EFFECTIVE THERMAL CONDUCTIVITY AND ELECTRICAL CONDUCTIVITY OF ANISOTROPIC SOLIDS OF LOW POROSITY

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UDC 536.21+537.311

Equations are derived to determine the effective thermal and electrical conductivities of anisotropic media of low porosity. The influence of porosity on the thermal and electrical conductivities of anisotropic ternary alloys is established.

A number of materials produced by the pressing of powders comprising anisotropic particles is widely employed at the present time. Such materials include, in particular, ternary alloys of the $Bi_2Te_3 + Sb_2Te_3$ and $Bi_2Te_3 + Bi_2Se_3$ types [1] used in thermoelectricity for making the branches of thermocouples.

On molding these materials under a high pressure, thermocouple branches with porosities of up to about 5%, having very anisotropic electrical and thermal conductivities, are created [1-4].

Since the thermoelectric efficiency of the branches of a thermocouple is determined by the ratio of their electrical and thermal conductivities ($z = \alpha^2\sigma/\varkappa$), it is desirable to establish the influence of porosity on the coefficients $\varkappa$ and σ and hence the z values of these branches, which consist of particles anisotropic with respect to σ and $\varkappa$.

We assume that the thermal and electrical conductivity tensors $\varkappa_{ik}$ and σ_{ik} of the continuous material are already known. We shall simulate the pores by ellipsoids of the form

$$\frac{x_1^2}{a_1^2} + \frac{x_2^2}{a_2^2} + \frac{x_3^2}{a_3^2} = 1, \tag{1}$$

where x_1, x_2, x_3 is a rectangular Cartesian coordinate system, the x_1, x_2, x_3 axes being directed along the axes of the $\varkappa_{ik}$ and σ_{ik} tensors. Thus, the quantities a_1, a_2, a_3 will characterize the dimensions of the pore. We accordingly assume that the pores are formed in such a way that the semiaxes of the ellipsoid are parallel to the principal axes of the thermal and electrical conductivity tensors (Fig. 1).

The space occupied by a pore may be filled with a gas of some kind (used as an atmosphere for the pressing operation), and a certain flow of heat may pass through the pore. However, we shall consider that the thermal and electrical conductivities of the substances filling the pores are equal to zero.

Let us determine the corrections introduced by the presence of a single pore. For this purpose we must determine the distortions introduced by the pore into the temperature distribution existing in the case of a homogeneous solid. We shall execute the calculation for the thermal conductivity only, since the relationships for the electrical conductivity are of exactly the same form after simply replacing $\varkappa$ by σ.

The general expression describing heat transfer by conduction in an anisotropic medium in terms of the principal axes of the tensor $\varkappa_{ik}$ under steady-state conditions takes the form [5]

A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Leningrad. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 30, No. 4, pp. 686-692, April, 1976. Original article submitted June 11, 1975.

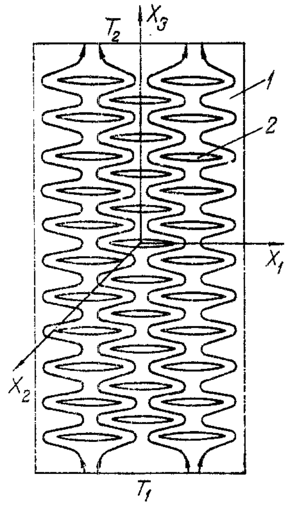

Fig. 1. Character of the current (stream) lines in the presence of lens-shaped pores in the sample: 1) Sample; 2) pore.

$$\varkappa_{11}\frac{\partial^2 T}{\partial x_1^2}+\varkappa_{22}\frac{\partial^2 T}{\partial x_2^2}+\varkappa_{33}\frac{\partial^2 T}{\partial x_3^2}=-\dot{q}. \quad (2)$$

Thus, in order to determine the temperature field in an anisotropic medium containing a pore we must solve Eq. (2) subject to the condition that the normal component of the heat flow to the surface of the pore is equal to zero. If we use the substitutions [5]

$$x_i=(\varkappa_{11}\varkappa_{22}\varkappa_{33})^{-\frac{1}{6}}\varkappa_{ii}^{\frac{1}{2}}X_i=\sqrt{\frac{\varkappa_{ii}}{\varkappa}}X_i, \quad (3)$$

where i takes the values 1, 2, 3, Eq. (2) transforms to

$$(\varkappa_{11}\varkappa_{22}\varkappa_{33})^{\frac{1}{3}}\left(\frac{\partial^2 T}{\partial X_1^2}+\frac{\partial^2 T}{\partial X_2^2}+\frac{\partial^2 T}{\partial X_3^2}\right)=-\dot{q}. \quad (4)$$

