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Theory of thermodiffusion for solids

WALENTY DUDZIAK and STEFAN JAN KOWALSKI
Institute of Fundamental Technological Research, Polish Academy of Sciences,
ul. Mielżyńskiego 27/29, 61-725 Poznań, Poland

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Abstract—The aim of this work is the derivation of a complete set of differential equations of thermodiffusion in solids, accounting, at the same time, for simultaneous action of the mechanical, temperature and concentration fields. The analysis is based on the thermodynamics of irreversible processes with the usual assumptions made in the theory of thermoelasticity and an additional assumption that there is no chemical reaction and that the local temperatures of the matrix and the diffusive substance are the same. Generalized laws of heat and mass flow are also introduced in the paper. Such a theory can be used to describe, for example, the thermochemical treatment of metals.

1. INTRODUCTION

THE AIM of this paper is to develop a set of equations describing the deformation of a solid when under the simultaneous influence of mechanical, temperature and concentration fields, as well as to introduce generalized laws of heat and mass flow.

The above problem was taken up by Podstrigac in 1961 [1] and by Nowacki in 1971 [2]. The latter presented a general outline of Podstrigac's concept, extending it by a number of generalizations from the thermodynamical standpoint. Some suggestions concerning solutions of the derived equations are also given. Both authors ignored the influence of the changes in the volume of the body on the distribution of the concentration in the equation of mass continuity for the diffusive mass. Moreover, the energy transported by the diffusing substance was not taken into account in the energy balance equation. This has a meaning when deriving the heat and mass transport equations on the basis of the second law of thermodynamics.

This paper shows that the equations of mass and heat transport result as conclusions from the Clausius–Duhem inequality. Phenomenological equations obtained in this way, contrary to the Onsager postulates, make possible the clear interpretation of the coefficients introduced.

In our considerations, the following simplifying assumptions have been made: the solid body in question is elastic and isotropic; the concentration and temperature fields cause only volume deformations of the solid; the mass of the diffusing substance in the solid is small when compared with the mass of the solid; ideal exchange of heat between the diffusing substance and the solid is assumed, implying that the temperatures of these two components are locally the same. Chemical reactions possibly accompanying the thermodiffusion process are not considered—that is, the solid is assumed to be chemically inactive.

The main aim of this paper is to solve the system of differential equations describing the distribution of deformations, temperature and concentration of the diffusing mass in a solid involved in the thermodiffusion process. Such a system can be used to describe, for example, the thermochemical treatment of metals.

2. EQUATION OF MASS CONTINUITY

The analysis of atomic diffusion mechanisms enables us to draw the conclusion that in a given time interval a certain number of diffusing substance particles in a solid body will not change their position with respect to the matrix, i.e. they are fixed to the solid. Observation of a sufficiently large number of particles makes it possible to estimate this number as about 40% [3]. This phenomenon will be taken into account in our present considerations, where the following kinematic model is established. There exists a solid the particles of which, being a continuum in Euclidean space, possess the velocity field $\mathbf{v}$. The density of the solid related to the unit of total volume is denoted by ρ_s. The other continuum, the diffusing substance, has bulk density ρ_d. A certain number of its particles are convected by the solid, whereas the remaining part is 'drifting' with mean velocity $\mathbf{w}$. The bulk density of the latter is denoted by ρ^*. The total density of the medium considered is $\rho = \rho_s + \rho_d = \rho_s(1+c)$, where

$$c = \frac{\rho_d}{\rho_s} \tag{1}$$

will be termed the concentration of diffusing mass.

In this paper, until the sixth section, all the quantities are functions of the position vector $\mathbf{x}$ and time t. In order to derive the equations of mass continuity, a certain random volume v will be separated mentally from the space. The volume is assumed to

NOMENCLATURE

a	body bound surface [m^2]
$\mathbf{b}$	body force [N kg^{-1}]
c	concentration, ρ_d/ρ_s
c_p	specific heat of the medium at constant pressure per unit volume [J m^{-3} K^{-1}]
c_v	specific heat of the medium at constant volume per unit volume [J m^{-3} K^{-1}]
$\mathbf{D}$	strain rate tensor [s^{-1}]
$\mathbf{E}$	Green strain tensor
$\mathcal{K}$	kinetic energy [J]
$\mathcal{P}$	mechanical power [W]
$\mathcal{Q}$	non-mechanical power [W]
$\mathbf{q}$	heat flux [W m^{-2}]
S	entropy per unit bulk volume [J m^{-3} K^{-1}]
$\mathcal{S}$	entropy [J K^{-1}]
s	total bulk entropy per unit mass of the solid, s_s+cs_d [J kg^{-1} K^{-1}]
s_d	bulk entropy of the diffusing substance per unit of its mass [J kg^{-1} K^{-1}]
s_s	bulk entropy of the solid per unit of its mass [J kg^{-1} K^{-1}]
T	absolute temperature [K]
$\mathbf{T}$	total stress tensor [N m^{-2}]
t	time [s]
U, F, G	internal energy, free energy, free enthalpy in that order per unit volume [J m^{-3}]
u	total bulk internal energy per unit mass of the solid, u_s+cu_d
$\mathbf{u}$	displacement vector of the solid, $(\mathbf{x}-\mathbf{X})$
$\mathcal{U}$	internal energy [J]
u_d	bulk internal energy of the diffusing substance per unit of its mass [J kg^{-1}]
u_s	bulk internal energy of the solid per unit of its mass [J kg^{-1}]
v	body volume [m^3]
$\mathbf{v}$	velocity vector of the solid [m s^{-1}]
$\mathbf{w}$	average velocity of 'drifting' particles of the diffusing substance [m s^{-1}]
$\mathbf{x}, \mathbf{X}$	position vectors [m].

Greek symbols

α_c	coefficient of linear diffusive expansion
α_ϑ	coefficient of linear thermal expansion [K^{-1}]
$\boldsymbol{\eta}$	diffusing mass flux [kg m^{-2} s^{-1}]
ϑ	relative temperature, $T-T_0$ [K]
Λ_ϑ	thermal conductivity [W m^{-1} K^{-1}]
Λ_m	diffusive conductivity [kg s^{-1} m^{-3}]
μ_d	chemical potential [J kg^{-1}]
μ, λ	Lamé constants [N m^{-2}]
ρ_d	bulk mass density of the diffusing substance [kg m^{-3}]
ρ_s	bulk mass density of the solid [kg m^{-3}].

be bounded by a smooth surface a, oriented in space by the normal unit vector $\mathbf{n}$ (Fig. 1).

