such a characteristic as surface conductivity can be assigned to pores.

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References

1. S. Kirkpatrick, *Rev. Mat. Phys.*, 1973, **454**, 547.
2. V. E. Dubrov, M. E. Levinshtein, and M. S. Shur, *Zh. Eksp. Teor. Fiz.*, 1976, **70**, 2014 [*J. Exp. Theor. Phys.*, 1976 (Engl. Transl.)].

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* Earlier,[7] pores accessible to pictometric measurements have been considered to be macroscopic.

3. L. A. Abramova, S. P. Baranov, and A. A. Dulov, *Izv. Akad. Nauk, Ser. Khim.* 1993, 1868 [*Russ. Chem. Bull.*, 1993, **42**, 1782 (Engl. Transl.)]; L. A. Abramova, S. P. Baranov, and A. A. Dulov, *Izv. Akad. Nauk, Ser. Khim.* 1993, 1874 [*Russ. Chem. Bull.*, 1993, **42**, 1788 (Engl. Transl.)].
4. H. Gould and J. Tobochnik, *An Introduction to Computer Simulation Methods. Application to Physical Systems*, Addison-Wesley Publishing Company, 1988, Part 1.
5. K. Okazaki and H. Igarashi, *Ferroelectrics*, 1980, **27**, 263.
6. D. M. Grannan, J. C. Garland, and D. B. Tanner, *Phys. Rev. Lett.*, 1981, **46**, 375.
7. I. Ya. Levintovich, A. S. Kotosonov, and G. M. Butyrin, *Izv. Akad Nauk SSSR, Ser. Neorg. Mater.*, 1991, **27**, 2546 [*Bull. Acad. Sci. USSR, Inorg. Mater.*, 1991, **27** Engl. Transl.)]
8. B. I. Shklovskii and A. L. Efros, *Usp. Fiz. Nauk*, 1975, **117**, 401 [*Sov. Phys. Uspekhi*, 1975, **117** (Engl. Transl.)].

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