

Původní práce

THE EFFECT OF FIRING TEMPERATURE ON THE PROPERTIES OF MODEL THICK-FILM RESISTORS

II. Critical Coefficients of the Percolation Theory

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Conceptions of the development of structure in thick-film resistors in the course of firing [1] can be verified by measuring the dependence of the critical coefficients of the percolation theory on firing temperature. The deviations of critical coefficients from the theoretical values are theoretically explained by the assumed formation of impurity states in the glass, as a result of diffusion of Ru during the firing. The estimated activation energy of the diffusion should amount to about 1.5 eV.

INTRODUCTION

Thick-film resistors are composite materials containing glass and a conductive pigment as the main components. Screen printing on insulating substrates (mostly Al_2O_3 — based ceramics) and firing in a tunnel kiln are the basic technological operations used in the manufacture of TFR. The present paper is the second of a series devoted to the effect of firing temperature on the basic properties of resistor films. Similarly to the previous paper [1], the experimental work was also carried out on model films prepared from pastes containing only glass and a conductive pigment in its inorganic component. The experimental results are not therefore affected by the presence of additional modifying oxides which are added to commercial pastes in order to adjust the temperature coefficient of resistance and to improve the long-term stability of parameters. The resistivity of the films can be controlled over a wide range through concentration of the conductive component in the paste. This is why the dependence of area resistivity R_{\square} on volume concentration v of the conductive component is of decisive significance.

Several theories describing the $R_{\square} - v$ relationship in heterogeneous systems of conductive and insulating particles, or of conductive particles in a matrix of an insulating medium, have been published in recent years [2—7]. Applicability of the individual theories is restricted by the limit concentrations of the conductive components and by the type of the structure (morphology) of the heterogeneous system. The present paper is concerned with the application of the percolation theory on the $R_{\square} - v$ dependence of thick-film resistor systems.

The following equation is provided by the percolation theory for the conductivity of the resistor lattice [8]:

$$G = A' (p - p_c)^{\nu}. \quad (1)$$

The range of validity of this relation amounts approximately to $p_c < p \leq p_c + 0.2$, where p is the probability that an arbitrary lattice site is occupied by a conductive particle (in the so-called site problem), or conductive connection of neighbouring sites (in the so-called bond problem). The critical probability (percolation limit), p_c , is defined so that within the limits of an infinitely large specimen it holds for $p \leq p_c$ that $G = 0$, and for $p > p_c$ that $G > 0$. The value of p_c depends on the type of the lattice and on the respective problem, i.e. if the site problem or the bond problem is considered [9]. The critical exponent, γ , depends solely on the number of dimensions of the specimen in the mathematical percolation theory. The applicability of the percolation theory on TFR specimens was experimentally verified in [10–12] on the assumption that probability p can be put equal to volume concentration of conductive component v . On designating the critical concentration v_c , which corresponds to the percolation limit (conduction threshold), the concentration dependence of area resistivity over the range $v_c < v \leq v_c + 0.2$ is given by the equation

$$R_{\square} = A (v - v_c)^{-\gamma}. \quad (2)$$

Experimental verification [10–12] provided a very satisfactory qualitative agreement with equation (2); however, the experimental values of the critical coefficients did not correspond to the theoretical values obtained by computer modelling. The critical concentrations in TFR specimens are mostly much smaller (0.02–0.10) than the theoretical ones (0.12–0.31) [9], and on the contrary, the critical exponents for TFR were much higher (2–7) than the theoretical value for 3D systems (1.6 ~ 1.7) [8, 13]. The extremely low values of v_c of specimens with a segregated structure agree well with the theory suggested in [15]. In the present part of the study, the authors will attempt to explain the disagreement between the experimental values of critical coefficients for thick-film resistors and the theoretical ones. However, the main purpose of this paper is to demonstrate the effect of firing temperature on the values of critical coefficients and their relationship with the structure of the films and the properties of initial materials.

SPECIMENS AND EXPERIMENTAL METHODS

The preparation and shape of specimens and the experimental methods were described in detail in [1]. The present paper is concerned with the study of model materials using the $\text{Bi}_2\text{Ru}_2\text{O}_7$ conductive component at BET specific area of $5 \text{ m}^2 \text{ g}^{-1}$. A paste based on RuO_2 with a BET specific area of $8.9 \text{ m}^2 \text{ g}^{-1}$ was used in one experiment only. These conductive components were combined with three types of glasses, whose composition and basic properties are listed in Table I. The ground frit of glass *A* was classified according to grain size in the same ways as in [1].

In the experiments described below, use was made of glass frit fractions with the following BET specific areas (ratio of mean sizes of conductive and glass grains respectively): 0.51 (0.052), 0.78 (0.080), 2.24 (0.230) $\text{m}^2 \text{ g}^{-1}$. The percolation coefficients were calculated from equation (2) adjusted to the form

$$\lg R_{\square} = \lg A - \gamma \lg (v - v_c). \quad (3)$$

The computer method was based on finding the critical concentration v_c at which the linear regression gave the minimum standard deviation.

Table I
Chemical composition and properties of glasses

Glass designation	Composition (wt. %)				t_g °C	t_d °C	ST °C
	PbO	SiO ₂	B ₂ O ₃	Al ₂ O ₃			
A	66	32.5	—	1.5	490	525	790
B	69	22	7.5	1.5	425	462	595
C	57	28	12	3	467	498	705

ST = sintering temperature, t_g — dilatometric transformation temperature, t_d — dilatometric softening temperature.