The equations of mass continuity result from the law of conservation of mass for the solid and the diffusive substance separately, as we have assumed non-occurrence of chemical reactions. Changes of mass in the volume v result from their outflow through the control surface a. This is expressed as

$$\int_v \frac{\partial \rho_s}{\partial t}\,\mathrm{d}v = -\int_a \rho_s \mathbf{v}\cdot\mathbf{n}\,\mathrm{d}a \tag{2}$$

for the solid body and

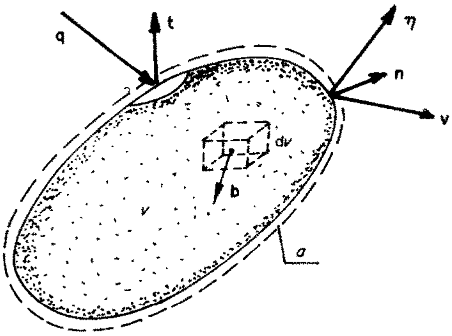

FIG. 1.

$$\int_v \frac{\partial \rho_d}{\partial t}\,\mathrm{d}v = -\int_a [(\rho_d-\rho^*)\mathbf{v}+\rho^*\mathbf{w}]\cdot\mathbf{n}\,\mathrm{d}a \tag{3}$$

for the diffusing substance.

Applying the Gauss–Ostrogradsky theorem and the fact that the volume v was arbitrarily chosen, it is possible to write the above mass balance equations locally. Thus, for the solid body

$$\frac{\partial \rho_s}{\partial t} + \operatorname{div} \rho_s \mathbf{v} = 0\,; \tag{4}$$

and for the diffusing substance

$$\frac{\partial \rho_d}{\partial t} + \operatorname{div} \rho_d \mathbf{v} = -\operatorname{div} \boldsymbol{\eta} \tag{5}$$

or

$$\rho_s \frac{\mathrm{d}c}{\mathrm{d}t} = -\operatorname{div} \boldsymbol{\eta}, \quad \frac{\mathrm{d}(\cdot)}{\mathrm{d}t} = \frac{\partial(\cdot)}{\partial t} + \mathbf{v}\cdot\operatorname{grad}(\cdot) \tag{6}$$

where

$$\boldsymbol{\eta} = \rho^*(\mathbf{w}-\mathbf{v}) \tag{7}$$

will be called the flux of mass of the diffusive substance through the control surface 'fixed' to the solid.

3. EQUATIONS OF MOTION

From the dynamics point of view the existence of the diffusive substance in a solid is of no great significance. Its mass is negligibly small when compared with the mass of the solid contained in a given volume, i.e. $c \ll 1$. Also, the momentum of the flux of diffusing mass is negligible when compared with that of the solid. Taking into account the kinematic model adopted in the previous section, we can express the momentum of the medium as

$$\mathbf{P} = \int_v [(\rho-\rho^*)\mathbf{v}+\rho^*\mathbf{w}]\,\mathrm{d}v = \int_v (\rho\mathbf{v}+\boldsymbol{\eta})\,\mathrm{d}v \cong \int_v \rho_s\mathbf{v}\,\mathrm{d}v. \tag{8}$$

The time change of momentum of the medium is therefore equal to the time derivative of momentum of the solid, i.e.

$$\dot{\mathbf{P}} = \int_v \rho_s\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t}\,\mathrm{d}v. \tag{9}$$

The equation of mass continuity (equation (3)) was used in the above operations. Since the momentum of the diffusing substance is disregarded in the global balance of the momentum, we shall also ignore the mechanical interactions resulting from the relative motion of the two components (dilatational interactions, however, will be taken into account). Thus, we shall assume that the change of momentum is caused by the action of the surface and body forces on the solid, i.e.

$$\dot{\mathbf{P}} = \int_a \mathbf{t}\,\mathrm{d}a+\int_v \rho_s\mathbf{b}\,\mathrm{d}v \tag{10}$$

where $\mathbf{t}$ denotes the stress vector and $\mathbf{b}$ the body force. The stress vector is expressed by the Cauchy stress tensor

$$\mathbf{t} = \mathbf{T}\cdot\mathbf{n} \tag{11}$$

where $\mathbf{T} = \mathbf{T}^{\mathrm{T}}$ is the stress tensor for the medium as a whole. One can deduce that it consists of a part $\mathbf{T}_s$ and a part $T_d\mathbf{I}$ arising from the presence of the diffusive substance in the solid, i.e.

$$\mathbf{T} = \mathbf{T}_s+T_d\mathbf{I} \tag{12}$$

where $\mathbf{I}$ denotes the unit tensor. Changing the surface integral into the volume integral in equation (10) and comparing equations (10) and (9), we arrive at an equation of motion of the form

$$\operatorname{div}\mathbf{T}+\rho_s\mathbf{b} = \rho_s\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t}. \tag{13}$$

As can be seen, this equation is analogous to that for the solid alone, owing to the foregoing simplifications.

4. BALANCE OF ENERGY

The definition of a thermodynamic system is essential in balancing the energy of multicomponent media. The reference system here will be a solid body with a control surface fixed to it. Thus, the energy balance will be derived for any arbitrarily chosen volume (Fig. 1), being bounded by a smooth surface fixed to the solid. The system defined in this way is an open system, i.e. not only the heat but also the diffusive mass flow through the surface a. The global equation of the energy balance is

$$\dot{\mathcal{U}}+\dot{\mathcal{K}} = \mathcal{L}+\mathcal{Q} \tag{14}$$

where dots denote time energy changes with convective velocity $\mathbf{v}$. Here $\mathcal{U}$ denotes the internal energy of the substance contained in the volume v. It consists of the internal energy of the solid and of the internal energy of the diffusing substance, i.e.

$$\mathcal{U} = \int_v (\rho_s u_s+\rho_d u_d)\,\mathrm{d}v \tag{15}$$

where u_s and u_d denote the internal energy per unit mass of the solid and of the diffusive substance, respectively. The time derivative of this energy is expressed as

$$\dot{\mathcal{U}} = \int_v \rho_s\frac{\mathrm{d}u}{\mathrm{d}t}\,\mathrm{d}v+\int_a u_d\boldsymbol{\eta}\cdot\mathbf{n}\,\mathrm{d}a \tag{16}$$

where

$$u = u_s+cu_d \tag{17}$$

is the internal energy of the medium as a whole per unit mass of the solid.