However, Eq. (4) is the equation of the temperature distribution created by a source $\dot{q}$ in an isotropic medium with a thermal conductivity

$$\varkappa=(\varkappa_{11}\varkappa_{22}\varkappa_{33})^{\frac{1}{3}}. \quad (5)$$

Using the substitutions (3), Eq. (1) transforms to the form

$$\frac{X_1^2}{b_1^2}+\frac{X_2^2}{b_2^2}+\frac{X_3^2}{b_3^2}=1, \quad (6)$$

where

$$b_1=\frac{a_1^2}{\varkappa_{11}}\varkappa;\quad b_2=\frac{a_2^2}{\varkappa_{22}}\varkappa;\quad b_3=\frac{a_3^2}{\varkappa_{33}}\varkappa. \quad (7)$$

The problem of determining the temperature field (or potential field in the case of electrical conductivity) in an anisotropic medium thus reduces to that of determining the temperature field in a homogeneous, isotropic medium.

Let us determine the effective thermal conductivity. Let us suppose that in the absence of a pore there is constant temperature gradient, for example, in the x_1 direction:

$$\operatorname{grad} T=\frac{\partial T}{\partial x_1}=k_1. \quad (8)$$

The temperature field will then be given by the relationship

$$T_0 = k_1 x_1. \tag{9}$$

In the presence of a pore the temperature field given by Eq. (9) will be distorted. Since in the present case there are no heat sources anywhere except on the boundaries of the sample, we have $\dot{q} = 0$, and in order to determine the temperature field we must solve the equation

$$\frac{\partial^2 T}{\partial X_1^2} + \frac{\partial^2 T}{\partial X_2^2} + \frac{\partial^2 T}{\partial X_3^2} = 0 \tag{10}$$

subject to the condition

$$T \to T_0 \quad \text{when} \quad x_i \to \infty.$$

The normal component of the heat flow to the surface described by Eq. (6) is equal to zero (since the thermal conductivity of the material filling the pore is assumed negligible):

$$Q_n = \varkappa \frac{\partial T}{\partial n} = 0. \tag{11}$$

However, this problem is analogous to the well-known problem of a dielectric ellipsoid with a dielectric constant ε_1 situated in a homogeneous dielectric with a constant ε_2, an electric field E_{01} being applied in the direction of the x_1 axis inside the latter, and the euqation of the ellipsoid surface being described by Eq. (6). If we thus make use of the solution to the ellipsoid problem given in [6] [considering that the dielectric constant of the medium filling the pore is equal to zero, which is mathematically equivalent to condition (11)], we shall have

$$T = T_0 \frac{1 - \dfrac{b_1 b_2 b_3}{2} \displaystyle\int_0^{\nu} \frac{ds}{(s + b_1^2) R_s}}{1 - \dfrac{b_1 b_2 b_3}{2} \displaystyle\int_0^{\infty} \frac{ds}{(s + b_1^2) R_s}}, \tag{12}$$

where T_0 is taken from (9) and

$$R_s = \sqrt{(b_1^2 + s)(b_2^2 + s)(b_3^2 + s)};$$

ν is the parameter of a system of ellipsoids confocal with the specified ellipsoid $\nu = 6$ corresponding to Eq. (6).

The thermal flux through the surface ν = const embracing the pore will then be

$$Q = -\varkappa \int_{-b_1^2}^{-b_2^2} \int_{-b_2^2}^{-b_3^2} \frac{1}{h_1} \cdot \frac{\partial T}{\partial \nu} h_2 h_3 d\eta d\xi. \tag{13}$$

If there is no pore, the thermal flux through this surface will be

$$Q_0 = -\varkappa \int_{-b_1^2}^{-b_2^2} \int_{-b_2^2}^{-b_3^2} \frac{1}{h_1} \cdot \frac{\partial T_0}{\partial \nu} h_2 h_3 d\eta d\xi, \tag{14}$$

where η and ξ are the parameters of confocal hyperboloids and serve to define the position of the point on the ellipsoids ν = const, i.e., ν, η, ξ are ellipsoidal coordinates.

