THERMAL CONDUCTIVITY OF MULTICOMPONENT MIXTURES

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The authors propose a method of calculating the effective thermal conductivity of multicomponent mixtures as a function of their structure, the thermal conductivities of the components, their concentrations, and other parameters.

We call a system consisting of two or more materials with different physical properties a multicomponent mixture. Multicomponent mixtures can be divided into three principal structural classes: I) structure with noncommunicating components, II) structure with communicating components, and III) intermediate structure, a combination of structures I) and II). The first class of mixtures includes those with a structure composed of individual noncommunicating inclusions 2, 3 of arbitrary shape randomly or regularly distributed in a matrix 1 (Fig. 1a). The second class includes structures composed of interconnecting inclusions 2, 3 in a matrix substance 1 (Fig. 1b). The distinction between inclusions and matrix is an arbitrary one, since the structural components 2 and 3 could be called the matrix and component 1 an inclusion. The second and third classes of mixtures embrace a much greater number of natural and artificial materials than the first: for example, solids with intercommunicating pores, reinforced structures, fibrous and granular materials, mixtures of different solids, some alloys, liquid-permeated soils, etc.

Since the end of the nineteenth century many attempts have been made to obtain theoretical expressions relating the thermal conductivity and other transport coefficients (electrical conductivity, dielectric constant, etc.) with the characteristic parameters, in particular: the structure of the mixture, the shape and size of the inclusions, their orientation relative to the flow, and the thermal conductivity and concentration of the individual components. These studies were made for mixtures of the first class and for the most part reduced to a determination of the effect of the shape of the inclusions and their orientation on the effective transport coefficients. The fullest review of the results of this research may be found in [1, 2].

Heat transfer processes in mixtures of the first class have been investigated by a number of authors of whom V. I. Odelevskii [3], in our opinion, adopted the most correct approach. Odelevskii proposed the following expression for the effective thermal conductivity of a two-component mixture:

$$\lambda = \lambda_1\left[1 - \frac{P}{1/(1-\nu)-(1-P)/3}\right], \quad \nu = \frac{\lambda_2}{\lambda_1}. \qquad (1)$$

The effective thermal conductivity of mixtures with communicating inclusions has received less attention. In [4] Dul'nev established a theoretical relation between the effective thermal conductivity and the characteristic parameters for a two-component mixture of this class. Comparison of calculation and experiment for various building materials, porous ceramics, refractories [5], some alloys, water- or oil-saturated soils, and other materials indicates satisfactory agreement.

As far as we know, λ for mixtures of the first and second classes has been theoretically investigated only for two-component mixtures.* However, in practice, extensive use is being made of systems with more than two components. The theoretical investigation of the effective thermal conductivity of such systems is of definite importance. The problem consists in establishing the form of the functional dependence of λ on the characteristic parameters, i.e.,

$$\lambda = \Phi(\lambda_1, \lambda_2, \lambda_3, \ldots, \lambda_i, P_1, P_2, P_3, \ldots, P_i). \qquad (2)$$

We have been unable to find in the literature analytical relations for determining the effective thermal conductivity of mixtures with more than two components. The only exceptions are certain relations for gas mixtures [8]. An analytic expression for the effective thermal conductivity of multicomponent mixtures can be obtained in various ways:

1. By simultaneously allowing for the thermal conductivity and concentration of all the components of the multicomponent structure.

2. By successively reducing the structure of the multicomponent mixture to the structure of a two-component mixture whose effective thermal conductivity is determined using known analytic relations.

We will examine both these methods with reference to the example of a three-component mixture with noncommunicating inclusions. Let this mixture consist of a matrix 1 and separate inclusions 2 and 3 whose thermal conductivities and volume concentrations are respectively equal to $\lambda_1, \lambda_2, \lambda_3$ and P_1, P_2, P_3. We impose the following restrictions:

1. The components do not interreact.

2. The dimensions of the inclusions are similar in the three principal directions (differ by a factor of not more than 2), and are much smaller than the dimensions of the mixture.

*As shown in [7], at the limits Odelevskii's formula for multicomponent statistical mixtures [6] leads to contradictory results.

