COMPENSATION FOR THE TEMPERATURE COEFFICIENT OF RESISTANCE OF HETEROGENEOUS RESISTIVE MATERIALS

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General expressions are obtained for the temperature coefficients of resistance of a two-component system on the basis of the theory of effective media. Conditions are analyzed for compensation for the coefficient of thick-film resistors by the addition of a semiconductor.

The materials of modern resistors, including both thin- and thick-film materials and bulk composite materials, are heterogeneous systems in which the two main phases are a dielectric phase (silicon dioxide, glasses, polymers) and a conducting phase (silicides of metals, ruthenates, noble metals, carbon). The concentration behavior of the resistance of such systems includes a region in which there is an abrupt, thresholdlike change in resistance attributable to a concentration-induced "phase transition" connected with current effects. Analysis of the temperature-concentration behavior of such systems is very important regarding the problem of significantly reducing the temperature coefficient of resistance (TCR) of resistors, i.e., in connection with the development of temperature-compensated resistive materials [1].

Here, we derive a general expression for the TCR of two-component mixtures in an effective medium approximation and we analyze the conditions for compensation of the TCR. As an example, we use a low-resistance ruthenium-containing cermet with additions of a semiconductor. This material is to be used in thick-film resistors.

The electrophysical parameters of heterogeneous materials will be examined within the framework of the theory of effective media [2-4]. In this theory it is assumed that the macroscopic particles of a given phase are "immersed" in a homogeneous effective medium. In this medium, the self-consistent values of the specific parameters coincide with their actual values for the composite as a whole. Such an approximation has been used successfully to describe the properties of heterogeneous composites [5-8].

In the effective medium approximation, the electrical resistivity ρ of a two-component mixture of materials with resistivities ρ_1 and ρ_2 has the form

$$\rho = \frac{1}{2x_c}(\rho_+ + R),\ R = (\rho_+^2 + 4x_c\bar{x}_c\rho_1\rho_2)^{1/2}, \tag{1}$$

where $\rho_\pm = \rho_1(x_c - x_2) \pm \rho_2(x_c - x_1)$; $x_1 + x_2 = 1$; $\bar{x}_c = 1 - x_c$. Equation (1) is essentially the Landauer–Bruggeman formula [2] or Odelevskii formula for statistical mixtures [3] and is a direct consequence of the effective medium approximation [4, 5].* For the case of clearly heterogeneous mixtures

$$\rho = \begin{cases} \rho_2 \dfrac{(x_c - x_1)^q}{x_c}, & x_1 < x_c, \\ \left(\dfrac{\bar{x}_c}{x_c}\right)^{1/2} (\rho_1\rho_2)^s, & x_1 = x_c, \\ \rho_1 \dfrac{\bar{x}_c}{(x_1 - x_c)^t}, & x_1 > x_c, \end{cases} \tag{2}$$

*Equation (1) is valid for the case of low frequencies: $f \ll f_{cr}$; at frequencies $f \gtrsim f_{cr}$, allowance should be made for the high-frequency threshold increase in conductivity due to the coupling of the active and capacitive components of the current [6]. For example, if $\rho_2 \gg \rho_1 \sim 1\ \Omega\cdot$cm and $\varepsilon_{r2} \sim 10$, then $f_{cr} = (2\pi\varepsilon_{r2}\varepsilon_0\rho_1)^{-1} \sim 2\cdot10^{11}$ Hz. If $\rho_2 \sim 10^{10}$-$10^{14}\ \Omega\cdot$cm $\gg \rho_1 \sim 10^5\ \Omega\cdot$cm (semiconductor), then $f_{cr} \sim 2$ MHz.