We may write the thermal flux through the surface ν = const in the presence of a single pore in the following way:

$$Q = -\varkappa'_{1\,\mathrm{eff}} \int\limits_{-b_1^2}^{-b_2^2} \int\limits_{-b_2^2}^{-b_3^2} \frac{1}{h_1} \cdot \frac{\partial T_0}{\partial \nu} h_2 h_3 d\eta d\xi. \tag{15}$$

Thus, the ratio

$$\frac{Q}{Q_0} = \frac{\varkappa'_{1\,\mathrm{eff}}}{\varkappa}. \tag{16}$$

It should be noted that, since the dimensions of the sample are regarded as much greater than any of the dimensions a_1, a_2, a_3 of the pore, when calculating the correction to the thermal resistance introduced by a single pore we must put $\nu \gg a_1, a_2, a_3$.

Thus, bearing in mind Eqs. (12)-(16),

$$\frac{\varkappa'_{1\mathrm{eff}}}{\varkappa} = \frac{Q}{Q_0} = 1 + \frac{b_1 b_2 b_3}{1 - A_1}\left[\frac{1}{2}\int\limits_{\nu}^{\infty} \frac{ds}{(s+b_1^2)} - \frac{1}{R_\nu}\right], \tag{17}$$

where

$$A_1 = \frac{b_1 b_2 b_3}{2} \int\limits_0^{\infty} \frac{ds}{(s+b_1^2) R_s}.$$

For $\nu \gg b_1, b_2, b_3$ we shall have

$$\int\limits_{\nu}^{\infty} \frac{ds}{(s+b_1^2) R_s} \approx \frac{2}{3} \cdot \frac{1}{R_\nu} \approx \frac{2}{3} \cdot \frac{1}{\nu^{3/2}}, \tag{18}$$

where

$$R_\nu = \sqrt{(b_1^2+\nu)(b_2^2+\nu)(b_3^2+\nu)}.$$

Thus, on allowing for (17) and (18) we may write the following for the effective thermal conductivity $\varkappa'_{1\mathrm{eff}}$ in the presence of only a single pore after taking account of Eq. (15):

$$\varkappa'_{1\mathrm{eff}} = \varkappa\left[1 - \frac{2}{3} \cdot \frac{b_1 b_2 b_3}{1 - A_1} \cdot \frac{1}{\nu^{3/2}}\right]. \tag{19}$$

The volume limited by the surface ν = const (for $\nu \gg a_1, a_2, a_3$) is

$$v = \frac{4}{3}\pi \nu^{3/2}. \tag{20}$$

In addition to this, the volume of a single pore will be

$$v_0 = \frac{4}{3}\pi a_1 a_2 a_3 = \frac{4}{3}\pi b_1 b_2 b_3. \tag{21}$$

Thus, from (19)-(21) we deduce

$$\varkappa'_{1\mathrm{eff}} = \varkappa\left[1 - \frac{2}{3} \cdot \frac{v_0}{v} \cdot \frac{1}{(1 - A_1)}\right]. \tag{22}$$

Transforming to the coordinates x_i and allowing for (3) and (5), we find that

$$\varkappa''_{1\mathrm{eff}} = \varkappa_{11}\left[1 - \frac{2}{3}\cdot\frac{v_0}{v}\cdot\frac{1}{(1-A_1)}\right].$$

If the sample contains not one but no pores, the corrections introduced by the individual pores will be additive, since in the case of a low porosity we may neglect their mutual influence. We shall thus have

$$\varkappa_{1\mathrm{eff}} = \varkappa_{11}\left[1 - \frac{2}{3}\cdot\frac{v_0}{v}\cdot\frac{1}{(1-A_1)}\,n\right] = \varkappa_{11}\left[1 - \frac{2}{3}\,v_0 n_0\,\frac{1}{(1-A_1)}\right], \tag{23}$$

where $n_0 = n/v$ is the number of pores in unit volume. However, since $\beta = v_0 n_0$, we shall finally have

$$\varkappa_{1\mathrm{eff}} = \varkappa_{11}\left[1 - \frac{2}{3}\cdot\frac{\beta}{(1-A_1)}\right]. \tag{24}$$

If the temperature gradient is directed along the x_i axis, then for $\varkappa_{i\mathrm{eff}}$ we shall clearly obtain

$$\varkappa_{i\mathrm{eff}} = \varkappa_{ii}\left[1 - \frac{2}{3}\cdot\frac{\beta}{1-A_i}\right], \tag{25}$$

where

$$A_i = \frac{b_1 b_2 b_3}{2}\int_0^\infty \frac{d\nu}{(b_i^2+\nu)R_\nu}. \tag{26}$$

It should be noted that the condition of low porosity corresponds to the equation $\frac{2}{3}\cdot[\beta/(1-A_i)] \ll 1$.

