THERMAL AND ELECTRICAL CONDUCTIVITIES OF BINARY-ALLOY MIXTURES

G. N. Dul'nev and Yu. P. Zarichnyak

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Let us examine the processes of heat and electricity transport in alloy mixtures. An analytical method is proposed for the determination of the effective thermal and electrical conductivities of such alloys, depending on the coefficients of thermal and electrical conductivity of the components, their volume concentration, and the structure of the alloy.

A substantial number of theoretical and experimental investigations—which are reviewed in [1, 2]—has been

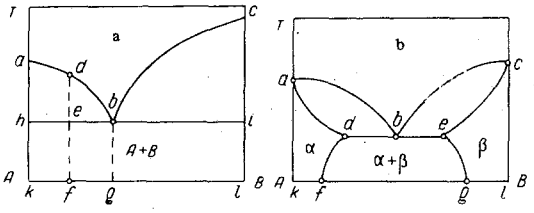

Fig. 1. Diagrams of state for the alloys under study: a) components are virtually insoluble; b) components are partially soluble.

devoted to the processes of heat and electricity transfer in alloys. That review also notes the absence of a complete theory of transport in alloys, thus making it possible to determine the coefficients of thermal and electrical conductivity for alloys with the required degree of accuracy. From among the many binary alloys, we can isolate three basic groups:

1) alloys with unlimited solubility of the components (solid solutions);

2) alloys with limited solubility of the components (solid solutions with a eutectic);

3) alloys with virtually insoluble components (eutectic alloys, alloy mixtures).

Let us consider this last group of alloys which, in the solid state, are nonhomogeneous, representing a mixture of two insoluble components. The diagram of state shown in Fig. 1a corresponds to such alloys. We know that for a concentration of components A and B corresponding to the point b of the diagram of state a eutectic alloy is formed, i.e., a mechanical mixture of uniformly distributed components A and B. With concentrations greater than g, the solid alloy is composed of two structural components: of the crystals of the pure component B and of the eutectic mixture (in the case of a eutectic alloy). The structure of the preeutectic alloys consists of the crystals of the pure component A and of the eutectic [3]. Consequently, over the entire range of variation in the concentration of the components the alloy under consideration represents a mechanical mixture of two components. In this case, the distribution of the components is statistically random in nature. Let us make the following assumption: the effective thermal conductivity of the statistical mixture is equal to the effective thermal conductivity of the ordered structure, if the values of the thermal conductivities of the components and of their concentrations are identical for the statistical and ordered structures. (All of these comments are equally valid for electrical conductivity.) We will return to the justification of this assumption later on. It is possible to consider the various classes of the alloy-mixture structures as follows: a) isolated inclusions (granules) of component B (Fig. 2a) have penetrated into the binder component A; b) the components A and B form an interpenetrating macrolattice (Fig. 2b); c) the components form combined structures of interpenetrating macrolattices and isolated inclusions (Fig. 2c).

All of the above-enumerated structural types are unordered statistical mixtures in which the study of the heat and electricity transport is associated with considerable difficulties. Based on the above assumptions, we will represent the unordered statistical mixture in the form of an ordered structure, retaining the concentration and characteristics of the components. For any ordered structure, the existence of long-range order is characteristic in the distribution of the components. This makes it possible to isolate the "elementary cell" from the entire structure (see Fig. 3)—the minimum volume element whose effective thermal conductivity is equal to the thermal conductivity of

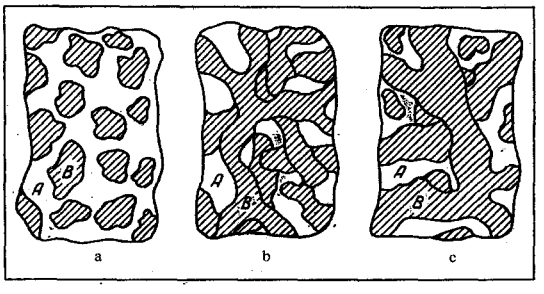

Fig. 2. Structures of alloy-mixtures: a) with isolated inclusions; b) with interpiercing inclusions; c) combined.

the entire structure, and so we continue the study of transport processes only in the elementary cell [4, 5].

