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TEMPERATURE RESISTANCE COEFFICIENT OF COMPOSITE RESISTIVE MATERIALS IN THE MIXED-STRUCTURE APPROXIMATION

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A method of calculating the temperature resistance coefficient and its temperature dependence for resistive materials in the approximation of a matrix–statistical structure is outlined.

Recently, the traditional empirical selection of optimal compositions of composite structures has been gradually replaced by a calculation based on the approximation of real heterogeneous systems by hypothetical structural models: The matrix model (with isolated inclusions of one phase in the other); the statistical model (with interpenetrating phases forming continuous three-dimensional "networks"); and the mixed model, which is a combination of the matrix and statistical models [1, 2].

Resistive cermet materials may be adequately represented by the two latter models, corresponding to the two conduction mechanisms discussed in the literature [3]: the contact mechanism (statistical structure) and the tunnel–barrier mechanism (mixed structure).

The most effective method of reducing the temperature resistance coefficient (TRC) of composite resistors is to use the thermocompensation effect [4], when the conducting subsystem consists (as a minimum) of two phases with opposite types of temperature dependence of the electrical conduction; semiconducting and metallic.

To realize the statistical method in practice, it is necessary to have monodisperse filler powders with identical particle materials. In constructing resistive materials with a matrix–statistical structure, no such difficulties are observed.

The aim of the present work is to calculate the TRC of resistive materials in the approximation of a matrix–statistical structure, which may be represented in the form of a heterogeneous system consisting of two subsystems: The conducting subsystem and the dielectric subsystem. The conducting subsystem is of matrix type and consists either of a semiconductor dispersed in a metallic matrix, or of a metal dispersed in a semiconducting matrix.

First, consider the calculation of the electrical conductivity of the conducting subsystem, in the form of a metallic matrix with inclusions of spherical semiconducting particles.

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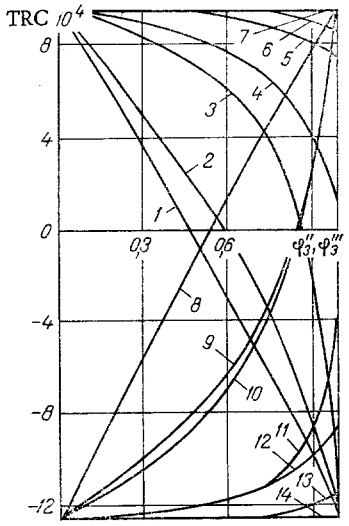

Fig. 1

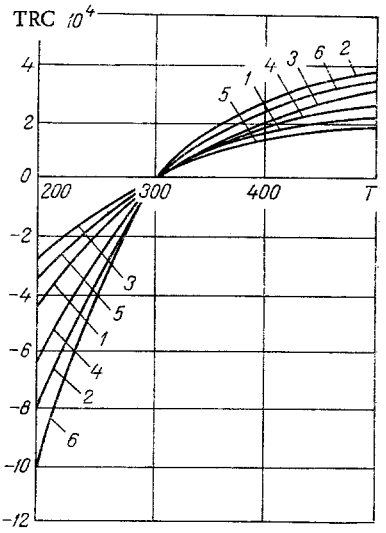

Fig. 2

Fig. 1. Dependence of TRC (deg^{-1}) on volume fraction of semiconductor ϕ_3'' and metallic ϕ_2''' inclusions for $\alpha = 10^{-3}$ deg^{-1}, E = 10^{-2} eV, ϕ_1 = 0.3, 0.4, 0.5. For ϕ_3'', AB = 1 (1), 10 (2), 10^{-1} (3), 10^2 (4), 10^{-2} (5), 10^3 (6), 10^{-3}, 10^{-4}, 10^{-5}, 10^4, 10^5 (7); for ϕ_3''', AB = 1 (8), 10^{-1} (9), 10 (10), 10^{-2} (11), 10^2 (12), 10^{-3} (13), 10^3, 10^4, 10^5, 10^{-4}, 10^{-5} (14).