All the formulas for the electrical conductivity σ may be obtained from (24) and (25) if we replace $\varkappa_i$ by σ_i, and there is therefore no need to present them in detail at this point.

It should be noted that a number of authors has considered the question of the effective electrical conductivity [7] and dielectric constant [8] of a heterogeneous system. The system which these authors considered consisted of an isotropic conducting medium (or isotropic dielectric) containing embedded spherical particles with a different electrical conductivity (or dielectric constant), the volumetric concentration of the spherical particles (or the porosity if the spheres are regarded as pores) being low. Clearly, the mathematical formalism for determining the effective thermal and electrical conductivities is exactly the same as for the dielectric constant of such a heterogeneous system.

If the electrical conductivity of the dielectric constant of the spherical particles is equal to zero, the expressions for the effective values of these quantities (in terms of the thermal conductivity) given in [7, 8] take the following form:

$$\varkappa_{\mathrm{eff}} = \varkappa(1 - c\beta), \tag{27}$$

where c is a numerical coefficient approximately equal to unity ($c \sim 1$).

The value of this coefficient depends to some extent on the means of averaging. Comparing (27) and (25), we see that Eq. (25) may be regarded as a generalization of the equations proposed in [7, 8] for the case of anisotropic media.

Let us consider the case in which $\varkappa_{11} = \varkappa_{22} = \varkappa_{33}$ and $a_1 > a_2 > a_3$. Since $A_1 \neq A_2 \neq A_3$, it follows from (24)-(26) that $\varkappa_{1\mathrm{eff}} \neq \varkappa_{2\mathrm{eff}} \neq \varkappa_{3\mathrm{eff}}$. Thus, anisotropy of the thermal and electrical conductivities arises in this case as a result of the different cross-sectional areas of the pores in different directions. This explains the appearance of anisotropy in the pressed samples of [2-4].

Using Eq. (25) we may estimate the anisotropy which arises from the different cross-sectional areas of the pores in different directions. In pressing thermocouples from the ternary alloys indicated above, the porosities were usually less than 5% [1, 2].

We direct the x_3 axis parallel to the pressing direction. Since in the course of the pressing operation all the directions perpendicular to the pressing direction are equivalent, we may consider that $a_1 = a_2$. In view of the strong cleavage properties of Bi_2Te_3, the powder particles from which the thermocouples are pressed assume a disk-like shape. The ratio of the thickness of such a disk to its diameter is approximately equal to 1/3. We shall consider that the pores have the same shape, i.e., $a_1/a_3 \approx 3$. Neglecting the influence of the pores on the thermal and electrical conductivities in the direction of the x_1 and x_2 axes (i.e., considering that $\varkappa_{11} = \varkappa_{22} = \varkappa = \varkappa_{1eff}$ and $\sigma_{11} = \sigma_{22} = \sigma = \sigma_{1eff}$) from Eq. (25) we deduce

$$\frac{\Delta\varkappa}{\varkappa_{1\,eff}} = \frac{\varkappa_{1\,eff} - \varkappa_{3\,eff}}{\varkappa_{1\,eff}} = \frac{\sigma_{1eff} - \sigma_{3\,eff}}{\sigma_{1\,eff}} = \frac{\Delta\sigma}{\sigma_{1\,eff}} \lesssim 0.03.$$

That is, the degree of anisotropy which may arise as a result of the presence of lens-shaped pores is less than 3%. Actually, according to [4]

$$\frac{\Delta\varkappa}{\varkappa_{1\,eff}} \approx 0.08 \quad \text{and} \quad \frac{\Delta\sigma}{\sigma_{1eff}} \approx 0.5,$$

while, according to [2], $\Delta\sigma/\sigma_{1eff} \approx 0.8$.

We thus see that, first, the degrees of anisotropy of the thermal and electrical conductivities are not equal to one another and, secondly, they may be greater than our own value of 3%.