As can be seen, the convection of internal energy by the diffusing substance is taken into account in equation (16) (second integral). Analogously to the way of balancing the momentum, we shall disregard the kinetic energy of the diffusing substance and write

$$\mathcal{K} = \frac{1}{2}\int_v [(\rho-\rho^*)\mathbf{v}\cdot\mathbf{v}+\rho^*\mathbf{w}\cdot\mathbf{w}]\,\mathrm{d}v \cong \frac{1}{2}\int_v \rho_s\mathbf{v}\cdot\mathbf{v}\,\mathrm{d}v. \tag{18}$$

The time changes of this energy will then be expressed as

$$\dot{\mathcal{K}} = \int_v \rho_s\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t}\cdot\mathbf{v}\,\mathrm{d}v. \tag{19}$$

The mechanical power $\mathcal{L}$ consists of the surface force and the body force powers acting on the solid, i.e.

$$\mathcal{L} = \int_a \left(\mathbf{T}\mathbf{v}+\frac{1}{\rho_d}T_d\boldsymbol{\eta}\right)\cdot\mathbf{n}\,\mathrm{d}a+\int_v (\rho\mathbf{v}+\boldsymbol{\eta})\cdot\mathbf{b}\,\mathrm{d}v. \tag{20}$$

As can be seen, the mechanical power of the relative motion of the diffusive substance with respect to the solid is also taken into consideration. The Cauchy formula for stresses has been used in equation (20). We can rewrite equation (20) using the Gauss–Ostrogradsky theorem, and the equation of motion (13) as

$$\mathscr{L} = \int_v \left(\operatorname{tr} \mathbf{TD} + \rho_s \frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} \cdot \mathbf{v} + \operatorname{div} \frac{1}{\rho_d} T_d \boldsymbol{\eta} \right) \mathrm{d}v \quad (21)$$

where $\rho \cong \rho_s$ and $\boldsymbol{\eta} \cdot \mathbf{b} \cong 0$ were substituted and

$$\mathbf{D} = \tfrac{1}{2}[\operatorname{grad} \mathbf{v} + (\operatorname{grad} \mathbf{v})^T]. \quad (22)$$

D denotes the symmetric strain rate tensor.

Some mechanical effects connected with the movement of the diffusive mass have been neglected. From the energetic point of view, however, the energy generated by the diffusing substance may play an important role in the global energy balance. The diffusion process in solids is known to be a thermally activated process. The flux of mass diffusing in the body may carry a considerable amount of energy (heat). The energy of the mass flux is expressed by a non-mechanical power $\boldsymbol{\eta} s_d T$. Globally, the heat supplied to the system is therefore equal, in our case, to the flux **q**, which results from the heat conduction and the heat transported by diffusing mass $\boldsymbol{\eta} s_d T$

$$\mathscr{Q} = \int_a (-\mathbf{q} + s_d T \boldsymbol{\eta}) \cdot \mathbf{n} \, \mathrm{d}a$$
$$= \int_v \operatorname{div} (-\mathbf{q} + s_d T \boldsymbol{\eta}) \, \mathrm{d}v. \quad (23)$$

Substituting these components of energy balance into the global equation (14) we obtain the following equation expressing the first principle of thermodynamics (here we write at once its local form):

$$\rho_s \dot{u} = \operatorname{tr} \mathbf{TD} + \rho_s \mu_d \dot{c} - \operatorname{div} \mathbf{q} - \boldsymbol{\eta} \operatorname{grad} \mu_d \quad (24)$$

where

$$\mu_d = u_d - \frac{1}{\rho_d} T_d - s_d T \quad (25)$$

will be called the chemical potential (free enthalpy density). According to this equation, the changes of the internal energy in our system are due to energy supplied by the mechanical power of the solid (first term), by the changes of the concentration of the diffusing mass (second term) and by the non-mechanical energy supplied (third and fourth terms).

5. BALANCE OF ENTROPY

Total entropy $\mathscr{S}$ in the volume v can be divided into entropy $\mathscr{S}_e$ exchangeable with the surroundings through the surface a and the entropy produced inside the system $\mathscr{S}_i$. The latter is always nonnegative, and in accord with the second principle of thermodynamics satisfies the inequality

$$\dot{\mathscr{S}}_i = \dot{\mathscr{S}} - \dot{\mathscr{S}}_e \geqslant 0. \quad (26)$$

The total entropy $\mathscr{S}$ consists of the entropy of the solid and the entropy of diffusing mass, i.e.

$$\mathscr{S} = \int_v (\rho_s s_s + \rho_d s_d) \, \mathrm{d}v. \quad (27)$$

Its time derivative takes the form

$$\dot{\mathscr{S}} = \int_v \rho_s \dot{s} \, \mathrm{d}v + \int_a s_d \boldsymbol{\eta} \cdot \mathbf{n} \, \mathrm{d}a \quad (28)$$

where

$$s = s_s + c s_d \quad (29)$$

is the total entropy per unit mass of the solid.

The entropy exchangeable with the surroundings is assumed to be equal to the total non-mechanical power exchanged with the ambient medium referred to the absolute temperature, i.e.

$$\dot{\mathscr{S}}_e = \int_a \frac{-\mathbf{q} + \boldsymbol{\eta} s_d T}{T} \cdot \mathbf{n} \, \mathrm{d}a. \quad (30)$$

Inequality (26) can now be written in a local form as

$$\rho_s \dot{s} T + \operatorname{div} \mathbf{q} - \frac{\mathbf{q}}{T} \cdot \operatorname{grad} \vartheta \geqslant 0 \quad (31)$$

where $\vartheta = T - T_0$ denotes the relative temperature referred to the temperature of the natural state T_0. Equation (24) will help to exclude div **q** from inequality (29)

$$-\rho_s(\dot{u} - \dot{s}T) + \operatorname{tr} (\mathbf{TD}) + \rho_s \mu_d \dot{c}$$
$$- \boldsymbol{\eta} \operatorname{grad} \mu_d - \frac{\mathbf{q}}{T} \operatorname{grad} \vartheta \geqslant 0. \quad (32)$$

Equation (32) shows the Clausius–Duhem inequality for the medium contained in unit volume of a particular configuration of the solid, i.e. it is expressed by the space variables $(\mathbf{x}, t)$. Its form expressed in terms of the material variables $(\mathbf{X}, t)$ (reference configuration of the solid) is

$$-\dot{U} + \dot{S}T + \operatorname{tr} \mathbf{T}^R \dot{\mathbf{E}} + M_d \dot{c} + D \geqslant 0 \quad (33)$$

where $U = \rho_{0s} u$, $S = \rho_{0s} s$, $M_d = \rho_{0s} \mu_d$, $\rho_{0s} = \rho_s J$ are respectively the internal energy, entropy, chemical potential and solid mass density, all per unit volume of the reference configuration, and $J = \det \mathbf{F}$ is the Jacobian, i.e. the determinant of the deformation gradient. $\mathbf{T}^R$ denotes the second Piola–Kirchhoff stress tensor. **E** the Green strain tensor and

$$D = -\boldsymbol{\eta}_0 \cdot \operatorname{Grad} \mu_d - \frac{\mathbf{q}_0}{T} \operatorname{Grad} \vartheta \quad (34)$$

where $\boldsymbol{\eta}_0$ and $\mathbf{q}_0$ are the flux of diffusing mass and the heat flux, respectively, measured per unit area of the reference configuration, and Grad is the gradient operator with respect to material coordinate **X**.