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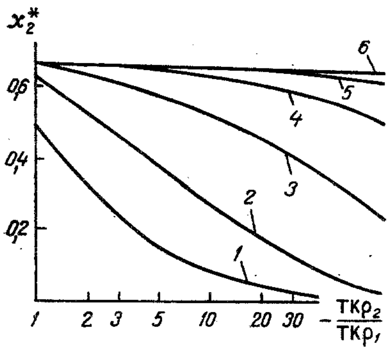


Fig. 1

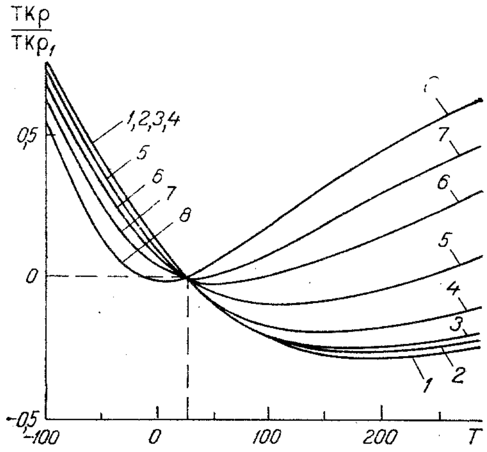


Fig. 2

Fig. 1. Dependence of the volume fraction of the compensating addition of semiconductor x_2* on the TKρ ratio of the semiconductor and cermet ($-TK\rho_2/TK\rho_1$) at the values $\nu = 1$ (1), 10^{-1} (2), 10^{-2} (3), 10^{-3} (4), 10^{-4} (5), and 10^{-5} (6).

Fig. 2. Temperature dependences of the ratio $TK\rho/TK\rho_1$ at values of A = 1000 ppM·K^{-1}, B = 1000 K and $\nu_0 = 10^{-4}$ (1), 10^{-3} (2), 10^{-2} (3), 0.1 (4), 0.2 (5), 0.4 (6), 0.6 (7), 1 (8).

$$q = t = 1, \; s = 1/2. \tag{2a}$$

These equations make clear the physical significance of the critical concentration (current threshold) x_c: with an increase in the concentration of the "metal" 1 inside the "dielectric" 2 to $x_1 = x_c$, the effective resistivity ρ decreases sharply to "zero" – to the value $\sim\rho_1 \ll \rho_2$, i.e., the system begins to conduct current through the metal. In short, a concentration-induced dielectric–metal phase transition takes place. With an increase in the concentration of the "dielectric" 2 inside the "metal" 1 at $x_1 = x_c$ ($x_2 = \bar{x}_c$), the effective resistivity ρ increases sharply to "infinity" – to the value $\sim\rho_2 \gg \rho_1$, i.e., a metal–dielectric phase transition takes place.

In a narrow concentration region near the threshold $|x_1 - x_c| \lesssim 0.1$, the critical indices q, t, and s may differ from the values (2a) found by the effective medium approximation (see [6, 7]). However, the values found in a broad concentration range are obviously quite suitable [8, 9].

The effective medium approximation has already been used to analyze the thermal behavior of the resistance of thick-film resistors [11].

With allowance for the temperature dependence of the resistivities of the components $\rho_1(T)$ and $\rho_2(T)$, we obtain the following from (1) for the temperature coefficient of resistance of the mixture $K = \mathrm{TK}\rho = \frac{1}{\rho}\frac{d\rho}{dT}$

$$K = \frac{1}{2}(K_1 + K_2) + \frac{1}{2}(K_1 - K_2)\frac{\rho_-}{R}, \tag{3}$$

where $K_{1,2} = TK\rho_{1,2}$.* For clearly heterogeneous mixtures ($\rho_2 \gg \rho_1$), we express TKρ as follows on the basis of (2)

*It is easily shown that the corrections for the bulk concentrations of the components due to the different coefficients of cubical expansion of materials 1 and 2 do not exceed ~10^{-3} in the temperature range $T - T_0 \sim 100$ K. However, these corrections may turn out to be substantial in certain special cases.

$$K = \begin{cases} K_2, & x_1 < x_c, \\ \frac{1}{2}(K_1 + K_2), & x_1 = x_c, \\ K_1, & x_1 > x_c. \end{cases} \tag{4}$$

Thus, it is evident from (4) and (2) that for clearly heterogeneous mixtures (for example, mixtures in which medium 1 is a "metal," with $K_1 > 0$, and medium 2 is a "dielectric," with $K_2 < 0$), the TCR can be compensated for through the concentration. This provides a natural explanation for the familiar U-shaped relation $\rho(T)$ (with a minimum) of materials used in thick-film resistors [10].