EXPERIMENTAL RESULTS

The values of percolation coefficients were measured on concentration series of specimens fired at peak temperatures between 450 and 900 °C. The condition $v_c < v \leq v_c + 0.2$ was maintained during the computer processing of the results.

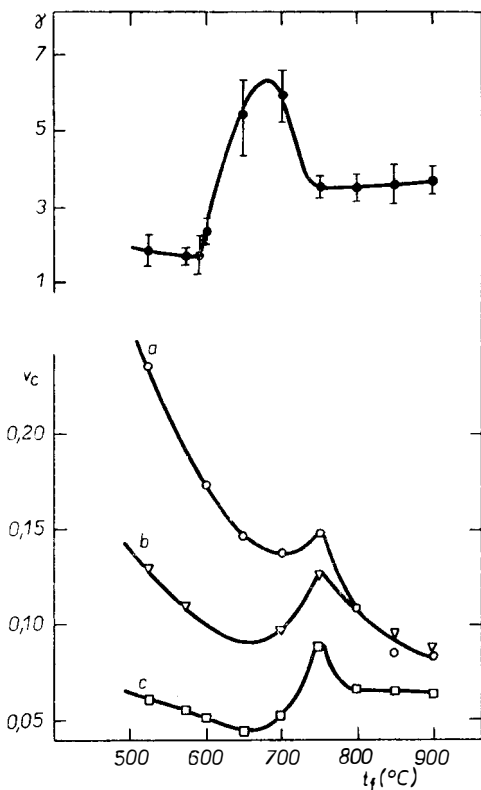


Fig. 1. Percolation coefficients v_c, γ in terms of the peak firing temperature of films based on $\text{Bi}_2\text{Ru}_2\text{O}_7$ and three grain size fractions of glass A with the respective surface areas ($\text{m}^2 \text{g}^{-1}$) of; a — 2.24, b — 0.78, c — 0.51.

Fig. 1 shows a plot of critical coefficients v_c and γ under peak firing temperature t_f of $\text{Bi}_2\text{Ru}_2\text{O}_7$ - based specimens with three different grain sizes of frit *A* in the initial paste. The glass granulometry appears to have the greatest effect on the critical concentration k_c in the region of the low firing temperatures. The effect

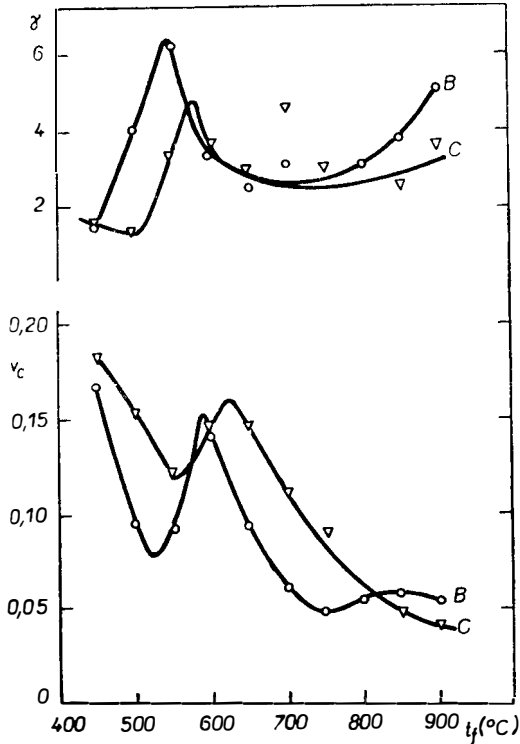


Fig. 2. Percolation coefficients vs. peak firing temperature of films based on $\text{Bi}_2\text{Ru}_2\text{O}_7$ and glasses *B* and *C*.

of granulometry diminishes gradually with increasing t_f . Within the framework of measuring errors, the critical exponent γ does not depend on the mean particle size of glass particles in the paste. Fig. 2 shows the plot of percolation critical coefficients vs. firing temperature for films with the $\text{Bi}_2\text{Ru}_2\text{O}_7$ conductive component and glasses *B* and *C*, whose frits were not classified according to particle size. The dispersion of experimental points around the regression curve 3 is apparent from the typical course shown in Fig. 3, exhibited by specimens made from $\text{Bi}_2\text{Ru}_2\text{O}_7$ and unclassified frits of glass *A*, fired at a peak temperature of 850 °C ($v_c = 0.0721$, $\gamma = 3.07$).

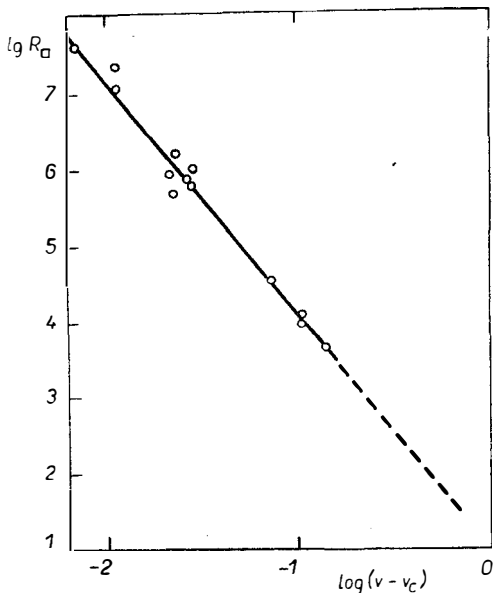


Fig. 3. An example of the dependence of planar resistivity on volume concentration of the conductive components, plotted according to equation (3) for films based on $\text{Bi}_2\text{Ru}_2\text{O}_7$, and unclassified frit of glass A ($v = 0.0721$, $\gamma = 3.07$).

