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STRUCTURAL EFFECT OF THE TEMPERATURE COEFFICIENT OF RESISTIVITY OF ELECTRICALLY CONDUCTING HETEROGENEOUS SYSTEMS

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The temperature dependence of the electrical resistivity of heterogeneous filled systems on the thermomechanical properties of their components and the filler particle dimensions and the contact spots between them is derived and confirmed experimentally.

Heterogeneous electrically conducting systems that are a dielectric matrix filled with conducting particles are applied extensively in practice, consequently, their development and the investigation of their properties has received a great deal of attention [1-4]. For instance, lacquer–carbon black thick-film resistors, polymer current-conducting glues, and composites are utilized extensively in electrons and the radio industry. One of the most important characteristics of such systems is the temperature coefficient of the resistivity α determined from the formula

$$\alpha = \frac{1}{R}\frac{dR}{dt}. \tag{1}$$

An attempt at a mathematical description of the dependence of α on the mechanical-temperature constants of the conducting filler and binder is made in [5, 6] in an example of ceramic resistive composites:

$$\alpha = \frac{1}{T(1+mT)} - \frac{2}{T}, \tag{2}$$

where m is the coefficient characterizing the linear thermal expansion of a spherical filler particle in an elastic matrix and is a function of μ, β, E of the matrix and the filler.

It is assumed in the derivation of (2) that the centers of the particles in the conducting chains remain fixed as the temperature increases while α is determined by the change in resistivity of the hypothetical contact film between the particles. However, verification shows that the dependence (2) is inaccurate and does not reflect fully the processes proceeding in the contacts as the temperature changes. Indeed, if it is assumed that equality of the coefficient m to zero is achieved by selecting the heterogeneous system components by means of their mechanical-temperature constants, then evidently α should equal zero. According to (2), for $m = 0$ $\alpha = -1/T$.

In contrast to [5, 6], we examined a heterogeneous system model whose conducting particles make direct contact. According to [7], the particle resistivity in this case will be due mainly to contraction of the current lines of force at the contact spots whose area is

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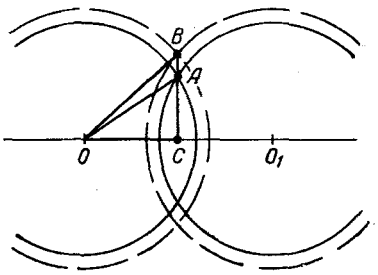

Fig. 1. Diagram of the mechanical and electrical contact of spherical particles.

quite small as compared with the particle section along the diameter, consequently, it is called the shrinkage resistivity R_s:

$$R_s = \rho/2c. \tag{3}$$

The resistance of a heterogeneous electrically conducting system (HES) will be comprised of series connected R_s in chains connected in parallel in this case.

Such an approach permits taking account of the contribution to the heterogeneous system α of the shrinkage resistivity and the α of the conducting filler independently of whether current flows over the particles in direct contact or also overcomes the dielectric gaps between them.

Let us examine the contact between two identical spherical particles with fixed centers O and O_1 (Fig. 1). For t_1 let the particle radius be b = OA, then the radius of the contact spot is c = AC; for $t_2 > t_1$ the radius of the expanding particle becomes greater, b_t = OB, correspondingly c_t = BC. We find from the right triangles OCA and OCB how the radius c_t of the contact spot varies as a function of the temperature and the quantities c and b:

$$BC = \sqrt{OB^2 - OC^2},$$

where $OB = b + bmt$; $OC = \sqrt{b^2 - c^2}$; $t = t_2 - t_1$, then

$$c_t = \sqrt{b^2 mt(2 + mt) + c^2}. \tag{4}$$

Substituting (3) into (1) and taking account of (4), we obtain as a result of differentiation

$$\alpha = \frac{2c_t}{\rho}\,\frac{d}{dt}\,\frac{\rho}{2c_t} = -\frac{b^2 m(1 + mt)}{b^2 mt(2 + mt) + c^2}. \tag{5}$$

If c^2/b^2m is denoted by n then (5) takes the simpler form

$$\alpha = -\frac{1 + mt}{t(2 + mt) + n}. \tag{6}$$

In contrast to (2), the relationship vanishes for m = 0. It is also seen that the HES α is negative for m > 0. If the particles making contact in the conducting chains should be compressed during HES heating, then α will be positive. In this case the thermomechanical properties of the HES components should specify a negative value of the coefficient m. In this case we obtain the equation for α by substituting $|m|$ into (6) instead of m:

$$\alpha = \frac{1 - |m|t}{t(|m|t - 2) + n}. \tag{7}$$

Formulas (6) and (7) are derived for HES with particles in direct contact and reflect the influence of just the HES structure on α. We called this influence the structural effect α (SE α). In addition its HES α can be determined by the intrinsic α_0 of the filler. The influence of α_0 can be taken into account by inserting it into (3): $\rho_t = \rho(1 + \alpha_0 t)$. Then

$$\alpha = \frac{2c_t}{\rho(1 + \alpha_0 t)}\,\frac{d}{dt}\left[\frac{\rho(1 + \alpha_0 t)}{2c_t}\right] = \frac{\alpha_0}{1 + \alpha_0 t} - \frac{1 + mt}{t(2 + mt) + n}. \tag{8}$$

Formula (8) is derived for HES whose structural effect α is negative. In the case of a positive structural effect α of the HES, formula (8) takes the following form

$$\alpha = \frac{\alpha_0}{1 + \alpha_0 t} + \frac{1 - |m| t}{t(|m| t - 2) + n}. \quad (9)$$

The α_0 in (8) and (9) can be represented exactly as the HES α in two components. The first should take account of details of the electronic structure and atomic configuration of the filler, and the second the structural effect α_0.