The global function of free enthalpy per unit volume of the reference configuration is defined as

$$G \overset{\text{def}}{=} U - TS - \operatorname{tr} \mathbf{T}^R \mathbf{E} \quad (35)$$

and inequality (33) can now be expressed with the help of this function. As a final result we obtain

$$-\dot{G}-S\dot{\vartheta}-\operatorname{tr}\dot{\mathbf{T}}^{\mathrm{R}}\mathbf{E}+M_{\mathrm{d}}\dot{c}+D \geqslant 0. \qquad (36)$$

Consequences resulting from this inequality will be discussed in the next section.

6. EQUATIONS OF STATE: PHYSICAL RELATIONS

Our considerations are based on the grounds of the classical theory of irreversible processes, i.e. processes occurring close to the states of equilibrium. The description of a non-equilibrium state is provided by the adoption of the principle of the local state, which recognizes that each of the independent quantities of the equilibrium end-states must now be replaced by an instantaneous field.

Constitutive relations, which describe inner properties of the medium, are expressed by two sets of equations. In our case they are the basic equation of state

$$G = G(\mathbf{T}^{\mathrm{R}}, \vartheta, c, G_1, G_2) \qquad (37)$$

where $G_1 = |\operatorname{Grad}\vartheta|$, $G_2 = |\operatorname{Grad}\mu_{\mathrm{d}}|$, and the rate equations (transport equations), which relate the fluxes and generalized forces appearing in the expression for entropy production. It should be emphasized that the rate equations do not have to be linear, and the transport coefficients are, in a general case, functions of the parameters of state. In the case of linear equations the appropriate transport coefficients satisfy Onsager's relations.

The independent variables in our case are the stress tensor $\mathbf{T}^{\mathrm{R}}$, the relative temperature ϑ, the concentration of diffusing mass c, the temperature gradient $\mathbf{G}_1 = \operatorname{Grad}\vartheta$ and the gradient of chemical potential $\mathbf{G}_2 = \operatorname{Grad}\mu_{\mathrm{d}}$. The first three variables are at the same time parameters of the 'local equilibrium', i.e. they fully describe the state of the system isolated from the surroundings by an adiabatic boundary.

We shall differentiate the function of free enthalpy (equation (37)) with respect to time and we shall substitute it into inequality (36). This leads to

$$-\operatorname{tr}\left(\mathbf{E}+\frac{\partial G}{\partial \mathbf{T}^{\mathrm{R}}}\right)\dot{\mathbf{T}}^{\mathrm{R}}-\left(S+\frac{\partial G}{\partial \vartheta}\right)\dot{\vartheta}+\left(M_{\mathrm{d}}-\frac{\partial G}{\partial c}\right)\dot{c}$$
$$-\frac{\partial G}{\partial G_1}\dot{G}_1-\frac{\partial G}{\partial G_2}\dot{G}_2-\frac{\mathbf{q}_0}{T}\cdot\mathbf{G}_1-\boldsymbol{\eta}_0\cdot\mathbf{G}_2 \geqslant 0. \qquad (38)$$

This inequality must be satisfied at every instant and at every place for any arbitrary imaginary process and also in the state of equilibrium. The first five terms in inequality (38) are linear with respect to $\dot{\mathbf{T}}^{\mathrm{R}}$, $\dot{\vartheta}$, $\dot{c}$, $\dot{G}_1$ and $\dot{G}_2$, as none of the coefficients of these variables depend on them. Furthermore, the variables $\dot{\mathbf{T}}^{\mathrm{R}}$, $\dot{\vartheta}$, $\dot{c}$, $\dot{G}_1$, $\dot{G}_2$ are independent of each other and can be arbitrarily chosen, so they can take positive and negative values. Then, in order to make the process admissible in each case, the linear terms must disappear. We therefore obtain

$$\mathbf{E} = -\left(\frac{\partial G}{\partial \mathbf{T}^{\mathrm{R}}}\right)_{\vartheta, c, G_1, G_2}$$
$$S = -\left(\frac{\partial G}{\partial \vartheta}\right)_{\mathbf{T}^{\mathrm{R}}, c, G_1, G_2}$$
$$M_{\mathrm{d}} = \left(\frac{\partial G}{\partial c}\right)_{\mathbf{T}^{\mathrm{R}}, \vartheta, G_1, G_2}$$
$$\left.\frac{\partial G}{\partial G_1}\right|_{\mathbf{T}^{\mathrm{R}}, \vartheta, c, G_2} = 0$$
$$\left.\frac{\partial G}{\partial G_2}\right|_{\mathbf{T}^{\mathrm{R}}, \vartheta, c, G_1} = 0. \qquad (39)$$

The above are the basic equations of state.

We see that the Gibbs function G does not depend on the modulus of gradients G_1 and G_2.

Application of equations (39) leads to obtaining from equation (38) a residual inequality of the form

$$D = -\boldsymbol{\eta}_0 \operatorname{Grad}\mu_{\mathrm{d}}-\frac{\mathbf{q}_0}{T}\operatorname{Grad}\vartheta \geqslant 0. \qquad (40)$$

We assume D (the dissipation function) to be a positive defined quadratic form. Then the fluxes $\boldsymbol{\eta}_0$ and $\mathbf{q}_0$ must be of the form

$$\boldsymbol{\eta}_0 = -\eta_1 \operatorname{Grad}\mu_{\mathrm{d}}-\eta_2 \operatorname{Grad}\vartheta \qquad (41\mathrm{a})$$
$$\mathbf{q}_0/T = -q_1 \operatorname{Grad}\mu_{\mathrm{d}}-q_2 \operatorname{Grad}\vartheta \qquad (41\mathrm{b})$$

where coefficients η_1, η_2, q_1 and q_2 must satisfy the Silvester criterion

$$\eta_1 \geqslant 0, \quad \eta_1 q_2 \geqslant \left(\frac{\eta_2+q_1}{2}\right)^2. \qquad (42)$$

Equation (41a) forms a generalized mass flux of the diffusing substance and equation (42) a generalized flux of heat.

