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The migration of metal melts in sintered composite materials

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Abstract—The phenomenon of the imbibition of metal melts by a sintered pore-free composition consisting of refractory particles and a binder is described from a thermodynamic point of view. The results of experiments on metal melt migration in the volume of sintered bodies are presented and phenomenological analysis of the process is given.

INTRODUCTION

THE OBJECTS of this investigation are sintered composite materials consisting of refractory particles and a binding metal, for instance, tungsten carbide-based (WC—Co, WC—Ni, WC—Ni, Fe)—, titanium carbide-based (TiC—Co, TiC—Ni, Mo)—, and chromium carbide-based (Cr_3C_2—Ni)— sintered carbides, and others. Above the melting point of the binding metal, particles in these materials from a refractory skeleton pervaded the metal melt. In this case the composite materials in question may be considered as a two-phase disperse structural system 'solid–liquid'.

Earlier studies [1] revealed the then unknown phenomenon consisting of the fact that at temperatures above the melting point of a binding metal the pore-free composite materials imbibe their own melts.

In the process of the imbibition of metal melts the liquid phase flows in the body through the channels formed by refractory particles with the accompanying reconstruction of the refractory skeleton and increase in the sintered body volume. This type of mass transport, called by the present author the migration of a liquid, occurs in a chemical equilibrium pore-free system 'metal melt–sintered body'. It cannot be described on the basis of the diffusion of components or capillary theory.

This work is concerned with the study of the motive forces and the kinetics of the process. The solution of these problems will enable one to develop a new generation of sintered articles with controlled inhomogeneous phase distribution throughout the volume and corresponding differentiation of properties within it.

THE THERMODYNAMICS OF THE LIQUID PHASE MIGRATION IN SINTERED COMPOSITE BODIES

The theoretical studies were carried out on a model which reflects the specific features of the above composite materials.

Consider a system, which in its initial state comprises region I filled with a liquid phase and region II consisting exclusively of *n* refractory particles of equal size. Regions I and II are separated by diaphragm III permeable only for the liquid phase. In its final state, the liquid phase migrates through the diaphragm into region II and completely separates the particles one from another (Fig. 1).

Let the contact zone between two particles be a layer of definite thickness with the surface energy concentrated in it. It is possible to draw such a conditional separating surface in this layer, each particle of which will have surface energy equal to $A_s\bar{\gamma}_{ss}/2$, where $\bar{\gamma}_{ss}$ is the face-averaged surface tension. The following limitations are imposed on the system considered:

$$V_s + V_l = V = \text{const.},$$

$$T_s = T_l = T_{ss} = T_{sl} = T = \text{const.},$$

$$m_i^s + m_i^l + m_i^{ss} + m_i^{sl} = m_i = \text{const.},$$

$$\mu_i^s = \mu_i^l = \mu_i^{ss} = \mu_i^{sl}. \tag{1}$$

From these limitations it follows that the process of liquid penetration occurs at the constant volume of the system and constant temperature. The system consists of independent components, with the phases and phase interfaces being in chemical equilibrium, that is, all the processes associated with the equalization of chemical potentials (diffusion, solving and the like) have terminated. Moreover, it is taken into account that in the case of the separation of particles by liquid:

$$\Delta A_{sl} = -2\Delta A_{ss}.$$

When the liquid phase penetrates region II and separates particles, the 'solid–solid' interface is replaced by the phase interface 'solid–liquid'. From the thermodynamic point of view this is analogous to the transfer of a body from one medium into another. Using the results given in ref. [2] and limitations (1), the following expression for the system of interest was obtained which describes the change in the Helmholtz energy of the system (free energy):

NOMENCLATURE

A	phase surface area [m^2]
b	coefficient [N m^{-1}]
C	coefficient [m^2 N^{-1}]
d	particle size [m]
F	force [N]
$\mathscr{F}$	Helmholtz energy (free energy) [N m]
i	number of components in a system
j	number of phases
K	coefficient
k	coefficient
k_m	migration coefficient [m^4 N^{-1} s^{-1}]
k_p	permeability coefficient [m^2]
l	length [m]
m	mass [kg]
n	number of particles
n_r	number of channels
P	pressure [Pa]
q	flux [m^3 m^{-2} s^{-1}]
r	radius [m]
T	temperature [K]
u	volumetric content of liquid phase expressed in fractions
V	volume of a phase [m^3]
v	liquid velocity [m s^{-1}]
W	work [N m]
x, y, z	coordinates.