THEORY AND ITS EXPERIMENTAL VERIFICATION

The quasihomogeneous structure, as defined in the previous paper [1], is characterized by a roughly uniform distribution of conductive particles throughout the glass matrix. Calculation of the theoretical value of critical concentration for the conductive component is based on the following assumptions:

(i) The shape of conductive particles can be approximated with the use of effective spheres with a constant diameter d , defined by equality of the volume of this effective sphere and the mean volume of the conductive particle.

(ii) The conductive particles are distributed at sites sc of the lattice jointly with fictive particles of glass having the same diameter d (lattice parameter d).

(iii) The space of the lattice between the spheres is filled with glass (Fig. 4).

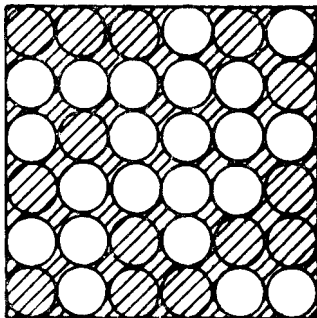


Fig. 4. Model for deriving the critical concentration in a quasihomogeneous structure of TFR

The critical concentration corresponding to the site problem in the *sc* lattice is $v_c(sc) = 0.307$ [8, 9]. The packing of empty lattice space with glass (transition to a structure with conductive spheres distributed throughout the glass matrix) can be calculated with the help of so-called packing fraction of spheres, which amounts to $f = 0.5236$ for the *sc* lattice. The following equation then holds for the critical concentration of the conductive component:

$$v_{c0} = v_c(sc) f. \quad (4)$$

On substituting into this equation, one finds $v_{c0} = 0.161$, which is the critical concentration of the conductive component in a structure characterized by direct contacts between the conductive grains. It appears [14, 9] that the product $v_c f$ is virtually constant (independent of the lattice type), and is dependent only on the number of dimensions. In 3D systems, it varies between 0.144 and 0.165 [9].

In studies [1, 16] the present authors suggested a model of electron transport in TFR based on assumed existence of impurity states in glass, consisting of Ru atoms that have diffused from the conductive grains into the glass in the course of firing. Transport of electrons between the localized impurity states proceeds by phonon assisted tunnelling, and the resistivity depends on the concentration of impurities N according to the equations [17, 18, 19]:

$$\rho \sim N^{-2/3} \exp(\eta\alpha N^{-1/3}), \quad (5)$$

where α^{-1} is Bohr's radius of the impurity centre and $\eta = 1.78$ [18]. From the symmetry it follows that the minimum concentration of localized states, N_{\min} , lies at half the distance between the surfaces of neighbouring conductive particles. If this minimum concentration falls below a critical value N_k , at which the probability of tunnelling is already negligible, the resistivity will increase to a value having the order of the resistivity of glass. The critical concentration of the impurity states N_k corresponds to the critical concentration of the conductive component, v_c .

The following relationship can be used for the concentration N of diffusing Ru atoms in the first approximation:

$$N = N_0 \exp\left(-\frac{x^2}{4D\tau}\right), \quad (6)$$

where x is the distance from the surface of the conductive particle, $D = D_0 \exp(E_{\text{diff}}/kT)$ is the coefficient of diffusion and τ is the time which is regarded as a constant in the case of firing in tunnel kilns. To simplify the problem, N_0 is considered to be constant.

The approximate equation (6) is applicable for very low concentrations of N only. On designating the distance between the surfaces of neighbouring conductive particles s , it is possible to write:

$$N_{\min} = N_0 \exp\left(-\frac{s^2}{16D\tau}\right). \quad (7)$$

At the critical concentration of the conductive pigment, $v = v_c$, $N_{\min} = N_k$ and to this corresponds the critical distance between the surfaces of neighbouring conductive particles, δ . This means that the critical concentration of impurities N_k occurs at the distance $\delta/2$ from the surface of the conductive particles.

The theoretical value of critical concentration in the given model will again be sought with the help of the percolation system of sites in the *sc* lattice, but using the effective diameter of conductive particles and that of the fictive glass particles equal to $d + \delta$. The number of conductive particles in a unit volume for the case $\sigma = 0$ will be designated n_{c0} and n_c for $\delta > 0$. The following equations then hold for the critical concentration in the individual cases:

$$v_{c0} = (\pi/6) d^3 n_{c0} \quad \text{for } \delta = 0, \quad (8)$$

$$v_{cc} = (\pi/6) (d + \delta)^3 n_c \quad \text{for } \delta > 0. \quad (9)$$

Comparison of the two equations yields the relationship

$$\frac{n_c}{n_{c0}} = \left(1 + \frac{\delta}{d}\right)^{-3}. \quad (10)$$

The critical concentration v_c at $\delta > 0$ (for diffusion of Ru into the glass) is given by the equation

$$v_c = \frac{\pi}{6} d^3 n_c \quad (11)$$

which jointly with (9) and $v_{c0} = 0.161$ gives the following equation after simple rearrangement:

$$\frac{\delta}{d} = (0.161 v_c^{-1})^{1/3} - 1. \quad (12)$$

In the given glass-conductive component system, N_k is considered to be constant, and thus it follows from equation (7) and from the expression for the temperature dependence of the coefficient of diffusion D that

$$\frac{\delta^2}{16 D_0 \tau} \exp \frac{E_{dif}}{k T_f} = \text{const.} \quad (13)$$

and hence

$$\ln \frac{\delta}{d} = \text{const.} - \frac{E_{dif}}{2k T_f} \quad (14)$$

where T_f is the firing temperature in Kelvins.