7. LINEAR CONSTITUTIVE EQUATIONS

We shall now specify the linear physical relations. The difference between the Piola–Kirchhoff stress tensor and that of the Cauchy one is negligible in a linear theory, i.e. $\mathbf{T}^{\mathrm{R}} \cong \mathbf{T}$. We shall expand the function of free enthalpy G into a Taylor series in the surroundings of a mechanically non-deformed state and at a concentration equal to zero

$$G(\mathbf{T}, \vartheta, c) = G(0, \vartheta, 0)+\frac{\partial G(0, \vartheta, 0)}{\partial \mathbf{T}}\cdot\mathbf{T}$$
$$+\frac{\partial G(0, \vartheta, 0)}{\partial c}c+\frac{1}{2}\frac{\partial^2 G(0, \vartheta, 0)}{\partial \mathbf{T}\otimes\partial \mathbf{T}}\cdot(\mathbf{T}\otimes\mathbf{T})$$
$$+\frac{\partial^2 G(0, \vartheta, 0)}{\partial \mathbf{T}\partial c}\cdot\mathbf{T}c+\frac{1}{2}\frac{\partial^2 G(0, \vartheta, 0)}{\partial c^2}c^2. \qquad (43)$$

Calculating the derivative of function G with respect to $\mathbf{T}$ we obtain the dependencies between strains and stresses (see equation (39))

$$-\mathbf{E} = \frac{\partial G(0,\vartheta,0)}{\partial \mathbf{T}} + \mathbf{A}^{(4)} \cdot \mathbf{T} + \mathbf{B}c \qquad (44)$$

where $\mathbf{A}^{(4)} = \partial^2 G(0,\vartheta,0)/\partial \mathbf{T} \otimes \partial \mathbf{T}$ and $\mathbf{B} = \partial^2 G(0,\vartheta,c)/\partial \mathbf{T}\partial c$ are some tensors of fourth and second order, dependent generally on the temperature. When the stress state equals zero and the content of the diffusing substance is also zero, only the following thermal deformations are possible:

$$\mathbf{E}^{\mathrm{T}} = \alpha_\vartheta \vartheta \mathbf{I} = -\frac{\partial G(0,\vartheta,0)}{\partial \mathbf{T}} \qquad (45)$$

where α_ϑ denotes the coefficient of linear thermal expansion. In a case where mechanical and temperature fields are nonexistent, deformations may be due to the concentration, so

$$\mathbf{E}^c = \alpha_c c \mathbf{I} = -\mathbf{B}c \qquad (46)$$

where α_c denotes the coefficient of linear diffusive expansion. When only the mechanical field is present

$$\mathbf{E}^{\mathrm{M}} = 2\mu' \mathbf{T} + \lambda' \operatorname{tr} \mathbf{T} \qquad (47)$$

and

$$2\mu' = \frac{1}{2\mu}, \quad \lambda' = -\frac{\lambda}{2\mu(2\mu+3\lambda)} \qquad (48)$$

where μ and λ are Lame constants. Thus equation (44) takes the form

$$\mathbf{E} = 2\mu'\mathbf{T} + (\lambda' \operatorname{tr} \mathbf{T} + \alpha_\vartheta \vartheta + \alpha_c c)\mathbf{I} \qquad (49)$$

where $(\mathbf{A}^{(4)})_{ijkl} = -[\lambda' \delta_{ij}\delta_{kl} + \mu'(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})]$ is an isotropic tensor of elasticity.

After the inversion with respect to stresses we get

$$\mathbf{T} = 2\mu\mathbf{E} + [\lambda \operatorname{tr} \mathbf{E} - \gamma_\vartheta \vartheta - \gamma_c c]\mathbf{I} \qquad (50)$$

where $\gamma_\vartheta = (2\mu+3\lambda)\alpha_\vartheta$, $\gamma_c = (2\mu+3\lambda)\gamma_c$. The chemical potential of the diffusing substance is

$$\rho_{0s}\mu_{\mathrm{d}} = \frac{\partial G(0,\vartheta,0)}{\partial c} - \alpha_c \operatorname{tr} \mathbf{T} + \Gamma_c c \qquad (51)$$

where $\Gamma_c = \partial^2 G(0,\vartheta,0)/\partial^2 c > 0$ determines the influence of the concentration on the chemical potential.

We assume $\partial G(0,\vartheta,0)/\partial c$ to be the following function of the temperature:

$$\frac{\partial G(0,\vartheta,0)}{\partial c} = \Gamma_\vartheta \vartheta. \qquad (52)$$

Coefficients Γ_ϑ, α_c, Γ_c are generally not constant. So, for the linear theory they ought to be taken as average values in the range of alterations of the state parameters. Clearer interpretation of these coefficients is possible when comparing the differential of equation (51) with the differential of equation (25) for an equilibrium state. We then obtain

$$\Gamma_\vartheta = -\frac{1}{c}\left[c_p^* \ln \frac{T}{T_0} + \left(\frac{\partial T_{\mathrm{d}}}{\partial \vartheta}\right)_{\operatorname{tr}\mathbf{T},c}\right]$$

$$\alpha_c = \frac{1}{c}\left(\frac{\partial T_{\mathrm{d}}}{\partial \operatorname{tr} \mathbf{T}}\right)_{\vartheta,c}$$

$$\Gamma_c = -\frac{1}{c}\left(\frac{\partial T_{\mathrm{d}}}{\partial c}\right)_{\operatorname{tr}\mathbf{T},\vartheta} \qquad (53)$$

where c_p^* is the specific heat of the diffusing substance at constant pressure per unit total volume. We can therefore determine coefficients Γ_ϑ, α_c and Γ_c by measuring the diffusive stress increase at the condition indicated by the subscripts in equations (53). Since

$$c_p = T\left(\frac{\partial S}{\partial T}\right)_{\mathbf{T},c} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{\mathbf{T},c} \qquad (54)$$

denotes the specific heat at constant pressure and concentration per unit total volume, double integration of equation (54) with respect to the temperature results in (see, e.g. ref. [2])

$$G|_{\mathbf{T},c} = G(0,\vartheta,0) = -\int_{T_0}^{T}\left(\int_{T_0}^{\xi} \frac{c_p}{\xi}\,\mathrm{d}\xi\right)\mathrm{d}\xi. \qquad (55)$$

