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Some Features of Mass Transfer in Composite Materials

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Abstract:

The paper deals with the process of mass transfer in a two-phase system which consists of a mobile phase (a liquid or a gas) and dispersed particles forming a spacial structure, i.e. a skeleton. It is shown that in systems like this the process of the mobile phase transfers is greatly affected by forces generated at both interfaces and particle boundaries. These forces are responsible for new regularities of the mass transfer in dispersed systems, in particular, a spontaneous increase in an intensive variable is a possibility.

Keywords: Mass transfer; Composite material; Structure.

Nomenclature

- C coefficient
d size of dispersed particles [m]
F Helmholtz free energy [N m], force [N]
g coefficient which allows for a variation of the surface area of dispersed particles in the process of mass transfer
I integral
K coefficient which allows for the dispersed particles shape and the mode of packing them
km migration coefficient [m⁴ N⁻¹ s⁻¹]
L Lagrange equation
l length [m]
P pressure [Pa]
q flow [m³ m⁻² s⁻¹]
S surface area [m²]
T temperature [K]
t time [s]
u volumetric content of mobile phase expressed in fractions
V volume [m³]
x coordinate [m]

Greek symbols

- γ surface tension [N m⁻¹]
 μ chemical potential [N m g⁻¹]

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Π migration pressure [Pa]

φ dihedral angle

τ relaxation time [s]

Subscripts

α solid phase,

β mobile phase (a gas, a liquid),

$\alpha\alpha$ solid–solid interface,

$\alpha\beta$ solid– mobile phase interface

1. Introduction

The mass transfer in dispersed systems is described at molecular-kinetic and phenomenological levels. The former permits the mechanism of proceeding processes to be revealed and provides the theoretical basis for the development of the phenomenological theory of the mass transfer. For the phenomenological description of the mass transfer process, parabolic differential equations are mainly used which are based on the Fick, Darcy, and capillarity laws. According to these laws, the flow of mass is proportional to the gradient of an intensive variable which causes this flow. Thus, the chemical potential gradient is responsible for diffusion flows of atoms.

Known mass transfer processes are governed by the following regularity: a flow q and the gradient of an intensive variable are oppositely directed and in the process of mass transfer the intensive variable gradient decreases and approaches zero. The gradient of the intensive variable is always normal to the equipotential surface and is directed to the side of a higher intensive variable, while the flow runs from the region having a higher intensive variable value to the region having a lower intensive variable value. It follows from this regularity that if in the system a gradient of the intensive variable exists, the mass transfer is involved in its volume, and vice versa if the system has no gradient of the intensive variable, the mass flows are not observed. The foregoing is true for systems in which processes proceed at atomic or molecular levels, i.e. the transfer of mass is by atoms or molecules. In dispersed structured systems, the mass transfer is greatly affected by highly developed interfaces, and what is more, dispersed particles may be involved in the mass transfer. These two factors violate the above regularity of the mass transfer.

Theory

Two-phase systems were studied. They consisted of a mobile phase (a liquid or a gas) and dispersed crystalline particles which formed a special structure, i.e. a skeleton. The WC-Co, WC-Ni, Cu-SiC [1], W-Ni, W-Co, W-Cu [2], TiB₂-Ni [3] composite materials heated above the melting point of a low-melting ingredient and compacts pressed from dispersed particles are examples of these systems. In the first case, a mobile phase is a metal melt, while in the second case a gas. We assign the quantities which correspond respectively to a solid phase, a mobile phase, particle boundaries and interfaces indexes α , β , $\alpha\alpha$, and $\alpha\beta$, and assume that the volumes of the systems under study have neither temperature gradient ($\text{grad } T = 0$) nor chemical potential gradient ($\text{grad } \mu = 0$).

During isothermal sintering of a compact pressed from dispersed particles, the mobile phase expels from the specimen. The variation of the Helmholtz free energy of this system is given by [4]:

$$\Delta F = \frac{1}{3} (\gamma_{\alpha\alpha} - 2g\gamma_{\alpha\beta}) \Delta S_{\alpha\alpha} \quad (1)$$

Variation of the contact surface area of particles ($\Delta S_{\alpha\alpha}$) as a function of the amount of the mobile phase (ΔV_{β}) is described by [5]:

$$\Delta S_{\alpha\alpha} = \frac{K}{d} \left(\frac{1-u}{u} \right)^{\frac{1}{3}} \Delta V_{\beta} \quad (2)$$

Substituting Eq. (2) into Eq. (1) yields:

$$\Delta F = \frac{K}{3d} (\gamma_{\alpha\alpha} - 2g\gamma_{\alpha\beta}) \left(\frac{1-u}{u} \right)^{\frac{1}{3}} \Delta V_{\beta} \quad (3)$$

It should be noted that Eq. (1) is more precise than Eq. (3), however, the latter has an advantage that lies in allowing for the phase relation in a composite, its structure, dispersion of particles, their geometry and the mode of packing, and the coordination number.