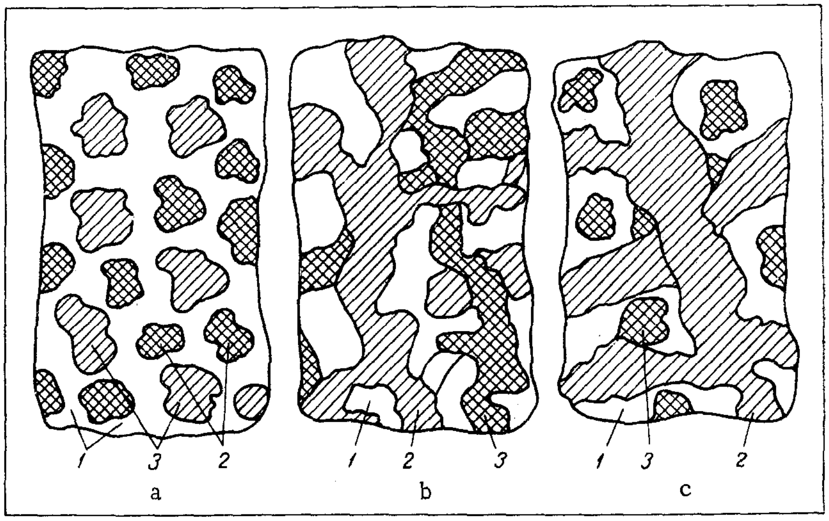

Fig. 1. Structural classes of multicomponent mixtures: a) structure with noncommunicating components, b) with communicating components, c) intermediate (combined) structure.

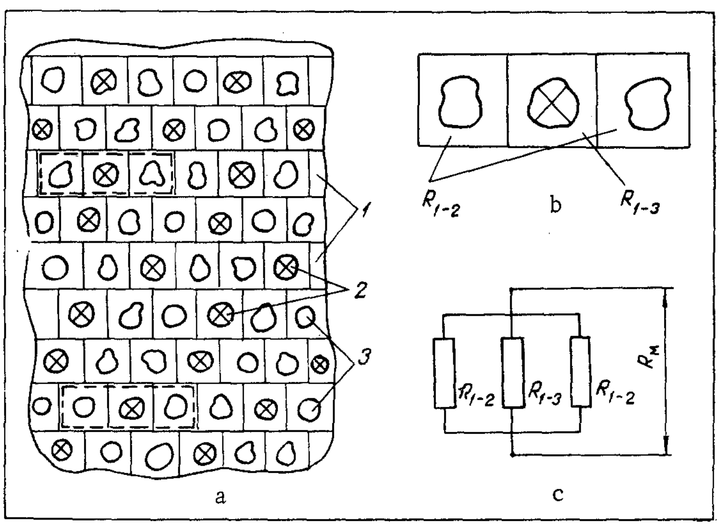

Fig. 2. Three-component mixture with noncommunicating components: a) schematic representation of mixture, b) elementary block, c) thermal resistance connection diagram.

EFFECTIVE THERMAL CONDUCTIVITY OF A MIXTURE WITH NONCOMMUNICATING INCLUSIONS

To analyze the heat transfer process we employed the method proposed in [4]. We assume that the inclusions 2 and 3 are uniformly distributed in the matrix 1, i.e., "long-range order" exists in the mixture. Such a mixture is represented schematically in Fig. 2a.

From this mixture we can separate individual layers perpendicular to the heat flow whose effective thermal conductivity is equal to that of the mixture. Upon examining the structure of the layer we can distinguish the "elementary blocks" (within the broken lines) which combine to form the entire mixture. Each block is composed of two types of cubical "unit cells" (Fig. 2b), the quantitative relationship between which is uniquely determined by the volume concentrations of the components P_2 and P_3. If we assume that the unit cells in a block are separated by infinitely thin adiabatic planes (Fig. 2c), we can define the thermal resistance of the block R_b as follows:

$$R_b = \frac{R_{1-2}R_{1-3}}{NR_{1-2}+KR_{1-3}} = \frac{l}{\lambda_b S_b}, \quad \lambda_b = \lambda, \tag{3}$$

where

$$S = (N+K)l^2.$$

Taking into account the relation between N, K, and P_2, P_3, we can bring Eq. (3) to the form

$$\lambda = \frac{P_2}{P_2+P_3}\frac{1}{lR_{1-2}} + \frac{P_3}{P_2+P_3}\frac{1}{lR_{1-3}}. \tag{4}$$

We find the thermal resistances of the unit cells R_{1-i} using Eq. (1):

$$R_{1-i} = \frac{1}{l\lambda_1}\left[1 - \frac{P_{1-i}}{1/(1-\nu_{1-i})-(1-P_{1-i})/3}\right]^{-1},$$

$$\nu_{1-i} = \frac{\lambda_i}{\lambda_1}, \quad P_{1-i} = P_2+P_3 = 1-P_1. \tag{5}$$

Substituting the value obtained for R_{1-i} in (4), after some simple transformations we obtain an expression for the effective thermal conductivity of a three-component mixture with noncommunicating inclusions:

$$\lambda = \lambda_1\left\{\frac{P_2}{1-P_1}\left[1 - \frac{1-P_1}{1/(1-\nu_{1-2})-P_1/3}\right] + \right.$$
$$\left. + \frac{P_3}{1-P_1}\left[1 - \frac{1-P_1}{1/(1-\nu_{1-3})-P_1/3}\right]\right\}. \tag{6}$$