Equation (3) leads to the following compensation condition with $K = 0$:

$$\frac{\rho_-}{R} = \frac{K_1 + K_2}{K_2 - K_1}. \tag{5}$$

This condition is the equation for the optimum concentration of one of the components of a two-phase system in which the material is temperature-compensated at the given temperature. Its solution:

$$x_2^* = \frac{1}{2}\frac{(K_1^2 + K_2^2)\rho_1\rho_2 - 2K_1K_2(\rho_1^2 x_c + \rho_2^2\bar{x}_c) \pm |K_1 + K_2|\sqrt{D}}{(K_1^2 + K_2^2)\rho_1\rho_2 - K_1K_2(\rho_1^2 + \rho_2^2)}, \tag{6}$$

$$D = \rho_1\rho_2[(K_1 - K_2)^2\rho_1\rho_2 - 4K_1K_2(\rho_1 - \rho_2)^2 x_c\bar{x}_c]$$

(with a + sign for $K_1 > |K_2|$ and a − sign for $K_1 < |K_2|$).

It is evident from (6) that the optimum concentration is a function of the ratios $\nu = \rho_1/\rho_2$ and $\varkappa = -K_2/K_1$. Figure 1 shows the dependence of the optimum concentration x_2^* on $\varkappa$ with different values of ν (here, we took $x_c = 1/3$, $\bar{x}_c = 2/3$).*

For clearly heterogeneous low-resistance thick-film resistors, approximate relations (4) lead to the compensation condition $K_1 = 0$ (at $x_1 > x_c$), i.e., the conducting phase should have a zero TCR. This criterion is widely used to select conducting materials for low-resistance thick-film resistors, with special conditions being adopted for the temperature compensation of the conducting phase [11]. However, this approximate criterion is completely inadequate for obtaining a temperature-compensated material. In fact, at $K_1 = 0$, exact relation (6) leads to the natural result $x_2^* = 0$, i.e., if the conducting material is temperature-compensated, then it makes no sense to dilute it with the dielectric. On the other hand, the use of a temperature-compensated conducting phase (lead rhodate and barium rhodate) will lead to significant changes in the TCR of a resistive material with variation of the concentration and type of dielectric phase (lead-barium borosilicate glasses) [11]. These results are easily explained on the basis of the above-derived relations with allowance for the contribution of the dielectric phase to the resistivity of the mixture at $x_1 > x_c$. The corrections to Eq. (2) and (4) for clearly heterogeneous mixtures ($\rho_2 \gg \rho_1$) at $x_1 > x_c$ are of the order $\sim\rho_1/\rho_2$ and increase as the current threshold is approached from the right [$\rho_1/\rho_2 \ll (x_1 - x_c)^2/x_1x_2$]:

$$\rho \approx \rho_1 \frac{\bar{x}_c}{x_1 - x_c}\left[1 - \frac{\rho_1}{\rho_2}\frac{x_1x_2}{(x_1 - x_c)^2}\right]; \; K \approx K_1 - (K_1 - K_2)\frac{\rho_1}{\rho_2}\frac{x_1x_2}{(x_1 - x_c)^2},$$

while the optimum concentration ($TK\rho = 0$) is shifted even more – $\sim(\rho_1/\rho_2)^{1/2}$ [see (6)]:

$$x_2^* \simeq \bar{x}_c - \frac{|K_1 + K_2|}{\sqrt{-K_1K_2}}(x_c\bar{x}_c)^{1/2}\left(\frac{\rho_1}{\rho_2}\right)^{1/2} (K_1 \neq 0, \; K_2 < 0).$$

Thus the concentration and properties of the dielectric phase have a significant effect on the degree of temperature compensation of low-resistance resistive materials based on clearly heterogeneous mixtures.