Using the dependence $P = -(\partial F / \partial V)_{T,m}$ [6] is obtained [4]:

$$P_{sh} = \frac{K}{3d} (2g\gamma_{\alpha\beta} - \gamma_{\alpha\alpha}) \left(\frac{1-u}{u} \right)^{\frac{1}{3}} \quad (4)$$

In Eq.(4) P_{sh} is the shrinkage pressure. Expressions (3) and (4) are fair only for composite materials with the open porosity.

The shrinkage pressure is a motive force for the mass transfer of a gas phase from the compact into its environment. In this case, the gas moves from the volume with a higher P_{sh} value into the volume with $P_{sh} = 0$, i.e. the gas flow q moves oppositely to the gradient of P_{sh} pressure. It follows from Eq.(4) that P_{sh} values increase as the gas moves away. This means that in the gas-compact system a spontaneous increase of the intensive variable gradient takes place concurrently with a decrease in the system's energy.

The findings of investigations [7] have allowed the conclusion that composite materials can be classed into two groups depending on the relation between the surface energy at the particle boundaries $\gamma_{\alpha\alpha}$ and that at the interfaces $\gamma_{\alpha\beta}$. Materials with $\gamma_{\alpha\alpha} > 2 \gamma_{\alpha\beta}$ fall into the first group, those with $\gamma_{\alpha\alpha} < 2 \gamma_{\alpha\beta}$ into the second group. A specimen which is prepared from a first-group composite material, heated to the temperature above the melting point of a binding phase and placed at this temperature into a metal melt, whose composition is identical with that of the liquid phase of the composite material, will imbibe the metal melt [8]. Due to the imbibition of the metal melt the liquid phase content of the specimen increases by a factor of 2 – 6, so does the specimen volume. The process proceeds spontaneously. The Helmholtz free energy variation in the specimen-metal melt system is described by the following expression [4]:

$$\Delta F = \frac{1}{3} (2g\gamma_{\alpha\beta} - \gamma_{\alpha\alpha}) \Delta S_{\alpha\alpha} \quad (5)$$

Substituting Eq. (2) into Eq. (5) yields:

$$\Delta F = \frac{K}{3d} (2g\gamma_{\alpha\beta} - \gamma_{\alpha\alpha}) \left(\frac{1-u}{u} \right)^{\frac{1}{3}} \Delta V_{\beta}$$

The liquid phase imbibition by a dispersed structured system is induced by the action of the migration pressure which has designated Π . According to the dependence $\Pi = -(\partial F / \partial V)_{T,m}$, is given by [4]:

$$\Pi = \frac{1}{3}(\gamma_{\alpha\alpha} - 2g\gamma_{\alpha\beta}) \frac{\partial S_{\alpha\alpha}}{\partial V_{\beta}} = \frac{k}{3r}(\gamma_{\alpha\alpha} - 2g\gamma_{\alpha\beta}) \left(\frac{1-u}{u}\right)^{\frac{1}{3}}$$

The liquid phase flow into the specimen from the surrounding volume is proportional to the migration pressure gradient [9]:

$$q_{\Pi} = k_m \text{grad}\Pi$$

A peculiarity of the process is that the direction of the liquid flow q and that of the gradient of the migration pressure coincide, i.e. the liquid goes from a low $-\Pi$ region (in a melt which surrounds the specimen $\Pi = 0$) into a high $-\Pi$ region (in the specimen $\Pi = \Pi_0$). The mass transfer causes the migration pressure gradient to lower and to tend to zero. Mass transfer of a liquid phase under the action of a Π pressure gradient is described by the following differential equation [9]:

$$F(\Pi) \frac{\partial \Pi}{\partial t} = -k_m \nabla^2 \Pi \quad (6)$$

where $F(\Pi) = -u_0 \exp(-C\Pi)$.

Perspective method of the solution of the nonlinear differential equation of mass transfer is variational [10]. For the solution of the nonlinear differential equation of mass transfer, it is necessary to find such function of parameters which provides a stationary state of some action integral ($\delta I = 0$). For the mass transfer of a melted metal under the action of a Π pressure gradient author [11] has given the following action integral:

$$\delta \iint L \left(t, \Pi, \frac{\partial \Pi}{\partial t}, \frac{\partial \Pi}{\partial x_i} \right) dV dt \quad (7)$$

where Lagrange function is presented by the expression:

$$L = \left[\frac{\tau}{2} \left(\frac{\partial \Pi}{\partial t} \right)^2 \exp(-C\Pi) + \frac{k_m}{2u_0 C} \left(\frac{\partial \Pi}{\partial x} \right)^2 \right] \exp\left(-\frac{t}{\tau}\right) \quad (8)$$

The integral (7) accepts the minimal value if Lagrange function (8) satisfies Euler- Lagrange equation:

$$\frac{\partial L}{\partial \Pi} - \frac{\partial}{\partial t} \frac{\partial L}{\partial \left(\frac{\partial \Pi}{\partial t} \right)} - \frac{\partial}{\partial x} \frac{\partial L}{\partial \left(\frac{\partial \Pi}{\partial x} \right)} = 0 \quad (9)$$