Since the end of the last century, many researchers have studied the processes of transport in structures

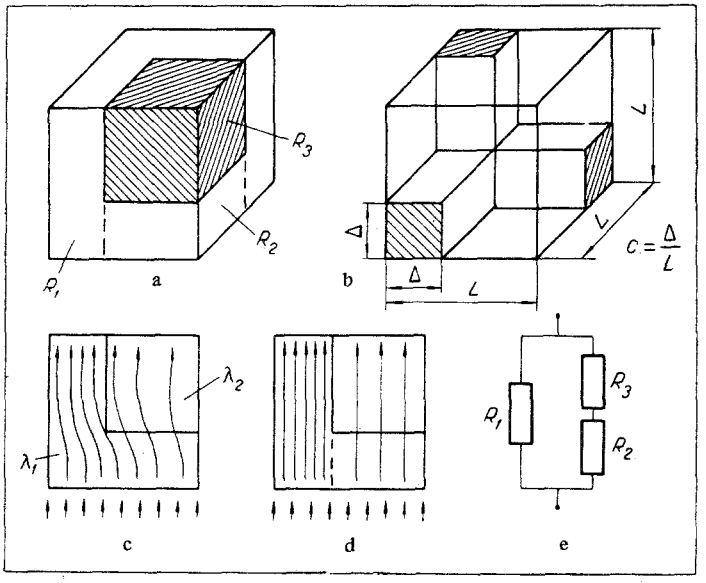

Fig. 3. Form of elementary cell and line of heat flux: a) structure with insulated inclusions; b) structure with interpiercing inclusions; c) current lines in cell; d) schematic presentation of current lines; e) connection diagram of thermal resistors.

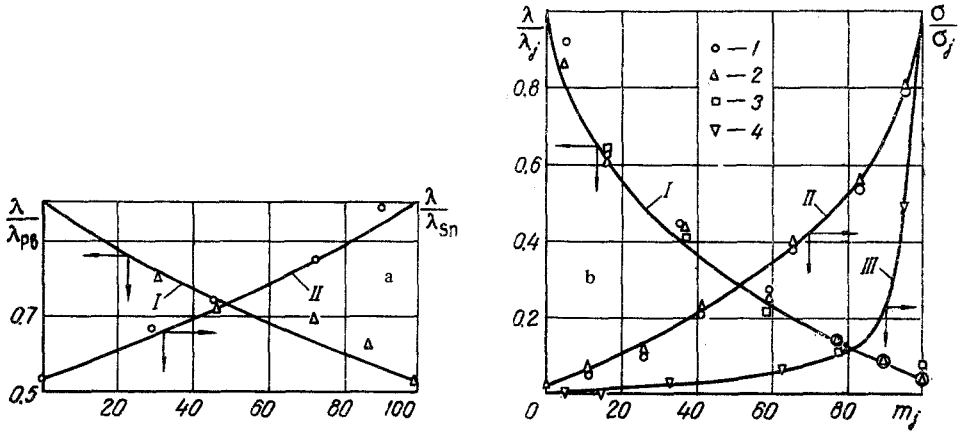

Fig. 4. Relationship between thermal conductivity and electric conductivity of binary alloys-mixtures with volume concentration of components, %: a) alloys with small difference in component characteristics [8] (I, Pb-Sb; II, Pb-Sn); b) alloys with high difference in component characteristics (I, Cd-Bi; 1, t = 50°C; 2, t = 100°C [1]; 3, t = 50°C [8]; II, Bi-Cd; 1, t = 50°C; 2, t = 100°C [1]; III, Bi-Ag; 4, t = 30°C [9]).

with isolated inclusions, their relation to the shape of the inclusions, the nature of the distribution within the binder component, the volume concentration of the inclusions, and the thermal conductivity of the components. The basic conclusions of this research are presented in [5, 6, 12]. In our opinion, Odelevskii [4] achieved the most correct derivation of the functional relationship associating the effective characteristics and the determining parameters of a structure with isolated inclusions, i. e., he proposed the following relationship:

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

The subscripts for the components in formula (1) cannot be interchanged, since in the light of the geometric disparity between the components, this might lead to substantial distortion of the calculation results [4].