*The current threshold x_c depends heavily on the granulometric composition of the powders, the manufacturing technology, and the structure of the material and may vary broadly [6, 7]. It is best to determine x_c empirically from the concentration relation $\rho(x_1)$ and to not consider it a "theoretical" parameter.

TABLE 1. Levels of Parameters of the Model

A, ppM	500, 1000, 1500
B, K	250, 500, 1000, 2000, 4000
ν_0	10^{-4}; 10^{-3}; 10^{-2}; 0,1; 0,2; 0,4; 0,6; 0,8; 1
T, °C	—100, —500, 0, 25. 50, 100, 150, 200, 250, 300
T_0, °C	25

For homogeneous (at the given temperature) mixtures $\rho_1 = \rho_2$ (but $TK\rho_1 \neq TK\rho_2$), we find from (3) that the temperature coefficient of resistance is additive

$$K = K_1 x_1 + K_2 x_2, \tag{7}$$

as actually occurs and, more generally, is reflected in Lichtenecker's formula [12]. Here, the optimum concentration (for temperature compensation at the same temperature) $x_2^* = K_1/(K_1 - K_2)$. This ratio is used to develop dielectrics which are temperature-compensated with respect to the TCR [13].

As an example of the specific use of the method of temperature compensation analyzed above, we will examine low-resistance ruthenium-containing metal-ceramic thick-film resistors characterized by a relatively large positive TCR = $+(500\text{-}1500)\cdot 10^{-6}$ K^{-1} [14]. A resistive material which was proposed in [15] is a metal-ceramic based on ruthenium dioxide. In order to reduce the TCR of this material, investigators added a semiconducting compound $(La_{0.35}Ca_{0.65})(Co_{0.3}Mn_{0.7})O_3$ with a relatively low negative TCR. We will examine this metal-ceramic material as a quasihomogeneous medium, with a resistivity ρ_1, which has been modified by the introduction of a semiconducting phase with the resistivity ρ_2.*

The problem then reduces to analysis of the TCR of a two-component heterogeneous system.† To analyze the temperature dependence of the TCR, it is necessary to concretize the temperature dependences of ρ_1 and ρ_2. For the cermet, we take

$$\rho_1 = \rho_{10}[1 + A(T - T_0)], \tag{8}$$

where ρ_{10} is the resistivity of the cermet at $T = T_0$ and A is a constant. Then $K_1 = A/[1 + A(T - T_0)]$ ($K_1|_{T=T_0} = A$). As usual, for the semiconductor we take

$$\rho_2 = \rho_{20}\exp[B(T^{-1} - T_0^{-1})], \tag{9}$$

where $B = \Delta E/2k$; E is the activation energy of conduction for the semiconductor; k is the Boltzmann constant; $\rho_{20} = \rho_2|_{T=T_0}$. Accordingly, $K_2 = -B/T^2$. The ratio of the resistivities

$$\nu = \frac{\rho_1}{\rho_2} = \nu_0[1 + A(T - T_0)]\exp[-B(T^{-1} - T_0^{-1})], \tag{10}$$

where $\nu_0 = \rho_{10}/\rho_{20}$. Thus, with allowance for (8)-(10), (3) gives a mathematical model of the TCR of a cermet with additions of a semiconductor. The parameters of the model are the volume fraction of the semiconductor x_2, the ratio of the conductivities ν_0 at $T = T_0$, the constants A and B determining the TCR of the cermet and semiconductor, and the temperature T. We analyzed the model on a computer at the levels of the parameters shown in Table 1. The TCR compensation was keyed to $T = T_0$.