We may thus conclude that the observed anisotropy cannot be explained by porosity alone, and another explanation is required for the observed effect, as, for example, in [9].

It is interesting to study the effect of porosity and pore shape on the ratio $\sigma/\varkappa$ of anisotropic solids and hence the efficiency of the thermocouples.

Let the x_3 axis lie in a direction in which the ratio of the coefficients $\sigma/\varkappa$ has its lowest value, i.e., the efficiency of the thermocouples reaches a minimum. It is then quite easy to show that the ratio

$$\frac{\sigma_{3eff}}{\varkappa_{3\,eff}} = \frac{\sigma_{33}}{\varkappa_{33}} \cdot \frac{1 - \frac{2}{3} \cdot \frac{\beta}{1 - A_3(\sigma)}}{1 - \frac{2}{3} \cdot \frac{\beta}{1 - A_3(\varkappa)}} > \frac{\sigma_3}{\varkappa_3}.$$

Thus, the existence of porosity increases the efficiency of an anisotropic thermocouple in the direction in which its value is lowest. This increment is greatest (assuming constant porosity) for a lenticular pore shape, i.e., $a_1, a_2 \gg a_3$. In the limiting case of large porosity the presence of lenticular pores may increase the ratio $\sigma/\varkappa$ corresponding to the worst direction until it reaches the value of $\sigma/\varkappa$ corresponding to the best.

From the physical point of view this effect in fact reduces to the organization of the thermal flux and electrical current by the lenticular pores in the direction in which $\sigma/\varkappa$ reaches its maximum (Fig. 1). Lenticular pores may be created in an anisotropic substance, for example, by extrusion through an elliptical (or severely "flattened") aperture.

NOTATION

z, thermoelectric efficiency; σ, electrical conductivity; $\varkappa$, thermal conductivity; α, thermo-emf; T, absolute temperature; q, total rate of heat evolution in unit volume of the crystal; dT/dn, temperature derivative along the normal to the pore surface; h_1, h_2, h_3, Lamé coefficients; $\varkappa_{1eff}$, $\varkappa_{2eff}$, $\varkappa_{3eff}$ and σ_{1eff}, σ_{2eff}, σ_{3eff}, effective thermal and electrical conductivities of the porous material in the direction of the x_1, x_2, x_3 axes; β, porosity; $A_i(\sigma)$ is obtained from Eq. (26) by substituting σ for $\varkappa$; $\varkappa_{ik}$, σ_{ik}, tensor components of thermal and electrical conductivities (i, k = 1, 2, 3); $\varkappa'_{1eff}$, effective thermal conductivity allowing for the influence of a single pore in coordinates X_i in the X_1 direction; $\varkappa''_{1eff}$, effective thermal conductivity allowing for the influence of a single pore in coordinates x_i in the x_1 direction.

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DETERMINATION OF THE COEFFICIENT OF THERMAL CONDUCTIVITY BY TWO-POINT PROBING OF THE SPECIMEN SURFACE

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UDC 536.2.08:620.179

A comparison method of determining the coefficient of thermal conductivity which permits direct measurement on specimens of arbitrary geometry without their destruction is elucidated. Experimental results on realization of the method are presented.

Methods to determine the coefficient of thermal conductivity, based on surface heat probing of the specimens, are of great practical interest. The main advantage of such methods is the possibility of conducting measurements on specimens of arbitrary geometry, for example, on fabricated items, without their destruction.

A number of instruments which solve this problem to some extent is described in [1]. Underlying the instruments is the principle of point heat probing of the specimen surface and recording the temperature difference at two points of the probe, which characterizes the heat exchange between the probe and the specimen across the zone of their continuity in an almost stationary mode. The coefficient of thermal conductivity is determined by a comparison with the results of similar meausrements on standard specimens with a known thermal conductivity. Hence, such instruments have been called thermal comparators. One of the most successful, which yields the possibility of reading the coefficient of thermal conductivity directly on the scale of a recording device, is the thermal comparator consisting of a bulk Constantan module and a thin rod standing off therefrom, whose end is in thermal contact with the specimen surface. A measure of the thermal conductivity is the temperature difference between the end of the rod in contact with the specimen and a preheated Constantan module at a higher temperature compared to the specimen temperature, recorded by using a differential thermocouple in the steady-state mode.

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Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 30, No. 4, pp. 693-699, April, 1976. Original article submitted May 27, 1975.