The thermodynamic functions can now be written in an explicit form. The Gibbs function (43) is therefore

$$G(\mathbf{T},\vartheta,0) = -\int_{T_0}^{T}\left(\int_{T_0}^{\xi} \frac{c_p}{\xi}\,\mathrm{d}\xi\right)\mathrm{d}\xi - \alpha_\vartheta \vartheta \operatorname{tr} \mathbf{T}$$
$$+\Gamma_\vartheta \vartheta c - \frac{1}{2}\lambda'(\operatorname{tr}\mathbf{T})^2 - \mu' \operatorname{tr}(\mathbf{T}\mathbf{T})$$
$$-\alpha_c \operatorname{tr} \mathbf{T} c + \tfrac{1}{2}\Gamma_c c^2. \qquad (56)$$

According to equation (39), the entropy of the medium is expressed as

$$S = \int_{T_0}^{T} \frac{c_p}{\xi}\,\mathrm{d}\xi + \alpha_\vartheta \operatorname{tr} \mathbf{T} - \Gamma_\vartheta c. \qquad (57)$$

The function of internal energy takes the form

$$U = \mu \operatorname{tr} \mathbf{E}\mathbf{E} + \tfrac{1}{2}\lambda(\operatorname{tr}\mathbf{E})^2 - (\gamma_\vartheta \vartheta + \gamma_c c)\operatorname{tr}\mathbf{E}$$
$$+\frac{3}{2(2\mu+3\lambda)}(\gamma_\vartheta \vartheta + \gamma_c c)^2 + \Gamma_\vartheta \vartheta c + \tfrac{1}{2}\Gamma c^2$$
$$+\gamma_\vartheta T \operatorname{tr}\mathbf{E} - 3\alpha_\vartheta T(\gamma_\vartheta \vartheta + \gamma_c c) - \Gamma_\vartheta T c$$
$$+T\int_{T_0}^{T} \frac{c_p}{\xi}\,\mathrm{d}\xi - \int_{T_0}^{T}\left(\int_{T_0}^{\xi} \frac{c_p}{\xi}\,\mathrm{d}\xi\right)\mathrm{d}\xi. \qquad (58)$$

In order to calculate the difference between specific heat at constant pressure and the specific heat at constant volume, we shall apply the function of free energy

$$F \overset{\mathrm{def}}{=} U - ST. \qquad (59)$$

We calculate the secondary derivative of this function with respect to the temperature, and obtain

$$c_\vartheta = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{\mathrm{E},c} = c_p - 3\alpha_\vartheta\gamma_\vartheta T \tag{60}$$

where c_ϑ denotes the total specific heat at constant volume per unit volume. Dependence (60) will be utilized in the equation of heat conduction.

8. LINEAR EQUATIONS OF HEAT AND MASS TRANSFER

In Section 6 the phenomenological equations of heat and mass transport were obtained. When taking into account the fact that there is a slight difference between an area in the current and reference configuration of a body in linear theory, so we can rewrite equations (41a) and (41b) as

$$\begin{aligned} \boldsymbol{\eta} &= -\eta_1 \operatorname{grad}\mu_{\mathrm{d}} - \eta_2 \operatorname{grad}\vartheta \\ \mathbf{q}/T &= -q_1 \operatorname{grad}\mu_{\mathrm{d}} - q_2 \operatorname{grad}\vartheta. \end{aligned} \tag{61}$$

The criteria

$$\eta_1 \geqslant 0 \quad \text{and} \quad \eta_1 q_2 \geqslant \left(\frac{\eta_2 + q_1}{2}\right)^2 \tag{62}$$

must be fulfilled for any process, and also when $\boldsymbol{\eta} = 0$ and $\mathbf{q} = 0$ but $\operatorname{grad}\mu \neq 0$ and $\operatorname{grad}\vartheta \neq 0$. In such a case the coefficients are related as follows (see also ref. [6])

$$\eta_1 q_2 = q_1 \eta_2. \tag{63}$$

In order to fulfil criteria (62)

$$q_1 = \eta_2. \tag{64}$$

The chemical potential of the diffusive substance is (see equation (51))

$$\mu_{\mathrm{d}} = \frac{1}{\rho_{\mathrm{s}}}(\Gamma_\vartheta\vartheta - \alpha_c \operatorname{tr}\mathbf{T} + \Gamma_c c). \tag{65}$$

Substituting the potential (65) with constant coefficients into equation (61) and after ordering we get

$$\begin{aligned} \boldsymbol{\eta} &= -D_\vartheta \operatorname{grad}\vartheta + D_{\mathrm{T}} \operatorname{grad}\operatorname{tr}\mathbf{T} - D_c \operatorname{grad} c \\ \mathbf{q} &= -\lambda_\vartheta \operatorname{grad}\vartheta + \lambda_{\mathrm{T}} \operatorname{grad}\operatorname{tr}\mathbf{T} - \lambda_c \operatorname{grad} c \end{aligned} \tag{66}$$

where

$$D_\vartheta = \eta_1\Gamma_\vartheta/\rho_{\mathrm{s}} + \eta_2$$

denotes the thermodiffusion coefficient (Soret effect)

$$D_{\mathrm{T}} = \eta_1\alpha_c/\rho_{\mathrm{s}}$$

denotes the coefficient of influence of the volume stress on the diffusion

$$D_c = \eta_1\Gamma_c/\rho_{\mathrm{s}}$$

denotes the diffusion coefficient

$$\lambda_\vartheta = Tq_1\Gamma_\vartheta/\rho_{\mathrm{s}} + Tq_2$$

denotes the thermal conductivity coefficients

$$\lambda_{\mathrm{T}} = Tq_1\alpha_c/\rho_{\mathrm{s}}$$

denotes the coefficient of influence of the volume stress on the heat flow, and

$$\lambda_c = Tq_1\Gamma_c/\rho_{\mathrm{s}}$$

denotes the coefficient of heat flow caused by the diffusion (Dufour effect). The coefficients in equation (64) are established experimentally. Some of them—D_ϑ, d_c, λ_ϑ, λ_c—are discussed in the literature dealing with heat and mass transfer (see, e.g. refs. [1–5]). Coefficients D_{T} and λ_{T} can be calculated from the formulae

$$\begin{aligned} D_{\mathrm{T}} &= D_c\alpha_c/\Gamma_c \\ \lambda_{\mathrm{T}} &= \lambda_c\alpha_c/\Gamma_c. \end{aligned} \tag{67}$$