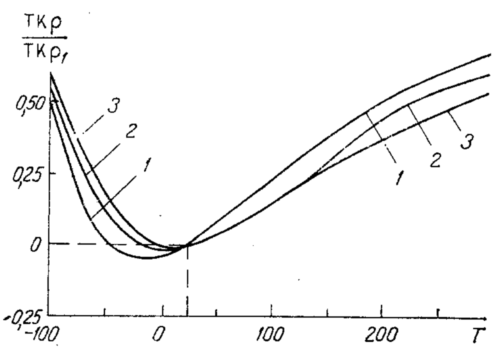
The values of x_2^* were calculated for each combination of levels (we took $x_c = 1/3$).

Figures 2, 3, and 4 show the temperature dependences for several combinations of parameter levels.

It follows from the data that the semiconductor additions can be used to markedly (by a factor greater than two) decrease the positive TCR of a cermet in the temperature range from −60 to 200°C.

*The characteristic dimensions of the discontinuities in the cermet were 100-1000 nm. The inclusions in the semiconductor had dimensions ≥10 μm.

†This system was regarded as a matrix system in [15]. The "matrix" properties are easily obtained from the relations in the present study if the concentration of one of the components is low.



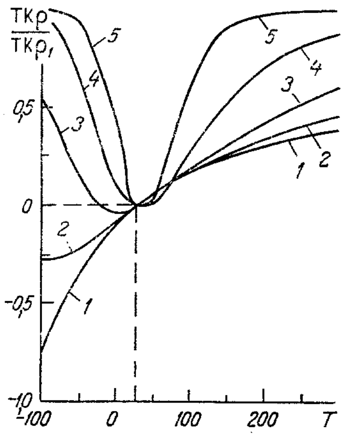


Fig. 3 Fig. 4

Fig. 3. Temperature dependences of the ratio $TK\rho/TK\rho_1$ at the values $\nu_0 = 1$, B = 1000 K and A = 500 (1), 1000 (2), and 1500 $ppM \cdot K^{-1}$ (3).

Fig. 4 Temperature dependences of the ratio $TK\rho/TK\rho_1$ at the values $\nu_0 = 1$; A = 1000 $ppM \cdot K^{-1}$ and B = 250 (1), 500 (2), 1000 (3), 2000 (4), and 4000 K (5).

It should be noted that we examined pointwise temperature compensation of a resistive material: $K(T_0) = 0$. In a number of cases, it is of interest to select compositions such that the TCR deviates as little as possible from zero in terms of its mean-square value (i.e., regardless of the sign) within a prescribed temperature interval (T_1, T_2). Then the criterion for selection of the concentration of the compensating addition has the form

$$\frac{1}{T_2 - T_1} \int_{T_1}^{T_2} K^2(T)\, dT \to \min_{x_2}, \tag{11}$$

where $K(T, x_2)$ is given by Eq. (3) (or an appropriate simplified formula).* Thus, for slightly heterogeneous mixtures for which Lichtenecker's formula (7) is valid, we find from condition (11) that $x_2^* = \langle K_1(K_1 - K_2)\rangle / \langle (K_1 - K_2)^2 \rangle$ [the symbol $\langle\rangle$ denotes averaging of temperature in the interval (T_1, T_2)]. It is evident that this optimum concentration of compensating addition differs quantitatively from the case of pointwise temperature compensation ($x_2^* = K_1(T_0)/[K_1(T_0) - K_2(T_0)]$).