Equation (6) satisfies the conditions at the limits. When P_2 or $P_3 = 0$, we arrive at Eq. (1). When $\nu_{1-i} = 1$ the effective thermal conductivity of the mixture $\lambda = \lambda_1$. Thus, Eq. (6) can be recommended for determining the effective thermal conductivity of a three-component mixture with noncommunicating components. However, as the number of components increases, Eq. (6) becomes rapidly more complicated and unsuitable for calculations.

We will use the second method of determining the effective thermal conductivity of the multicomponent mixture as a function of the characteristic parameters.

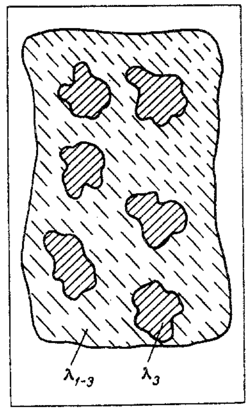

Fig. 3. Structure of a three-component mixture reduced to the structure of a two-component mixture.

We will consider a three-component mixture with noncommunicating inclusions. The solution is carried out in stages. In the first stage we imagine that the third component has been removed from the mixture (Fig. 1a). This reduces the three-component mixture to a two-component structure with noncommunicating inclusions. But in this case in the reduced two-component mixture it is necessary to take into account the change in the ratio of the component concentrations. We denote the volume concentration of the first component in the reduced two-component mixture by P_1', that of the second component by $P_2' = 1 - P_1'$. It is easy to show that P_1' and P_2' are related with P_1 and P_2 by the simple expression

$$P_1' = P_1/(P_1+P_2); \quad P_2' = P_2/(P_1+P_2). \tag{7}$$

Knowing the thermal conductivity of the components and the values of P_1' and P_2' we can determine the effective thermal conductivity of the reduced two-component mixture using Eq. (1), i.e.,

$$\lambda_{1-2} = f_1(\lambda_1, \lambda_2, P_1, P_2). \tag{8}$$

We can now assume that part of the volume of the three-component mixture corresponding to the volume concentration $P_{1-2} = P_1 + P_2$ has the effective thermal conductivity λ_{1-2} (Fig. 3).

In the second stage of the calculations we take into account the presence of the third component. We again obtain a two-component mixture with volume concentrations P_{1-2}, P_3 and thermal conductivities λ_{1-2} and λ_3, respectively. We again use Eq. (1) and determine the effective thermal conductivity of the initial three-component mixture

$$\lambda = \Phi_1(\lambda_1, \lambda_2, \lambda_3, P_1, P_2, P_3) =$$
$$= \varphi_1(\lambda_{1-2}, \lambda_3, P_{1-2}, P_3). \tag{9}$$

We note that in a mixture with noncommunicating inclusions the latter are geometrically nonequivalent.

i.e., the thermal conductivity of the matrix has a greater influence on the effective thermal conductivity of the mixture. Therefore, in Eq. (1) the indices of the matrix and the inclusions cannot be transposed, since this leads to a significant change in the value of the effective thermal conductivity of the mixture [3].

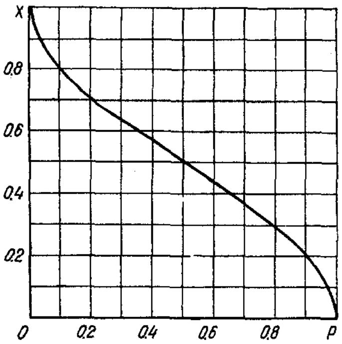

Fig. 4. Graph of the function X = X(P).

The sequence in which the inclusions are dealt with is a matter of indifference since the inclusions are geometrically equivalent.

EFFECTIVE THERMAL CONDUCTIVITY OF A MIXTURE WITH COMMUNICATING COMPONENTS

In order to determine the effective thermal conductivity of a mixture with communicating components we will also use the method of successive reduction of the structure of a multicomponent mixture to the structure of a two-component mixture (Fig. 1b). However, in such a structure the components are geometrically equivalent and may be combined in any order. In the first stage of calculation, taking any pair of components (for example, 2-3), we determine their effective thermal conductivity

$$\lambda_{2-3} = f_2(\lambda_2, \lambda_3, P_2', P_3') \tag{10}$$

as the effective thermal conductivity of a mixture with communicating components from their thermal conductivities and reduced volume concentrations using the expression proposed in [4]:

$$\lambda = \lambda_1 \left[X^2 + \nu(1-X)^2 + \frac{2\nu X(1-X)}{\nu X + (1-X)} \right]. \tag{11}$$

The parameter X is related with the volume concentration as follows:

$$P = 2X^3 - 3X^2 + 1. \tag{12}$$

Figures 4 and 5 are intended to facilitate the calculations.