The coefficient in equations (61) are related to those listed above as follows:

$$\begin{aligned} &\eta_1 = D_c\rho_{\mathrm{s}}/\Gamma_c = \lambda_{\mathrm{m}}, \quad \eta_2 = D_\vartheta - D_c\frac{\Gamma_\vartheta}{\Gamma_c} = \lambda_{\mathrm{m}}\delta_{\mathrm{m}} \\ &Tq_1 = \lambda_c\rho_{\mathrm{s}}/\Gamma_c, \quad Tq_2 = \lambda_\vartheta - \lambda_c\frac{\Gamma_\vartheta}{\Gamma_c} = \lambda_\vartheta\delta_\vartheta \end{aligned} \tag{68}$$

where

$$\delta_{\mathrm{m}} = \delta_{\mathrm{s}}\Gamma_c/\rho_{\mathrm{s}} - \Gamma_\vartheta/\rho_{\mathrm{s}}, \quad \delta_\vartheta = 1 - \delta_{\mathrm{D}}\Gamma_\vartheta/\Gamma_c \tag{69}$$

$\delta_{\mathrm{s}} = D_\vartheta/D_c$ is the Soret coefficient and $\delta_{\mathrm{D}} = \lambda_c/\lambda_\vartheta$ the Dufour coefficient.

It is accordingly pointed out in the literature dealing with heat and mass transfer (see, e.g. ref. [4]) that the Dufour effect has a slight importance in practical aspects; one usually assumes that $\delta_{\mathrm{D}} = 0$. So we then get $\delta_\vartheta = 1$ and $q_1 = \eta_2 = 0$. Owing to this simplification, we obtain finally

$$\begin{aligned} \boldsymbol{\eta} &= -\lambda_{\mathrm{m}} \operatorname{grad}\mu_{\mathrm{d}} \\ \mathbf{q} &= -\lambda_\vartheta \operatorname{grad}\vartheta. \end{aligned} \tag{70}$$

The transport equations (70) will be used later on.

9. DIFFERENTIAL EQUATIONS OF THE THEORY

The set of differential equations of the thermodiffusion for solids consists of the differential equations governing the heat and diffusion mass transfer and the equation describing the mechanical deformations.

To derive the equation of thermal conductivity one must calculate the time derivative of the internal energy equation (58) and compare it with that of equation (24). After some operations we get

$$T\dot{S} = -\operatorname{div}\mathbf{q} - \boldsymbol{\eta}\cdot\operatorname{grad}\mu_{\mathrm{d}}. \tag{71}$$

Utilizing the expression for entropy (57) and the transport equations (70), we arrive at the equation of heat conduction of the form

$$\lambda_\vartheta\nabla^2\vartheta = \kappa_\vartheta\dot{\vartheta} + \kappa_u \operatorname{div}\dot{\mathbf{u}} - \kappa_\mu\dot{\mu}_{\mathrm{d}} \tag{72}$$

where

$$\kappa_\vartheta = c_v - \frac{\Gamma_v + 3\alpha_c\gamma_\vartheta}{\Gamma_c + 3\alpha_c\gamma_c}\left(\frac{c_p - c_v}{\gamma_\vartheta}\gamma_c + \Gamma_\vartheta\right)$$

$$\kappa_u = \frac{c_p - c_v}{3\alpha_\vartheta} - \frac{\gamma_c}{\Gamma_c + 3\alpha_c\gamma_c}\left(\frac{c_p - c_v}{\gamma_\vartheta}\gamma_c + \Gamma_\vartheta\right)$$

$$\kappa_\mu = \frac{\rho_s}{\Gamma_c + 3\alpha_c\gamma_c}\left(\frac{c_p - c_v}{\gamma_\vartheta}\gamma_c + \Gamma_\vartheta\right). \tag{73}$$

The expression $\boldsymbol{\eta}\cdot\boldsymbol{\eta}$ is omitted in equation (72) as negligibly small.

Inserting equation (70) into the equation of mass continuity (6), we obtain the equation of thermodiffusion

$$\Lambda_m \nabla^2 \mu_d = -\lambda_\vartheta \dot{\vartheta} + \lambda_u \operatorname{div} \dot{\mathbf{u}} + \lambda_\mu \dot{\mu}_d \tag{74}$$

where

$$\lambda_\vartheta = \rho_s \frac{\Gamma_\vartheta + 3\alpha_c\gamma_\vartheta}{\Gamma_c + 3\alpha_c\gamma_c}$$

$$\lambda_u = \rho_s \frac{\gamma_c}{\Gamma_c + 3\alpha_c\gamma_c}$$

$$\lambda_\mu = \frac{\rho_s^2}{\Gamma_c + 3\alpha_c\gamma_c}. \tag{75}$$

The displacement equation of the theory is obtained by inserting physical relations (50) into the equation of motion (13).

After some operations and application of the strain tensor defined by the displacement vector

$$\mathbf{E} = \tfrac{1}{2}[\operatorname{grad} \mathbf{u} + (\operatorname{grad} \mathbf{u})^T] \tag{76}$$

the displacement equations take the form

$$\mu\nabla^2\mathbf{u} + \delta_u \operatorname{grad} \operatorname{div} \mathbf{u} + \rho_s \boldsymbol{b} = \rho_s \ddot{\mathbf{u}} + \delta_\vartheta \operatorname{grad} \vartheta + \delta_\mu \operatorname{grad} \mu_d \tag{77}$$

where

$$\delta_u = \lambda + \mu - \frac{\gamma_c^2}{\Gamma_c + 3\alpha_c\gamma_c}$$

$$\delta_\vartheta = \gamma_\vartheta - \frac{\Gamma_\vartheta + 3\alpha_c\gamma_\vartheta}{\Gamma_c + 3\alpha_c\gamma_c}$$

$$\delta_\mu = \frac{\rho_s}{\Gamma_c + 3\alpha_c\gamma_c}. \tag{78}$$

We have now obtained a complete set of equations of thermodiffusion for solids.There are five unknown functions, u_1, u_2, u_3, ϑ and μ_d, and the same number of differential equations.

The set of equations (72), (74) and (77) is a system of coupled parabolo-hyperbolic equations. Usually there are certain simplifications made, analogous to those used in Nowacki's coupled thermoelasticity and thermodiffusion [2].

The system of equations introduced in this paper enables us to determine the interdependence of the thermodiffusion process, i.e. deformation of a solid, with the process of mass and heat transfer.