In the derivation of relationship (1) it was assumed that cubic inclusions are oriented with respect to one of the faces, perpendicular to the heat flow. Analysis of the investigational results demonstrates that the divergence in the shape of the nonelongated inclusions (sphere, cube, twinned pyramid, nonoriented ellipsoids of revolution) and their orientation with respect to the direction of the heat flow have virtually no effect on the magnitude of the effective thermal conductivity of the system with isolated inclusions [7]. The transfer of heat in structures with interpenetrating components has been studied in [5] in which the following expression has been proposed for the determination of the effective thermal conductivity:

$$\lambda = \lambda_1 \left[c^2 + \nu (1-c)^2 + \frac{2\nu c (1-c)}{\nu c + (1-c)} \right], \quad (2)$$

where c is the geometric parameter of the lattice (see Fig. 3b), accociated with the volume concentration m of the second component by the equation

$$m = 2c^3 - 3c^2 + 1, \quad (3)$$

whose solution has the form

$$c = 0.5 + a \cos \frac{\varphi}{3} \quad (4)$$

when

$$0 \leqslant m \leqslant 0.5; \quad a = -1; \quad \varphi = \arccos (1 - 2m),$$

$$0.5 \leqslant m \leqslant 1.0; \quad a = 1; \quad \varphi = \arccos (2m - 1),$$

where

$$270^\circ \leqslant \varphi \leqslant 360^\circ.$$

In the structure with interpenetrating components, the subscripts of the components may be chosen arbitrarily, since in the light of the geometric similarity between the components, the substitution of the subscripts will not affect the results of the calculation.

To determine the boundaries of applicability for formulas (1) and (2), let us consider the assumptions and limitations which were employed in the determination of these relationships.

In references [4, 5] it was assumed that infinitely thin adiabatic interlayers have been introduced into the elementary cell (Fig. 3a, b) at the boundaries between heterogeneous bodies parallel to the heat flow. The introduction of these interlayers causes the streamlines of the heat flow within the elementary cell to become parallel, thus making it possible to reduce the problem under consideration to the simplest one-dimensional case. Figure 3c shows the heat-flow streamlines in the elementary cell (Fig. 3a) of a structure with isolated inclusions (for the special case of $\lambda_1 > \lambda_2$) without these adiabatic interlayers, while Fig. 3d shows the same situation in the presence of such adiabatic interlayers. Further, the elementary cell is divided into several parts with thermal resistances R_1, R_2, and R_3, which were calculated on the basis of the simple formulas for flat walls. The total thermal resistance of the elementary cell was found from the circuit shown in Fig. 3e. The elementary cell was then presented in the form of a homogeneous body with an effective thermal conductivity λ, and whose thermal resistance was also determined on the basis of the formula for a flat wall. Equating both expressions for the thermal resistance of the elementary cell, and expressing the geometric parameters in terms of the concentration, we derive the analytical expression (1). This same approach was also adopted for the elementary cell (Fig. 3b) of a system with interpenetrating components.

It was demonstrated in [5] that the assumption of parallel heat-flow streamlines has but a slight effect on the final result, i. e., we can assume the hypothesis to be valid.

The following constraint has been introduced implicitly into the mathematical realization of the above considerations: there are no additional physical or chemical effects present at the boundaries between heterogeneous components to alter the flow of heat to the elementary cell, i. e., the thermal conductivities of the original components remain unchanged after they have been brought into contact. This limitation narrows the range of applicability for relationships (1) and (2); they are valid for alloys whose structure is a mechanical mixture.