Technical carbon, utilized extensively as the filler in electrically conducting polymer composites (EPC), can be taken as an example. Its particles are HES in which the electrically conducting crystallites and the nonconducting matrix from amorphous carbon have different thermomechanical properties [8].

It should also be noted that a formula with negative SE α is most acceptable for EPC and technical carbon. This is explained by the fact that the thermomechanical properties of the matrix and filler in the mentioned cases most often specify expansion of the conducting filler particles during heating.

The significance of the deduced formulas for the HES α, including the EPC, is the following. Firstly, to achieve zero values of α (which is of most important practical value) two approaches can be utilized: let α_0 and m tend either to zero values or to equality of the components in (8) and (9) for identical signs for α_0 and m, as is achieved by selection of the components with definite magnitudes of μ, α_0, E, β, b and c. Secondly, it is seen that the greater the c (i.e., the greater the electrical conductivity of the heterogeneous systems), the smaller the dependence of the resistance on the temperature, other conditions being equal. This latter is confirmed practically in polymer resistors [1]. Thirdly, the greater the quantity b under other equal conditions the greater the HES SE α in absolute value. And finally, for corresponding relations of α_0 and m the HES α can be negative not only because the filler is a semiconductor but also because of the HES SE α. Let us note that the negative EPC α sometimes is taken as a proof of the presence of polymer layers between conducting particles [2]. Formula (8) shows that this opinion may be erroneous.

The disadvantage of (8) and (9) is that they, just as (2), are derived under the assumption of immobility of the spherical particle centers as the temperature changes. This results in the fact that the calculated quantities of α may differ somewhat from the measured values.

We conducted an experimental verification of (8) in the example of an EPC. The epoxy resin ÉD-20 solidified by polyethylene polyamines was used as binder, and electrically conducting fractionated schungite* powders ($2b = 55 \cdot 10^{-6}$ m) [9] for a volume fraction of τ, equal to 0.56, as the filler.

The thermomechanical and electrophysical characteristics of the EPC components were taken from [9-11]. The quantity c was evaluated by starting from the EPC ρ and the assumption that the shungite particles in the EPC form a simple cubic lattice ($\rho = 2R_S b$, $\tau = 0.52$). It would be possible to start from the assumption about the chaotic arrangement of the filler particles in the EPC ($\tau = 0.61$ [12]). However, the quantity c changes insignificantly here ($\rho = 1.73R_S b$). In passing we mention that $\rho = 1.64R_S b$ for the simplest filler particle stacking in the EPC. A computation using (8) and measurements in the 213-333 K range of temperatures afforded practically coincident values of the EPC α (from $-4 \cdot 10^{-3}$ K^{-1} to $-5 \cdot 10^{-3}$ K^{-1}). As the temperature increases further, the calculated and measured values of the EPC α start to differ abruptly. This is due to the change in the thermomechanical properties of the binder during heating, which we did not determine and did not take into account in (8).

It is known that to obtain high-resistance thick-film resistors several methods can be utilized. One is to diminish the layer thicknesses. However ρ and α grow here [1]. The answer to the question of why this occurs is not yet known. We analyzed the formation of contacts between filler particles as the lacquer–carbon black films hardened and we established that the radii of the contacting spots c between the particles of the upper film layers are less than the radii of the contacting spots between the lower layer particles. Hence, according to (3) the resistivity of the upper layers should be higher and the α according to (5) should be more negative as compared with the analogous quantities of the lower film layers. As the film thickness diminishes the fractional contribution of the ρ and α of the upper layers in them increases, consequently, the ρ of the films grows while the α becomes more negative.

*Shungite is a mountain alumosilicate rock containing carbon as filler in the form of globules of 20-50-nm dimension.

Let us mention one more example of taking account of the SE α in polymer thick-film resistors. To obtain high resistance resistors, the following method can also be utilized: Grind and introduce as filler in the binder a solidified resistive composite [1]. The resistance of the new resistive composite evidently grows, however, it is inconceivable why α here becomes more negative. This is explained by the fact that several SE α enter into the α of a high-resistance resistor according to (8): 1) the SE α of technical carbon; 2) the SE α of EPC as filler; 3) the SE α of a high-resistance resistor. As an illustration we present the experimental results of the quantities ρ and α of technical carbon: $5 \cdot 10^{-5}$ $\Omega \cdot m$ and $-5 \cdot 10^{-4}$ K^{-1}; shungite 0.05 $\Omega \cdot m$ and -10^{-3} K^{-1}; EPC filled with shungite: 10 $\Omega \cdot m$ and -4.5×10^{-3} K^{-1}. It is evident that α becomes more negative during the passage from technical carbon to shungite, and later to EPC because the contribution of the structural effects α of the listed substances increase successively in its value.

Therefore, the derived equation and the examples examined show that when studying the electrophysical properties of heterogeneous materials, particularly, electrically conducting polymer composites, and their application the structural effect of their temperature coefficients of resistivity should be taken into account and which can be governing for the magnitude and sign of the HES α in certain systems. The above refers fully to the fillers of electrically conducting heterogeneous systems also.

NOTATION

R, electrical resistivity, Ω; t, temperature, °C; T, absolute temperature, K; μ, Poisson ratio; β, coefficient of thermal linear expansion, K^{-1}; E, Young's modulus, N/m^2; ρ, specific electrical resistivity, $\Omega \cdot m$; c, radius of the contacting spots, m. Subscripts: s, shrink; t, values of corresponding quantities after a temperature change.

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