The metal melt migration into the semi-infinite space is described in research [11]. The studied system consists of the A semi-infinite space which is filled only by a liquid and the B semi-infinite space which consists of the liquid and particles. The particles form a special structure, i.e. a skeleton. The liquid migrates from the A space into the B space. Using variation method, the solution of the differential equation (6) is given in [11]. Author [11] obtained an analytical function which describes time dependence of metal melt penetration length l_i :

$$l_i = \sqrt{\frac{3}{2} \frac{k_m}{u_0 C I} t} \quad (10)$$

$$\text{where } I = \int_0^l \xi^3 \exp(-CI_0 \xi^{1.5}) d\xi, \quad \xi = \frac{x}{l_t}.$$

The experimental data [9] confirm the expression (10). An analytical function which describes the migration pressure change with space and time is:

$$II(x, t) = II_0 \left(\frac{x}{l_t} \right)^{1.5}$$

where l_t is Eq.(10).

3. Discussion

In dispersed structured systems, particles and a mobile phase are affected by surface forces whose resultant is directed either into the volume of the mobile phase when $\gamma_{\alpha\alpha} < 2\gamma_{\alpha\beta}\cos\varphi/2$ (see Fig. 1) or along the contact surface when $\gamma_{\alpha\alpha} > 2\gamma_{\alpha\beta}\cos\varphi/2$. According to these relations, particles rearrange such that either the contact surface $\alpha\alpha$ or the interface $\alpha\beta$ disappear in the limiting case. The rearrangement of particles causes the mass transfer of the mobile phase. In this case, new mass transfer mechanisms which differ from the known mechanism of the mass transfer on atomic and molecular levels come into play. The mechanism of liquid migration is described in [12].

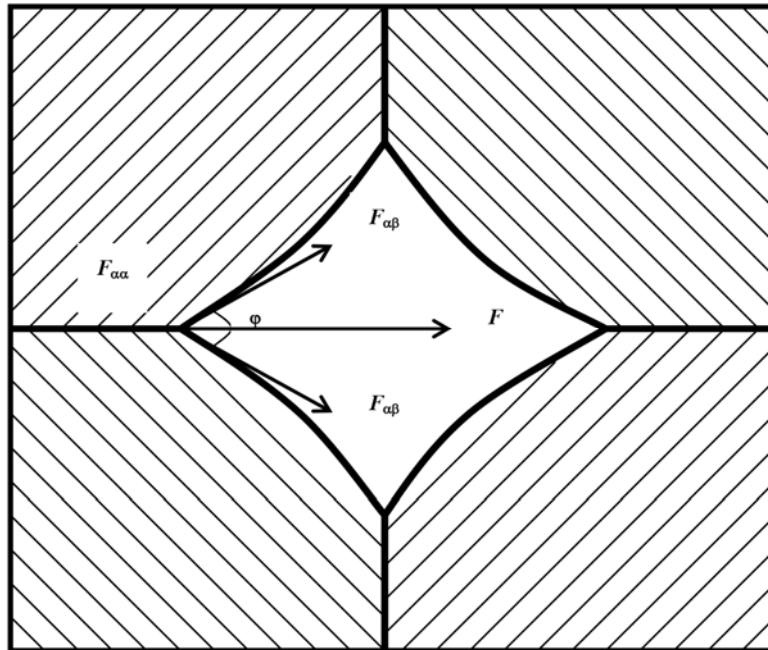


Fig. 1. Schematic representation of an action of surface forces in dispersed structured system.

4. Conclusion

In dispersed structured systems the under the action of particles new features of the mass transfer appear.

1. During the sintering in a volume of compact pressed from particles, the shrinkage pressure arises which increases at the gas removal from the compact. In the gas-compact

system, an increase of the shrinkage pressure gradient is concurrent with a decrease of the free energy of the system.

2. In the system of metal melt-sintered composite body imbibition of the metal melt by the sintered pore-free composite body takes place. In the volume of the composite body, a migration pressure appears. Under the action of the migration pressure the metal melt flows from an environment ($\Pi = 0$) into a composite body volume ($\Pi = \Pi_0$), i.e. the metal melt flows from a volume with a small value of migration pressure into a volume with a high migration pressure.

3. Unlike the mass transfer of the atomics or molecules (diffusion) in the metal melt-composite body system, the direction of the liquid flow and the migration pressure gradient coincide.

5. References

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Садржај: У овом раду се дискутује процес трансфера масе у двофазном систему, који се састоји од мобилне фазе (течности или гаса) и честица, који формирају просторну структуру која личи на костур. Показано је да у оваквом систему на процес транспорта мобилне фазе значајно утичу силе на границама фаза и на границама честица. Ове силе су одговорне за нове појаве у транспорту масе у диспергованом систему, као што је могући спонтани пораст интензитета променљивих.

Mass transfer; Composite material; Structure

Кључне речи: Транспорт масе, композитни материјал, структура