Using equations (14) and (12) it is possible to determine the activation energy of diffusion, E_{dif} .

The firing shrinkage of films was utilized for testing the model in the form of the *sc* lattice. This shrinkage, due to filling the empty spaces in the lattice during the first stages when a quasihomogeneous structure is formed, proceeds solely in the direction of thickness. The other two dimensions are fixed by adhesion to the substrate. From this it follows that the ratio of film thickness measured after firing ($t_f = 850^\circ\text{C}$) and after the lacquer components have burnt out ($t_f = 450^\circ\text{C}$) should be just equal to the packing factor $f(sc) = 52.4\%$ according to the given model. The fired film should of course be virtually free of pores, and this is actually the case [1]. The experimental values of shrinkage in the direction of thickness, established for various glass-conductive component systems, are on the average $50.3 \pm 2.9\%$, which is a very satisfactory agreement with theory.

Experimental verification of the theoretical value of critical concentration v_{c0} according to equation (4) encounters two major problems:

(i) The different grain sizes of the conductive component and the glass frit are responsible for deviations from the assumed quasihomogeneous structure of fired films in the direction towards the transient structure or a segregated structure [1].

(ii) In the last stage of formation of a quasihomogeneous structure in the course of firing it is necessary to consider beginning diffusion of Ru into the glass, which cannot be neglected [1]. For this reason it is possible to determine, on the curve of the $v_c(t_f)$ dependence, the point which would best correspond to the assumptions formulated in the derivation of equation (4).

The former problem can be resolved by extrapolating the experimental dependence of critical concentration on the ratio of mean sizes of conductive and glass grains $\langle a \rangle$ [4, 15, 20]:

$$v_c^{-1} = C_1 + C_2 \langle a \rangle^{-1} \quad (15)$$

where C_1 and C_2 are constants. The way of determining a from specific area measurements is described in [15]. The value of v_c is determined by extrapolation at $\langle a \rangle = 1$. The resolving of the other problem is much more difficult and there is probably no objective method for establishing $v_{c0}(\langle a \rangle)$ from the relationship $v_c(t_f)$. As the best estimate it is possible to consider the values corresponding to the peaks of the curves $v_c(t_f)$, lying at the boundary of the firing temperature range, over which the conductive particles become redistributed and wetted with glass, and the region where the diffusion has the prevailing effect on the electrical conductivity of the films [1]. The uncertainty of determining the correct value of v_{c0} is due to a certain overlapping of the two neighbouring regions of structural development. Experimental verification was carried out by means of the results of measuring the critical concentrations in films consisting of the $\text{Bi}_2\text{Ru}_2\text{O}_7$ system and classified fractions of glass *A* (Fig. 1). Extrapolation of the v_{c0} values towards $\langle a \rangle = 1$ is shown in Fig. 5 and provides $v_{c0} = 0.172$, which is a value quite well corresponding to the theoretical one when taking into account the approximations employed.

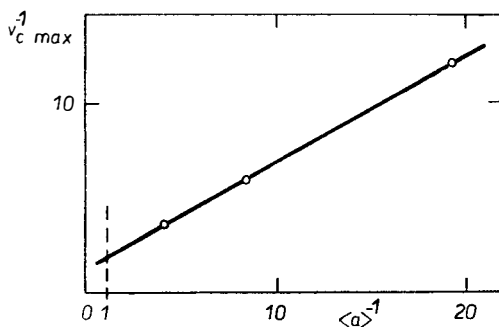


Fig. 5. Extrapolation of critical concentration $v_{c \max}$ towards the value $\langle a \rangle = 1$.

The dependence of critical diffusion lengths δ on the absolute firing temperature according to equation (14) for 3 types of films based on RuO_2 or $\text{Bi}_2\text{Ru}_2\text{O}_7$ and glasses *A*, *B* and *C* are plotted in Fig. 6. The corresponding values of the activation energy of diffusion are 1.55 eV (glass *A*), 1.58 eV (glass *B*) and 1.50 eV (glass *C*).

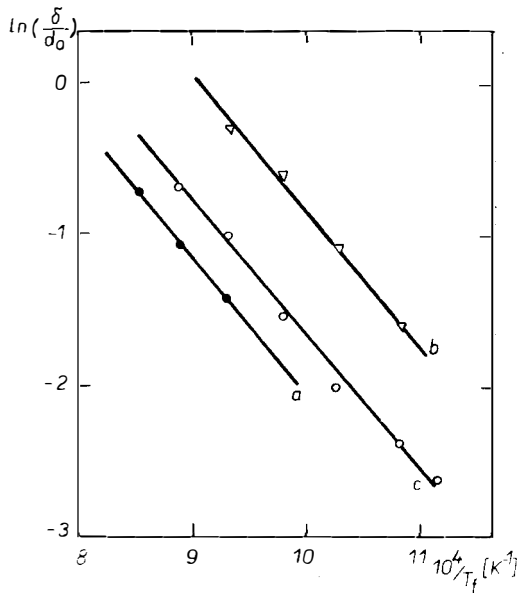


Fig. 6. Critical diffusion distance δ vs. firing temperature according to equation (14); a — RuO₂ + glass A, b — RuO₂ + glass B, c — Bi₂Ru₂O₇ + glass C.

