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Studies of Structure of Ceramic Materials Containing Molibdenum Particles Within the Framework of Theory of Non-Homogeneous Systems

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Abstract

The structure of ceramic materials containing molibdenum powder is considered within the framework of leakage theory. Determined are the density of the endless cluster, volumetric parts of the skeleton and dead ends, as well as their dependence on the component concentration.

Volumetric part of the skeleton near the threshold of leakage makes a negligible part of the full volume.

1. Introduction

Nowadays, devices based on electric conducting ceramic materials [1, 2] are being extensively used in various branches of technology. However, further development of investigations and application of such materials are inhibited by the absence of a distinct understanding of their structure.

The present work is dedicated to the investigation of the electric properties of ceramic materials containing molybdenum and finding out their structures within the theory of non-homogeneous systems.

2. Experimental Details

For this investigations used were local ceramic materials of the following composition (in percents):

$S10_2 - 61,7;$	$MgO - 0,94;$
$Fe_2O_3 - 3,87;$	$Na_20 - 1,78;$
$Al_2O_3 - 12,52;$	$K_2O - 0,72$
$OaO - 13,48;$	$MnO - 0,07;$

Admixtures of 4,9 %; and an electricity conducting component - molibdenum particles of around 10 mkm. Investigations were conducted on samples of 15 mm diameter with a thickness of 2 mm obtained by sintering (baking) of the tablets in vacuum under $1000°C$ and pressure $P = 2T/cm^2$, with their composition preliminary mixed in a ball grinder for 7 hours.

Table 1.

N	V_1	$P(V_1)$	V_1'	V_1''	V_1'''
1	0,26	0,18	0,013	$1,5*10^{-3}$	$1,2*10^{-2}$
2	0,28	0,28	0,040	$8,0*10^{-3}$	$3,2*10^{-2}$
3	0,30	0,32	0,060	$14,7*10^{-3}$	$4,5*10^{-2}$
4	0,32	0,38	0,093	$28.4*10^{-3}$	$6,5*10^{-2}$
5	0,34	0,43	0,120	$41.6*10^{-3}$	$7,8*10^{-2}$
6	0,36	0,46	0,146	$55.8*10^{-3}$	$9,0*10^{-2}$
7	0,38	0,50	0,173	$71.4*10^{-3}$	$10,1*10^{-2}$
8	0,40	0,53	0,200	$89.4*10^{-3}$	$11,1*10^{-2}$

Results and Discussions

Electric conductivity (δ) measurements of the composites depending on the volume fraction of the filler V_1 are represented by points on Fig. 1. In the zone of $V_1 = 0,25 - 0,33$ there is a sharp growth of electric conductivity, δ, of the matrix to the value of electric conductivity of the filler δ_1. Critical concentration of V_c (leakage threshold) for when the first time endless cluster (EC) is formed from filler particles is determined by differentiation of $1g\delta$ composite along V_1 (Fig. 1a) when its value was $V_c' = 0,25$.

It is known [3] that electric conductivity of two-phase systems consisting of components with sharply distinctive σ is depicted by the formulas:

$$\delta(V_1) = \delta_2 \left(\frac{V_c - V_1}{V_1}\right)^{-q} \quad \text{under} \quad V_1 < V_c, \tag{1}$$

$$\delta(V_1) = \delta_1 \left(\frac{V_1 - V_c}{1 - V_c}\right)^{t} \quad \text{under} \quad V_1 > V_c, \tag{2}$$

$$\delta(V_1) = h^s \delta_1 \quad \text{under} \quad V_1 \approx V_c, \tag{3}$$

where δ_1 is the conductivity of the filler; δ_2 - the conductivity of the linking $h = \delta_2/\delta_1$ - indices of the $'t',' q'$ degree and $'s'$ in (1), (2) and (3); as in the theory of phase transitions, are called critical indices with values for three-dimension systems equal to 1,7: 0,98: 0,62. There is a correlation between critical indices;

$$q = t\left(\frac{1}{S} - 1\right), \tag{4}$$

which is analogous to the ratio for similarity and phase transition theory.

As is seen from the Fig. 1a, the threshold filler concentration of the material under our investigation is much higher than the theoretical value of $V_c = 0.15$ [4]. The same phenomena was observed during investigations of epoxypolyster PE 933 + with fine dispersed powder group VIII metals.