Fig. 2. Dependence of TRC (deg^{-1}) on temperature (°K) in the region of optimal compositions for $\alpha = 10^{-3}$ deg^{-1}, E = 10^{-2} eV. For ϕ_3'', AB = 1, ϕ_3'' = 0.47 (1), 10, 0.59 (2); 10^{-1}, 0.87 (3); for ϕ_3'' = 0.55 (4); 10, 0.96 (5); 10^{-1}, 0.85 (6).

If no account is taken of the slight corrections introduced by some authors, all the formulas proposed for the calculation of the physical characteristics of matrix systems may be reduced to the following expression

$$\sigma_M = \sigma_2 \left(1 + \frac{\varphi_3'}{\frac{1-\varphi_3'}{3} + \frac{\sigma_2}{\sigma_3 - \sigma_2}}\right), \tag{1}$$

which, as shown in [1], is valid for the whole concentration range of inclusions and agrees with theoretical [5] and experimental [6] dependences of the critical concentration (threshold level) on the size ratio of the conducting and dielectric particles. Let $\sigma_2 = 1/\{B[1 + \alpha(T - 273)]\}$ and $\sigma_3 = A\exp(-E/kT)$. Then, calculating the electrical conductivity of the matrix conducting component σ_M its TRC may also be found

$$\alpha_M = -\frac{1}{\sigma_M}\frac{d\sigma_M}{dT}. \tag{2}$$

The derivative $d\sigma_M/dT$ in Eq. (2) is found by differentiating Eq. (1), which is preliminarily brought to the form

$$\sigma_M = \frac{\sigma_2\sigma_3(1 + 2\varphi_3') + 2\sigma_2^2(1 - \varphi_3')}{\sigma_3(1 - \varphi_3') + \sigma_2(2 + \varphi_3')}, \tag{3}$$

$$\frac{d\sigma_M}{dT} = \frac{[\sigma_2\sigma_3(1 + 2\varphi_3') + 2\sigma_2^2(1 - \varphi_3')]'\,[\sigma_3(1 - \varphi_3') + \sigma_2(2 + \varphi_3')]}{[\sigma_3(1 - \varphi_3') + \sigma_2(2 + \varphi_3')]^2} - \frac{[\sigma_2\sigma_3(1 + 2\varphi_3') + 2\sigma_2^2(1 - \varphi_3')]\,[\sigma_3(1 - \varphi_3') + \sigma_2(2 + \varphi_3')]'}{[\sigma_3(1 - \varphi_3') + \sigma_2(2 + \varphi_3')]^2}. \tag{4}$$

Taking account of the above values of σ_2 and σ_3, the final expression for $d\sigma_M/dT$ is written in the form

$$\frac{d\sigma_M}{dT} = \frac{\frac{d\sigma_2}{dT}\left[\sigma_3^2(1-\varphi_3')(1+2\varphi_3') + 4\sigma_2\sigma_3(1-\varphi_3')^2 + 2\sigma_2^2(1-\varphi_3')(2+\varphi_3')\right]}{\left[\sigma_3(1-\varphi_3') + \sigma_2(2+\varphi_3')\right]^2} + \frac{\frac{d\sigma_3}{dT}\sigma_2^2 9\varphi_3'}{\left[\sigma_3(1-\varphi_3') + \sigma_2(2+\varphi_3')\right]^2}, \quad (5)$$

where

$$\frac{d\sigma_2}{dT} = -\frac{\alpha}{B[1+\alpha(T-273)]^2}; \quad \frac{d\sigma_3}{dT} = \frac{EA\exp(-E/kT)}{kT^2}.$$

The electrical conductivity of the two-component statistical system calculated from the Bruggeman–Odelevskii generalized-conduction formula [1, 7] is in complete agreement with the dependence introduced on the basis of the theory of the conduction of an effective medium [8]

$$\frac{\sigma_1 - \sigma_c}{\sigma_1 + 2\sigma_c}\varphi_1 + \frac{\sigma_M - \sigma_c}{\sigma_M + 2\sigma_c}\varphi_M = 0, \quad (6)$$

where $\phi_M = 1 - \phi_1$.