DISCUSSION

The mechanisms involved in the structural development of TFR [1] obviously also determine the courses of the relationships of the critical coefficients at the peak firing temperature (Figs. 1 and 2). For this reason the curves $v_c(t_f)$ and $R_c(t_f)$ are similar. The differences in the positions of the extreme layouts are given by the dependence of the critical exponent on firing temperature and by the fact that the $R(t_f)$ curves were obtained at concentrations of the conductive component which were substantially higher than the critical one. The properties of the glass employed, characterized e.g. by the temperatures t_g , t_d and ST (cf. Table I) are projected into the dependence of the critical coefficients on the firing temperature, similarly to the course of $R_c(t_f)$ [1], particularly as regards the shifts of the curves towards the higher or lower firing temperatures. The development of structure (morphology) of the films, as described in the previous paper [1], gives a key to the explanation of the forms of the $v_c(t_f)$ and $\gamma(t_f)$ curves, and above all the difference between the experimental values of the critical coefficients measured on TFR, and the theoretical values provided by computer simulations [8, 9, 13].

In the range of the low firing temperatures, where the sintering of glass grains is the controlling mechanism of the film structural development, the size of the conductive and glassy particles in the paste has a significant influence. The ratio of mean diameters of these particles, $\langle a \rangle$, is the concrete parameter used in the relationships for critical concentrations. At $\langle a \rangle \ll 1$, a typical segregated structure with the conductive grains distributed at the boundaries of larger glass grains is formed in the firing temperature region considered [1, 15]. From the standpoint of the percolation theory this type of segregated structure is characterized by low

values of critical concentrations and also in that the critical exponent corresponds to the theoretical value for 3D structures (within the framework of measuring errors). The theory of critical concentration in segregated TFR structure was formulated in [15]. An increase in the peak firing temperature leads to the transient structure and eventually to the quasihomogeneous one [1]. An explanation of the low v_c values in TFR specimens with a quasihomogeneous structure was attempted in the paragraph above. If the paste employed contains larger glass particles (very small value of the $\langle a \rangle$ ratio), the relatively short time of firing is not sufficient for satisfactory homogenization of the system comprising the conductive component and glass, and the films fired at the usual temperature of 850 to 900 °C remain in the region of the transient structure. Evidence for this is provided by the micrographs shown in [1] and the courses of the $v_c(t_v)$ relationships at increasing firing temperature for specimens with various ratios of particle sizes in the paste (curves *a*, *b* in Fig. 1). The fact that the curve *c* (for the smallest value of $\langle a \rangle$) lies below the other two curves, over the entire interval of firing temperatures indicates (in agreement with the micrographs in [1]) that the transient structure survives to a temperature of up to 900 °C.

In the first approximation, the critical concentration of the conductive component in specimens with a transient structure can be calculated as follows: The total volume of film regions containing solely glass without any conductive pigment shall be designated V_1 (the residue of larger glass frit particles), the remaining volume with an approximately quasihomogeneous distribution of conductive particles in the glass is designated V_2 , and the volume of the conductive component proper will be V_3 . The mean concentration of the conductive component is therefore

$$v = V_3 / (V_1 + V_2) \quad (16)$$

and the effective concentration in the region of volume V_2 (providing the electrical conductivity of the film) is equal to

$$v_{\text{ef}} = V_3 / V_2 \quad (17)$$

The effective critical concentration v_{cef} corresponds to the theory outlined in the previous paragraph. For the critical (mean) concentration of the conductive component in the specimen with a transient structure, one obtains the following relationship from equations (16) and (17):

$$v_c = v_{\text{cef}} (1 + w)^{-1} \quad (18)$$

where $w = V_1 / V_2$. Fig. 1 and equation (18) indicate that in the specimen prepared from paste with a frit having a specific surface area of 0.51 m² g⁻¹ (curve *c*) by firing at 900 °C, the regions free of the conductive phase (having the volume V_1) take about 23 % of the film volume. In this estimate it was assumed that specimens prepared from paste containing frit with a surface area of 0.78 or 2.24 m² g⁻¹, fired at the same temperature, have a quasihomogeneous structure.

In conclusion, let us attempt to explain why the critical exponent values established experimentally in the quasihomogeneous structures of TFR deviate from theory, which specifies $\nu = 1.6 \div 1.7$ for the 3D systems. The mathematical percolation theory, leading to equation (1) or to equation (2) with respect to TFR, assumes a constant resistivity between the conductive grains (spheres) in the neighbouring lattice nodes, which is therefore independent of the concentration of the conductive component. In our model of electron transport in TFR, based on phonon-assisted

tunnelling between the localized impurity states in the glass, the resistance between two neighbouring conductive grains depends on their distance and thus on the concentration of the conductive component. The dependence of the distance between conductive grains is associated with the concentration of impurity centres N_{\min} introduced into the glass by diffusion at constant firing temperature and time. For this reason, in the case of TFR with a quasihomogeneous structure, it is necessary to consider coefficient A in equation (2) as being dependent on the concentration of the conductive component. The critical exponent is considered to correspond to theory and is taken as being equal to 1.7. Equation (2) can then be written in the form

$$R_{\square} = A(v) (v - v_c)^{-1.7}. \quad (19)$$

The resistivity of glass between neighbouring conductive particles is described by equation (5). In agreement with the results described in paragraph 4, it is possible to substitute N_{\min} from equation (7) into equation (5) for the concentration of impurity states, thus obtaining the following equation after rearrangement and in view of the assumed proportionality $A(v) \sim \varrho(N_{\min})$:

$$\ln A(v) = \text{const.} + (24\tau D_0)^{-1} (0.89\alpha N_0^{-1/3} - 1) \exp\left(\frac{E_{\text{dif}}}{kT_f}\right) s^2. \quad (20)$$