Let us illustrate the difference between pointwise and interval compensation by using the example of Lichtenecker's formula (7). Let the high TCR of a cermet $K_1(T_0) = A = 1000 \cdot 10^{-6}\ K^{-1}$ require compensation by the addition of a semiconductor with B = 500 K. In the case of pointwise compensation at room temperature T_0, the optimum concentration of the compensating addition $x_2^* = 15.2\%$, and the TCR of the mixture deviates little from zero in the temperature range from ~30 K to room temperature (see Fig. 4, for example). In the working temperature range, the rms value of the TCR turns out to be $\langle K^2 \rangle^{1/2} \simeq 700 \cdot 10^{-6}\ K^{-1}$. In the case of interval compensation (11) throughout the working range $T_2 - T_1 = 200$ K, the concentration of the compensating addition $x_2^* = 14.3\%$, while the minimum rms value of the TCR throughout the interval

$$\langle K^2 \rangle^{1/2}_{\min} = \left[\frac{\langle K_1^2 \rangle \langle K_2^2 \rangle - \langle K_1 K_2 \rangle^2}{\langle (K_1 - K_2)^2 \rangle} \right]^{1/2} \simeq 250 \cdot 10^{-6} K^{-1}.$$

Finally, along with temperature compensation, it is often important for a resistive material that the resistivity be within a prescribed range of the nominal value. In this

*If the actual amount of reduction in the TCR is different in different parts of the temperature interval (T_1, T_2), then it is possible to introduce a weight function $p(T)$, $\frac{1}{T_2 - T_1} \int_{T_1}^{T_2} p(T)\, dT = 1$ into (11).

case, system (1) and (3) (with pointwise compensation) or (1) and (11) (with interval compensation) determines the choice of initial materials ($\rho_{1,2}(T)$) and their optimum ratio ($x_{1,2}^*$).

NOTATION

ρ, electrical resistivity of the material; T, temperature; K, K_1, K_2, temperature coefficients of resistance of the heterogeneous material and the components 1 and 2; $x_{1,2}$, volume concentrations of the components; x_c, $\bar{x}_c$, critical concentrations of the conducting and nonconducting phases; ν, ratio of the resistivities of the conducting and nonconducting phases; A, TCR of the cermet at room temperature T_0; B, activation constant of semiconductor conduction.

LITERATURE CITED

1. K. I. Martyushov, Ob. Elektron. Tekh. Ser. 5. Radiodetali i Radiokomponenty, No. 2 (1108), 3-68 (1985).
2. R. Landauer, J. Appl. Phys., 23, 779-785 (1952).
3. V I. Odelevskii, Zh. Tekh. Fiz., 21, No. 6, 678-685 (1951).
4. S. Kirkpatrick, Phys. Rev. Lett., 27, No. 25, 1721-1725 (1971).
5. B. F. Last and D. F. Thouless, Phys. Rev. Lett., 27, No 25, 1719-1721 (1971).
6. E. V. Kharitonov, Dielectric Materials with a Heterogeneous Structure [in Russian], Moscow (1983).
7. K. A. Boitsov, N. N. Kolosova, E. V. Kharitonov, et al., Élektron. Tekh. Ser. 5. Radiodetali i Radiokomponenty, No. 3 (40), 22-24 (1980).
8. F. Webman, J. Jortner, and M. Cohen, Phys. Rev. B, 13, No. 2, 713-725 (1976).
9. F. Webman, J. Jortner, and M. Cohen, Phys. Rev. B, 11, No. 8, 2885-2893 (1975).
10. D. P. H. Smith and J. C. Anderson, Philos. Mag., B, 43, No. 5, 811-828 (1981).
11. A. H. Boonstra, C. A. H. A. Mutsaers, and F. Kruijs, Am. Ceram. Soc. Bull., 59, No. 8, 842-843 (1980).
12. K. Lichtenecker, Phys. Z., 10, No. 25, 1005-1008 (1909).
13. B. M. Tareev, Physics of Dielectric Materials [in Russian], Moscow (1982).
14. N. D. Koldashov, V. G. Krasov, V. Z. Petrova, and R. F. Shutov, Elektron. Tekh. Ser. 3. Mikroelektronika, No. 5 (77), 97-105 (1978).
15. Resistive Material, Inventor's Certificate, No. 1,048,523 USSR: MKI³N 01 S 7/00.