We can now assume that part of the volume of the three-component mixture corresponding to the volume concentration $P_{2-3} = P_2 + P_3$ has an effective thermal conductivity λ_{2-3}. In the second stage of the calculation we determine the effective thermal conductivity of the three-component mixture as a whole:

$$\lambda = \Phi_2(\lambda_1, \lambda_2, \lambda_3, P_1, P_2, P_3) = \\ = \varphi_2(\lambda_1, \lambda_{2-3}, P_1, P_{2-3}). \tag{13}$$

EFFECTIVE THERMAL CONDUCTIVITY OF COMBINED MIXTURES

The effective thermal conductivity of combined mixtures (Fig. 1c) may be determined by reduction to the structure of a two-component mixture. In combined mixtures the geometrical nonequivalence of the components is preserved. Therefore in the first stage of the calculation we determine the effective thermal conductivity of the part of the structure formed by the communicating components from their thermal conductivities and reduced volume concentrations. For this purpose we employ Eq. (11), i.e.,

$$\lambda_{1-3} = f_2(\lambda_1, \lambda_3, P_1', P_3'). \tag{14}$$

In the second stage of the calculation we determine the effective thermal conductivity of the three-component mixture reduced to the structure of a mixture with noncommunicating inclusions, i.e.,

$$\lambda = \Phi_3(\lambda_1, \lambda_2, \lambda_3, P_1, P_2, P_3) = \\ = \varphi_3(\lambda_{1-3}, \lambda_2, P_{1-3}, P_2). \tag{15}$$

We note that in the second stage of the calculation transposition of the indices of the matrix and the inclusions is not permissible.

By successive applications of the method proposed it is possible to determine the effective thermal conductivity of a mixture with any number of components.

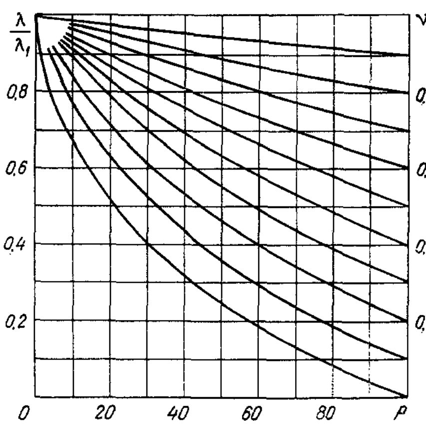

Fig. 5. Graph of the function $\lambda/\lambda_1 = f(P, \nu)$.

Since in multicomponent mixtures the concentrations of the components are often given by weight, it is worthwhile giving the relation between the concentrations by weight and volume n and P, respectively. By definition

$$P = v_2/v, \quad n = G_2/G, \tag{16}$$

where v_2 and v are the volumes of the admixture and the mixture; G_2 and G are the weights of the admixture and the mixture. Denoting by γ_1, γ_2, and γ the specific weight of the components and the mixture as a whole, we find

$$n = \frac{G_2}{G} = \frac{\gamma_2 v_2}{\gamma v} = P\frac{\gamma_2}{\gamma},$$

but

$$\gamma = \frac{G}{v} = \frac{\gamma_2 v_2 + \gamma_1(v - v_2)}{v} = \gamma_2 P + \gamma_1(1-P).$$

After simple transformations we obtain the relation between γ/γ_2 and P:

$$\frac{\gamma}{\gamma_2} = P + \frac{1}{\eta}(1-P), \quad \eta = \frac{\gamma_2}{\gamma_1}. \tag{17}$$

From (16) and (17) it follows that

$$P = \frac{n}{\eta + n(1-\eta)}. \tag{18}$$

If the concentrations of the components are given in at.%, we can use the relation between the concentration by weight and the atomic concentration proposed in [9]

$$n = 100a \Big/ \left[a + \frac{A}{B}(100-a) \right], \tag{19}$$

where A, B are the atomic weights of the components, and a is the concentration in at.%.

NOTATION

λ is the effective thermal conductivity of multicomponent mixture; λ_1 is the thermal conductivity of the matrix; λ_2 is the thermal conductivity of inclusions; P is the volume concentration of inclusions; λ_i is the thermal conductivity of the i-th component; P_i is the volume concentration of the i-th component; R is the thermal resistance; l is the dimension of the unit cell; n is the concentration by weight; N, K are the number of unit cells in the block.

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