The following approximation was used in the above rearrangements with respect to the very small distances between the surfaces of the neighbouring conductive particles:

$$\exp\left[s^2(12\tau D_0)^{-1} \exp\left(\frac{E_{\text{dif}}}{kT_f}\right)\right] \approx 1 + s^2(12\tau D_0)^{-1} \exp\left(\frac{E_{\text{dif}}}{kT_f}\right). \quad (21)$$

In equation (20) the constant coefficient in the second term of the right side will be designated μ_0 , thus obtaining an expression suitable for experimental verification:

$$\ln A(v) = \text{const.} + \mu(T_f) s^2 \quad (22)$$

where

$$\mu(T_f) = \mu_0 \exp\left(\frac{E_{\text{dif}}}{kT_f}\right). \quad (23)$$

It now remains to find the relationship between the mean distance of the surfaces of neighbouring particles in the conductive cluster and the concentration of conductive particles in the film. The solution will be based on the homogeneous model with particles distributed at all the nodes of the *sc* lattice on assuming that the actual distance between the centres of these particles is proportional to the lattice parameter of the model. The following equation then holds for the distance between the surface of conductive particles:

$$s = \text{const.} \left[\left(\frac{\pi}{6v}\right)^{1/3} - 1 \right] d \quad (24)$$

where d is again the mean value of the diameter of the conductive grains.

Equation (22) was verified experimentally by measuring films of the $\text{Bi}_2\text{Ru}_2\text{O}_7$ system with glass *C*. The specimens were prepared by firing at peak temperatures over the interval of 650 to 850 °C. In Fig. 7 the coefficients $A(v)$ are plotted for the various firing temperatures in dependence on the squared ratio of distances to the mean diameter of the conductive grain. The natural logarithms of the

slopes of the lines in Fig. 7 are plotted in Fig. 8 in terms of reciprocal absolute firing temperature according to equation (23). The activation energy of diffusion of Ru into glass determined in this way, $E_{dif} = 1.53$ eV, is in satisfactory agreement with the value of 1.50 eV obtained by another method in the previous paragraph. The agreement is considered as evidence for the correctness of the given conceptions suggested for the mechanism of electrical conductivity in TFR with a quasihomogeneous structure, and of their respective effects on the values of critical concentration and of the critical coefficient.

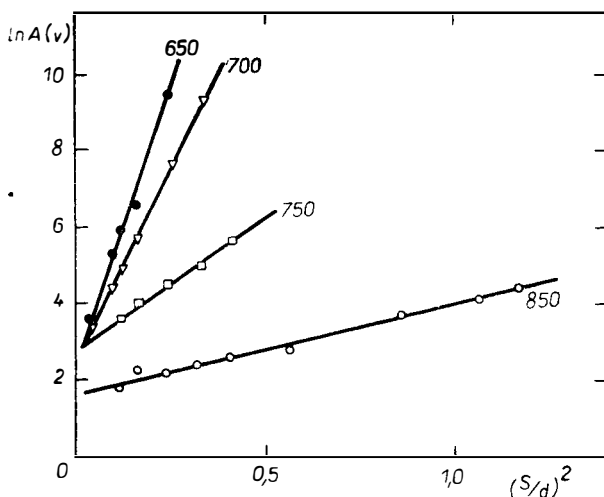


Fig. 7. Natural logarithm of coefficient $A(v)$ vs. the squared ratio of the mean distance between the surfaces of neighbouring conductive particles and their mean diameter, plotted according to equation (22) — $\text{Bi}_2\text{Ru}_2\text{O}_7$ + glass C.

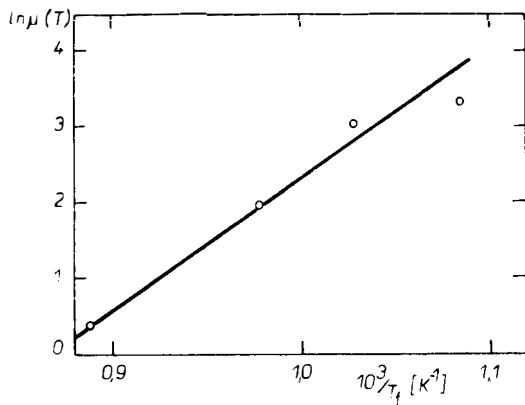


Fig. 8. Determination of the activation energy of diffusion according to equation (23) — the values were taken from Fig. 7.