For the case of a dielectric subsystem considered here, the composition–property function of the statistical model is of threshold type (with a threshold level equal to 2/3 for a cubic lattice), which is in good agreement with the numerous experimental data [9]. Taking into account that $\sigma_1 = 0$ and $\phi_1 \leq 2/3$, the solution of Eq. (6) is written in the form

$$\sigma_c = \frac{\sigma_M(2-3\varphi_1)}{2}. \quad (7)$$

The TRC of the mixed structure is determined by the TRC of the conducting substructure calculated from Eq. (5). This is confirmed by systematic transformation of an expression of the form

$$\sigma_c = -1/\sigma_c \cdot d\sigma_c/dT. \quad (8)$$

The electrical conductivity of the conducting subsystem, in the form of a semiconducting matrix with metallic inclusions, is calculated analogously.

Calculations are performed for typical parameters of fillers of precision resistive materials: $E = 10^{-2}$ eV, $\alpha = 10^{-3}$ deg^{-1}, $\phi_1 = 0.3$, 0.4, 0.5. The influence of the constants A and B on the TRC of the resistive material may be characterized by the product AB. It is a dimensionless parameter, which varies in the range 10^{-5}-10^5.

The dependence of the TRC on the volume fraction of semiconducting ϕ_3'' and metallic ϕ_3''' inclusions (Fig. 1) shows that a resistive material with "zero" TRC may only be obtained in a limited range of AB; 0.1-10. The dependences of the TRC on ϕ_3'' and ϕ_3''' obtained for AB < 0 and AB > 10 may be explained in that both when AB < 0.1 (the electrical conductivity of the metallic phase is higher than that of the semiconducting phase) and when AB > 10 (the opposite case), the resistance of the conducting subsystem may be written in the form of a series of parallel combination of two conductors. In both cases, however, it is determined by the resistance of the matrix.

It follows from the temperature dependence of the TRC in the region of optimal composition (Fig. 2) that with increase in temperature the TRC of the resistive material changes sign from negative to positive, reflecting the experimental U-shaped dependence of the resistance on the temperature [10].

NOTATION

σ_M, electrical conductivity of matrix system; σ_c, electrical conductivity of mixed system; σ_1, electrical conductivity of dielectric subsystem; σ_2, electrical conductivity of matrix phase; σ_3, electrical conductivity of inclusions; ϕ_1, volume fraction of dielectric subsystem; ϕ_M, volume fraction of conducting subsystem; ϕ_3', volume of fraction of inclusions with respect to matrix material; ϕ_3'', volume fraction of semiconducting inclusions with respect to matrix material; ϕ_3''', volume fraction of metallic inclusions with respect to matrix material; α, TRC of metal, α_M, TRC of matrix system; α_c, TRC of mixed system; B, resistivity of metal at 273°K; k, Boltzmann constant; A, electrical conductivity of semiconductor at infinitely large temperature; E, activation energy of electrical conductivity of semiconductor.

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MASS TRANSFER WITH "MEMORY" IN ELECTROCHEMICAL PROCESSES

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Diffusion processes in porous electrodes are investigated on the basis of mass-transfer equation with "memory." The equation is analyzed with the application of the Laplace transform.

The analysis of mass-transfer processes in porous electrodes is of major importance in the investigation of many electrochemical processes, in particular the operation of electrochemical current sources. A complicated interaction takes place between the electric and concentration fields in a porous electrode, where mass transfer is accompanied by electrochemical reactions. The large difference between the characteristic time constants of the diffusion and electrical processes means that they can be considered independently. The variation of the concentration field in the diffusion mode of operation of a porous electrode is described by an equation of the form [1]

$$\frac{\partial c}{\partial \tau} = D^* \Delta c - k_0 c. \tag{1}$$

This equation has been derived on the assumption that the expenditure or accumulation of active substance as a result of electrochemical reactions takes place uniformly. However, this assumption is an idealization, and in real electrodes the instantaneous mode of operation of the electrode is observed to depend on the nature of the process at previous times, i.e., on the history of the process.

Mass transfer of this nature can be modeled if the following expression is used to describe the transfer flux [2]:

$$q_m = -D^* \operatorname{grad} c - \int_0^\tau D^* D' (\tau - \theta) \operatorname{grad} c (\mathbf{r}, \theta)\, d\theta. \tag{2}$$

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