The nature of the alloy structure can be determined by studying microscopic sections and the diagram of state. If the components of the alloy are virtually insoluble (see Fig. 1a), the proposed method is suitable for the determination of the effective thermal conductivity of the alloy mixture in the region h-k-*l*-i. In the case of limited solubility for the components (see Fig. 1b), the proposed calculation method can be used in the zone *f*-d-e-g, i. e., in the region of mixed α β solid solutions. The original components in this case are the α and β solid solutions at the corresponding lines *f*-d and g-e.

To verify the suitability of the proposed method and to determine the region of its applicability, we compared the calculation results for the effective thermal and electrical conductivities of binary alloys with

virtually insoluble components against experimental data taken from [1, 4, 8, 9] (see Fig. 4).

The satisfactory coincidence of the calculation results and those of the experiment attest to the possibility of presenting a statistical mixture in the form of an ordered structure in the determination of the effective coefficient of mixture transport, i.e., the assumption may be regarded as having been validated experimentally. We note that despite the extensive publication, by various authors, of the experimental data obtained in the study of the thermal and electrical conductivities of alloys, only a few of these present results for a wide range of variation in component concentration. This explains the comparatively small volume of experimental data which we have presented to justify the proposed method of calculating the transport coefficients for the alloy mixtures. The validity of these assumptions is indirectly confirmed by the agreement between the calculation results and the experimental data with respect to the thermal conductivity of statistical mixtures not related to alloys [7, 11]. We felt it necessary to dwell in such detail on precisely this assumption, since the remaining assumptions have either been validated analytically or have been dropped through the introduction of limitations on the proposed method of calculating the effective transport coefficients.

Extensive use is made in the physics of metals of the rule relating the properties of alloys with the properties of the components and their concentrations, this rule known as the Kurnakov law. According to the Kurnakov law, the principle of additivity applies to alloy mixtures, i.e., a linear relationship between the properties of the alloy and the concentration of the components

$$\lambda = \lambda_1 m + \lambda_2 (1 - m). \qquad (5)$$

It is not difficult to demonstrate that relationship (5) is special in nature and applicable in the limited range of application for the parameter ν. Indeed, for $0.7 \leq \nu \leq 1.0$ relationships (1) and (2) are close to the linear (see Fig. 4a) and virtually coincide with relationship (5) over the entire range of variation in concentration. However, application of the Kurnakov law for the determination of the alloy-mixture properties in the region of low values for the parameter ($\nu < 0.5$) leads to substantial error.

In formulas (1) and (2), for the determination of the effective thermal conductivity the concentration is expressed in volume percent, whereas in the majority of cases it is the weight concentration of the components that is known for alloys. The relationship between the volume and weight concentrations of the component is specified by the expression

$$m = \frac{n}{\eta + n(1 + \eta)}, \quad \eta = \frac{\rho_2}{\rho_1}. \qquad (6)$$

In conclusion, let us examine the practical scheme of calculating the effective thermal and electrical conductivities of the alloy mixtures. First of all, we have to use the diagram of state to prove that the given alloy is a mechanical mixture. Further analysis of the microscopic sections enables us to determine the structure of the alloy (isolated inclusions, interpenetrating components, or a combination of these) and to select the calculational formula (1) or (2). The method of calculating the effective thermal and electrical conductivities for alloys of combined structure for any number of insoluble components—said method involving the use of relationships (1) and (2)—has been covered in detail in reference [10].

If we do not know the nature of the alloy's structure, for tentative calculations we can take the arithmetic mean of that value from formulas (1) and (2).

NOTATION

λ is the effective thermal conductivity of the mixture; λ_1 and λ_2 are the thermal-conductivity coefficients of the binders and inclusions, respectively; m is the volume concentration of inclusions; n is the weight concentration of components; ρ_i is the specific density of components.

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Institute of Precision Mechanics and Optics, Leningrad