CONCLUSION

The present study showed that the courses of the dependence of critical coefficients on firing temperature, as measured on TFR specimens, as well as the deviations of the values from the theoretical ones, can be explained by means of the mechanisms acting during the firing on the development of structure in the films, and by means of conceptions of the electrical conductivity of TFR with a quasi-homogeneous structure [1]. The suggested simple theory of critical concentration of the conductive component and the concentration dependence of coefficient $A(v)$ from equation (20) allowed the activation energy of diffusion of Ru in high-lead borosilicate glasses, used in TFR, to be estimated. The agreement of the E_{diff} values determined by the two methods is very satisfactory. There is the interesting finding that deviations in the composition of the glasses employed have virtually no effect on the value of

$$E_{\text{diff}} = 1.54 \pm 0.03 \text{ eV.}$$

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VLIV TEPLoty VÝPALU NA VLASTNOSTI MODELOVÝCH TLUSTOVRSTVÝCH REZISTORŮ; II. KRITICKÉ KOEFICIENTY TEORIE PERKOLACÍ

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Práce navazuje na článek [1], ve kterém byl navržen model vývoje struktury tlustovrstvých rezistorů (TFR), který je konzistentní s představou o mechanismu elektrické vodivosti ve vypálených vrstvách [16]. Tato práce je věnována vlivu teploty výpalu na hodnoty kritických koeficientů (v_c) teorie perkolace. Jak bylo dříve ukázáno [10—12], vztah (2) odvozený z teorie perkolace dobře popisuje průběhy koncentračních závislostí plošné rezistivity v oblasti koncentrací vodivé složky blízkých kritické. Změřené hodnoty kritických koeficientů

však nesouhlasí s hodnotami vyplývajícimi z matematické teorie. V článku je uvedena původní teorie kritické koncentrace vodivé složky v TFR s kvazihomogenní strukturou a vysvětlují se odchylky kritického exponentu od teorie. Vychází se z představy [1, 16] o přenosu elektronů mezi sousedními vodivými částicemi aktivovaným tunelováním mezi lokalizovanými příměsovémi stavy ve skle, tvořenými ionty ruthenia, které během výpalu vrstvy difundují z vodivých částic. Obě teorie umožňují nalézt aktivační energii difúze E_{dif} Ru do skle vyhodnocením experimentálních závislostí plošné rezistivity na koncentraci vodivé složky, získaných u série vzorků připravených při různých teplotách výpalu. Dobrý souhlas hodnot E_{dif} (1,53 eV a 1,50 eV) nalezených u systému $\text{Bi}_2\text{Ru}_2\text{O}_7$ + sklo C oběma metodami dokazuje správnost použitých představ.

Závislost kritických koeficientů na vrcholové teplotě výpalu je ukázána na několika příkladech (obr. 1 a 2), které současně dokumentují vliv parametrů použitého skle (tab. I), resp. typu vodivého pigmentu.

- Obr. 1. Perkolační koeficienty v_c , γ v závislosti na vrcholové teplotě výpalu vrstev na bázi $\text{Bi}_2\text{Ru}_2\text{O}_7$ a tří granulometrických frakcí skle A s BET měrným povrchem ($\text{m}^2 \text{g}^{-1}$); $a=2,24$, $b=0,78$, $c=0,51$.
- Obr. 2. Závislost perkolačních koeficientů na vrcholové teplotě výpalu vrstev na bázi $\text{Bi}_2\text{Ru}_2\text{O}_7$ a skel B, C.
- Obr. 3. Příklad závislosti plošné rezistivity na objemové koncentraci vodivé složky vynesené podle vztahu (3) pro vrstvy na bázi $\text{Bi}_2\text{Ru}_2\text{O}_7$ a netříděné frity skle A ($v_c = 0,0721$, $\gamma = 3,07$).
- Obr. 4. Model pro odvození kritické koncentrace v kvazihomogenní struktuře TFR.
- Obr. 5. Extrapolace kritické koncentrace $v_{c,\text{max}}$ k hodnotě $a = 1$.
- Obr. 6. Závislost kritické difúzní vzdálenosti na teplotě výpalu podle vztahu (14), $a - \text{RuO}_2$ + sklo A, $b - \text{RuO}_2$ + sklo B, $c - \text{Bi}_2\text{Ru}_2\text{O}_7$ + sklo C.
- Obr. 7. Závislost přirozeného logaritmu faktoru $A(v)$ na kvadrátu poměru střední vzdálenosti mezi povrchy sousedních vodivých částic a jejich středního průměru, vynesená podle rovnice (22) — $\text{Bi}_2\text{Ru}_2\text{O}_7$ + sklo C.
- Obr. 8. Stanovení aktivační energie difúze podle vztahu (23) — hodnoty z obr. 7.

ВЛИЯНИЕ ТЕМПЕРАТУРЫ ОБЖИГА НА СВОЙСТВА МОДЕЛЬНЫХ ТОЛСТОПЛОЧНЫХ РЕЗИСТИВНЫХ ЭЛЕМЕНТОВ; II. КРИТИЧЕСКИЕ ВЕЛИЧИНЫ ТЕОРИИ ПРОТЕКАНИЯ

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Предлагаемая работа является продолжением статьи [1], в которой была предложена модель развития структуры толстоплочных резисторов (TFR), которая является consistenteм с представлением о механизме электропроводности в обжигаемых слоях [16]. Данная работа посвящена влиянию температуры обжига на величины критических величин (v_c) теории протекания. Как уже было доказано [10—12], отношение [2], выведенное из теории протекания, хорошо описывает ход концентрационных зависимостей удельного поверхностного сопротивления в области концентраций проводящего компонента, близких критической величине. Однако измеренные величины критических величин не находятся в согласии с величинами, основывающимися на математической теории. В статье приводится исходная теория критической концентрации проводящего компонента (порога протекания) в TFR с квазигомогенной структурой и объясняются отклонения критического показателя от теории. Основой является представление [1, 16] о переносе электронов между соседними проводящими частями активированным туннелированием между локализованными примесными состояниями в стекле, образующимися ионами ruthenia, которые во время обжига слоя диффундируют из проводящих частиц. Обе теории представляют возможность устанавливать энергию активации диффузии E_{dif} Ru в стекло, оценивая экспериментальные зависимости удельного поверхностного сопротивления от концентрации проводящего компонента, полученные у серии образцов, приготовленных при разных температурах обжига. Хорошее согласие величин E_{dif} (1,53 эВ и 1,50 эВ), установ-

ленных у систем $\text{Bi}_2\text{Ru}_2\text{O}_7$ + стекло с помощью обоих методов является свидетельством правильно применяемых представлений.