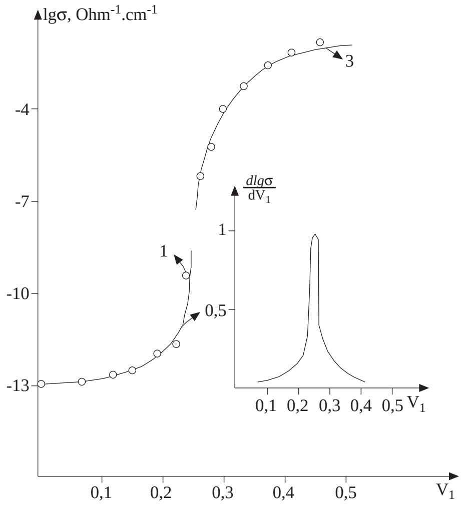

Figure 1. Dependence of the electric conductivity of composites based on ceramic volumetric share of V_1 of the filler (molydenum)
1. $\delta_{\exp}$;
2. δ_{est} equation No (1) under $q = 1,25$;
3. δ_{est} equation No (2) under $t = 2,1$ and $\delta = 0,1 (ohm^{-1} * cm^{-1})$.
a. dependence $dlg\delta/dV_1$ on the volumetric share of V_1 filler

Using basic ideas of the theory of the process of structuring of colloid particles in the solutions or polymers melts the authors [5] explained that incoincidence of the experimental value of V_c with the estimated one was due to formation of stable periodic colloid structures in the composition, since in case of overbearing of repelling forces over attracting forces the particles form stable periodic colloid structure. Then for the composites of equation (2) can be written as follows [5]: $\delta(V_1 - V_c')^t$, where $V_c' = V_c/a$ is the value of the threshold concentration, a- is a parameter which shows probability of belonging to the conducting class.

In order to determine parameters of equations (1) and (2) experimental results were built within the following coordinates:

$$1g\delta - 1g\left(\frac{V_c - V_s}{V_c}\right) \quad \text{and} \quad 1g\delta - 1g\left(\frac{V_1 - V_c}{1 - V_c}\right).$$

Out of inclinations tilt (slope, dependence) determined were the critical indices of $'q'$ and $'t'$ whose values for the composition were accordingly 1,25 and 2,1. These values are somewhat different from that cited above [3, 4]. However, as in [3, 4], our equation (4) was exercised with the exactness coinciding the exactness of calculations of the indices themselves.

Electric conductivity of the EC in the composition, whose value happened to be equal to $\delta_1 = 0,1 ohm^{-1} * cm^{-1}$, was determined by extrapolating the linear section of the dependence

$$1g\delta - 1g\left(\frac{V_1 - V_c}{1 - V_c}\right),$$

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and the electric conductivity value of pressed molindenum powder obtained at $2ton/cm^2.sq.$ pressure was $\delta = 0,06 ohm^{-1} * cm^{-1}$. The obtained result value of δ is much lower than the value of δ of pressed molybdenum powder. This can be explained by the contact resistance between the particles of the filler.

Thus, in the composite materials the value of δ depends basically on the properties of insulating films between contacting particles of the filler. In such systems one observes the so-called "contact leakage" which differs them from the model systems of the leakage theory under consideration, where contact resistance between contacting elements of the conducting particles is not taken into account (knot leakage).

In this case also, the value of $\delta(V_1)$ of two-component system near the threshold of leakage, as is indicated above, is determined by formulas (1), (2), (3). Closeness of the experimental values of the critical indices with estimated values shows that the ideas about the topology of the endless cluster [4] can be used in the case of contact leakage as well.

Methods of the theory of leakage enables to determine topology of the resistance net (topology of endless cluster). One of the properties of the non-homogeneous systems is the density of endless cluster $P(V_1)$. Near leakage threshold $P(V_1)$ has the following appearance [5]:

$$P(V_1) = D\left(\frac{V_1 - V_c}{1 - V_c}\right)^{\beta}, \qquad (5)$$

where D is a numerical factor of the unit order; and β is a critical index for three-dimension systems equal to 0,4.

Table 1 contains values of $P(V_1)$ calculated by formula (5) and volumetric share of EC calculated by formula [4]:

$$V_1' = \frac{V_1 - V_c}{1 - V_c},$$

where the value of $P(V_1)$ depending on value of V_1' increases with the increase of the distance from leakage threshold to the greater V_1 values. This means that the endless cluster gradually joining end clusters formed between molybdenum particles becomes much "denser". The value of V_1', as seen from the table, near the leakage threshold makes up a very minor part of V_1.

The value of Z/R calculated by formula [5],

$$\frac{Z}{R} = \left(\frac{V_1 - V_c}{1 - V_c}\right)^{(\xi - \nu)},$$

where $\xi = t - \nu$, $t = 2,1$ and $\nu = 0,9$, show that near the leakage threshold the endless cluster is very wavy. Knowing the length of the skeleton, δ_1, and resistance, r, of compositions we have calculated the value of volumetric share of the skeleton V_1'' in a single volume and share of the dead ends $V_1''' = V_1' - V_1''$ (see the Table).

Hence, study of the topology of EC in ceramic compositions shows that volumetric share of the skeleton near the leakage threshold belonging to the endless cluster makes 1-7 % of the shares of dead ends.

Dependence of the EC density, volumetric share of EC V_1', volumetric share of the skeleton EC and volumetric share of EC dead ends on the volumetric share of the conducting part V_1 of the composition based on ceremaics and molybdenum.

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