Now we shall formulate the initial and boundary conditions for the system of the thermomechanical diffusion equations. For temperature and concentration, the initial conditions are expressed by their distribution at the initial time $t = 0$ as a function of position

$$\vartheta(\mathrm{P},0) = l(\mathrm{P}), \quad \mathrm{P}\in\mathrm{B}, \quad t = 0$$

$$\mu_d(\mathrm{P},0) = k(\mathrm{P}), \quad \mathrm{P}\in\mathrm{B}, \quad t = 0 \tag{79}$$

where P denotes a point of region B, l and k are known functions. The displacement and the velocity fields in the solid at the initial time are determined by known functions g_i and f_i

$$u_i(\mathrm{P},0) = g_i(\mathrm{P}), \quad \dot{u}_i(\mathrm{P},0) = f_i(\mathrm{P}),$$

$$\mathrm{P}\in\mathrm{B}, \quad t = 0, \quad i = 1,2,3. \tag{80}$$

Boundary conditions may take several forms. The heat and diffusion conditions express interaction of the solid and its surroundings, and may be represented at the boundary surface by

$$\vartheta = h(\mathrm{P},t), \quad \mathrm{P}\in\mathrm{A}, \quad t > 0$$

$$\mu_d = m(\mathrm{P},t), \quad \mathrm{P}\in\mathrm{A}, \quad t > 0 \tag{81}$$

when temperature ϑ and chemical potential μ_d at surface A, being functions of the point and time, are known, by

$$\frac{\partial\vartheta}{\partial n} = r(\mathrm{P},t), \quad \mathrm{P}\in\mathrm{A}, \quad t > 0$$

$$\frac{\partial\mu_d}{\partial n} = s(\mathrm{P},t), \quad \mathrm{P}\in\mathrm{A}, \quad t > 0 \tag{82}$$

when temperature gradient $\partial\vartheta/\partial n$ and chemical potential gradient $\partial\mu_d/\partial n$ at surface A, being the function of the point and time, are known, and by

$$\left(\frac{\partial}{\partial n} + \alpha\right)\vartheta(\mathrm{P},t) = f(\mathrm{P},t), \quad \mathrm{P}\in\mathrm{A}, \quad t > 0$$

$$\left(\frac{\partial}{\partial n} + \beta\right)\mu_d(\mathrm{P},t) = g(\mathrm{P},t), \quad \mathrm{P}\in\mathrm{A}, \quad t > 0 \tag{83}$$

when the above functions are known and α and β are certain constant values.

Condition (82) is related to heat and mass flow through surface A. The case $\partial\vartheta/\partial n = 0$ and $\partial\mu_d/\partial n = 0$ is related to thermal and diffusive isolation at the boundary surface.

The mechanical boundary conditions may be simple or mixed. Simple conditions mean that at the boundary surface either external loading

$$\mathbf{p} = \mathbf{T}\cdot\mathbf{n} = \mathbf{p}(\mathrm{P},t), \quad \mathrm{P}\in\mathrm{A}, \quad t > 0 \tag{84}$$

or displacement $\mathbf{u}$ is present

$$u_i = u_i(\mathrm{P},t), \quad \mathrm{P}\in\mathrm{A}, \quad t > 0. \tag{85}$$

We deal with mixed boundary conditions frequently, which means that in such cases there are loadings in the A_p part and displacements in the A_u part of boundary surface $A_p \cup A_u = A$.

10. FINAL REMARKS

The system of equations of thermomechanical diffusion as introduced in this paper is complex; yet despite their complexity they are applied in solving particular boundary problems. Under some assumptions, they are used to describe such processes as thermomechanical treatment of metals (carbonizing, nitriding steel, etc.). These processes are thermally activated, their diffusing substance being, for example, nitrogen, carbon, etc. They are accompanied by deformations of the solid; these deformations, however, have been neglected so far in the theory of thermodiffusion in solids [6]. References [7, 8] indicate that the interaction of the deformation of the solid and the heat and mass flow is considerable and cannot always be ignored.

In order to solve differential equations of thermodiffusion, among others, methods of integral transformations, as in ref. [8], or methods of finite elements [9] are utilized.

Recently, attempts have been made to apply the theory of thermodiffusion in the description of thermomechanical treatment of porous media of sintered powder metals. The thermodiffusion method in improving the mechanical properties of products made of powder metals has been successfully applied in the last few years. It seems to be especially important to analyse the interrelation between dilatation changes and the process of thermodiffusion.

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THEORIE DE LA THERMODIFFUSION POUR LES SOLIDES

Résumé—Le but de cette étude est d'établir un système complet d'équations différentielles de la thermodiffusion dans les solides en tenant compte, en même temps, des champs mécanique, thermique et de masse. L'analyse est basée sur la thermodynamique des phénomènes irréversibles avec les hypothèses habituelles faites dans la théorie de la thermoélasticité et avec l'hypothèse supplémentaire qu'il n'y a pas de réaction chimique et que les températures locales de la matrice et de la substance diffusante sont les mêmes. Des lois générales des flux de chaleur et de masse sont aussi introduites. Avec cette théorie on peut décrire, par exemple, le traitement thermochimique des métaux.

THEORIE DER THERMODIFFUSION IN FESTEN KÖRPERN

Zusammenfassung—Das Ziel dieser Arbeit ist die Herleitung eines kompletten Satzes von Differentialgleichungen für die Thermodiffusion in festen Körpern, die unter Berücksichtigung der mechanischen, der Temperatur- und der Konzentrationsfelder gelten. Die Untersuchungen basieren auf der Thermodynamik der irreversiblen Prozesse bei den üblichen Annahmen der Thermoelastizität, verbunden mit den Annahmen, daß keine chemische Reaktion stattfindet und die lokalen Temperaturen der Matrix sowie die diffundierenden Substanzen erhalten bleiben. Verallgemeinerte Gesetze des Wärme- und Stofftransports werden ebenfalls in dieser Arbeit vorgestellt. Eine solche Theorie kann benutzt werden, um beispielsweise das thermochemische Verhalten von Metallen zu beschreiben.

ТЕОРИЯ ТЕРМОДИФФУЗИИ В ТВЕРДЫХ ТЕЛАХ

Аннотация—Дан вывод замкнутой системы дифференциальных уравнений, описывающих термодиффузию в твердых телах с учетом совместного действия механического, температурного и концентрационного полей. Анализ основан на положениях термодинамики необратимых процессов с учетом обычных допущений теории термоупругости и дополнительного предположения об отсутствии химической реакции и о том, что значения локальных температур решетки и диффундирущего вещества одинаковы. Представлены также обобщенные закономерности для теплового потока и потока массы. Предлагаемая теория может использоваться для описания, например, термохимической обработки металлов.