Зависимость критических величин от пиковой температуры обжига показывается на нескольких примерах (рис. 1 и 2), которые одновременно показывают влияние параметров применяемого стекла (табл. 1) или типа проводящего пигмента.

Рис. 1. Коэффициенты теории протекания v_c , γ в зависимости от пиковой температуры обжига слоев, состоящих из $\text{Bi}_2\text{Ru}_2\text{O}_7$ и трех гранулометрических фракций стекла А с ВЕТ удельной поверхностью ($\text{м}^2\text{г}^{-1}$): а — 2,24, б — 0,78, с — 0,51.

Рис. 2. Зависимость коэффициентов протекания от пиковой температуры обжига слоев, состоящих из $\text{Bi}_2\text{Ru}_2\text{O}_7$ и стекла В, С.

Рис. 3. Пример зависимости удельного поверхностного сопротивления от объемной концентрации проводящего компонента согласно отношению (3) для слоев, состоящих из $\text{Bi}_2\text{Ru}_2\text{O}_7$ и несортированной фритты стекла А ($v_c = 0,0721$, $\gamma = 3,07$).

Рис. 4. Модель для выведения критической концентрации в квазигомогенной структуре TFR.

Рис. 5. Экстраполяция критической концентрации $v_{c \text{ макс}}$ к величине $\langle a \rangle = 1$.

Рис. 6. Зависимость критического диффузионного расстояния δ от температуры обжига согласно отношению (14); а — RuO_2 + стекло А, б — RuO_2 + стекло В, с — $\text{Bi}_2\text{Ru}_2\text{O}_7$ + стекло С.

Рис. 7. Зависимость натурального логарифма фактора $A(v)$ от квадрата отношения среднего расстояния между поверхностями соседних проводящих частиц и их среднего диаметра, вынесенная согласно уравнению (22) — $\text{Bi}_2\text{Ru}_2\text{O}_7$ + стекло С.

Рис. 8. Определение энергии активации диффузии согласно отношению (23) — величины из рис. 7.

SPECIÁLNÍ SKLA TVOŘÍ NOVOU GENERACI SKELNÝCH MATERIÁLŮ

obsahujících některé speciální příměsi a vykazující vlastnosti využitelné v perspektivních technických i jiných oborech. Skla jsou v mnoha případech vyráběna buď syntetickou cestou, nebo výrobními technologiemi používanými při výrobě keramiky, např. slinováním předtavených práškových nebo chemicky upravených skel, procesem sol-gel, chemickým napařováním apod. Speciální skla zahrnují křemenná, křemičitá, boritokřemičitá, fosforečná, germanicitá, chalkogenidová a iontová (halogenidová, nitridová, síranová, uhličitánová) skla a skelně krystalické hmoty. Tato skla jsou používána v telekomunikacích v podobě optických vláken vyrobených většinou z křemenných skel dopovaných oxidy Ge a P. Kromě veřejných telekomunikačních sítí se používají optická vlákna i pro spojení mezi počítači, pro vojenské účely (opticky řízené střely), v lékařství (endoskopy i složité diagnostické přístroje), pro výrobu optických gyroskopů, senzorů a řídicích a kontrolních zařízení. Další generace optických vláken se bude vyrábět z fluoridových a fosforečných skel s obsahem těžkých kovů. V elektronice jsou speciální skla využívána jako izolační a pasivační vrstvy, tlustovrstvá dielektrika, rezistory a termistory, zátavové feritové materiály, elektronické displeje apod. Některá z těchto skel vykazují spínací a paměťové vlastnosti. Skleněné kompozitní materiály se používají především v leteckém průmyslu (např. sklo S-2 firmy Owens-Corning) k výrobě některých konstrukčních prvků letadel, raketových motorů, tlakových nádob i některých druhů sportovního nářadí. Kompozitní materiál využívající křemenná vlákna se používá k výrobě destiček pro tepelný štít kosmických raket. Mezi další perspektivní kompozitní materiály patří — sklo/ Al_2O_3 , kovová matrix zpevněná křemennými vlákny a skla zpevněvaná různými vlákny. Další oblastí využití speciálních skel je lékařství. Bioskla se používají jako protetický materiál v různých lékařských oborech a ve stomatologii. Příkladem tohoto materiálu je Ceravital. Kompozitní materiály na bázi skla nahrazují zubní amalgamy, sklokeramické materiály se používají k přípravě zubních korunek. Mezi speciální skla patří také ochranná skla proti působení rtg paprsků a γ -záření, skla pro ukládání radioaktivních materiálů a skla pro speciální optické použití — laserová skla dopovaná Nd nebo germanicitá skla propouštějící IČ záření. Do roku 1995 se předpokládá další zvýšení objemu výroby optických vláken (ze 41,8 % celkové výroby speciálních skel v roce 1985 na 57,6 % v roce 1995) na úkor speciálních skel pro elektroniku.

(Glass Ind., 68, 1987, č. 2, s. 8—10)

Fryntová