Greek symbols

γ	surface tension [N m^{-1}]
η	viscosity [Pa s]
μ	chemical potential [N m g^{-1}]
Π	migration pressure [Pa]
τ	time [s].

Subscripts

l	liquid
s	solid
sl	solid–liquid interface
ss	solid–solid interface.

$$\Delta\mathscr{F} = -V\Delta P_l + \tfrac{1}{3}(2k\bar{\gamma}_{sl} - \bar{\gamma}_{ss})\Delta A_{ss}. \qquad (2)$$

The liquid separating the particles alters their shape—it becomes equilibrated, characteristic for the surrounding liquid. This results in a change in the solid phase area which is taken into account by the coefficient k. The value ΔP_l in equation (2) is approximately equal to zero; consequently, the change of the Helmholtz energy for the system under consideration can be written with adequate accuracy as

$$\Delta\mathscr{F} = \tfrac{1}{3}(2k\bar{\gamma}_{sl} - \bar{\gamma}_{ss})\Delta A_{ss}. \qquad (3)$$

From equation (3) it follows that the process of liquid phase migration from region I to region II occurs spontaneously when $\bar{\gamma}_{ss} > 2k\bar{\gamma}_{sl}$. This inequality is the criterion which defines the class of composite materials revealing the ability to imbibe their own melts. It also follows from this equation that the process of liquid phase penetration takes place until the contact surface area A_{ss} diminishes. On complete separation of particles by the liquid $\Delta\mathscr{F} = 0$ and the process ceases. Variation of the contact surface (ΔA_{ss}) can be expressed in terms of the volume of liquid ΔV_l penetrated into region II, the particles size d and the volumetric fraction of the liquid u in region II [3]:

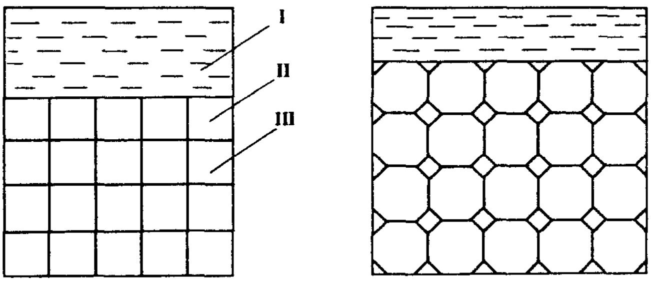
$$\Delta A_{ss} \simeq K\frac{1}{d}\left(\frac{1-u}{u}\right)^{1/3}\Delta V_l. \qquad (4)$$

The coefficient K takes into account the shape of the particles and the geometry of voids in region II which are filled with liquid.

Substituting equation (4) into equation (3) yields

$$\Delta\mathscr{F} = \frac{K}{3d}(2k\bar{\gamma}_{sl} - \bar{\gamma}_{ss})\left(\frac{1-u}{u}\right)^{1/3}\Delta V_l. \qquad (5)$$

During the passage of the volume of liquid ΔV_l from region I into region II, work W is done to shift diaphragm III:



(a) (b)

FIG. 1. The redistribution of a liquid phase in a disperse system 'solid–liquid': (a) initial state; (b) final state.

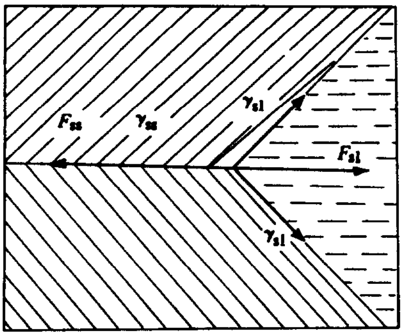


FIG. 2. The scheme of forces operating in the volume of a sintered body.

$$W = (P'' - P')\Delta V_1 \qquad (6)$$

where P' and P'' are the pressures in regions I and II, respectively.

The viscosity of liquid metals is 10^{-3} Pa s, therefore it is possible to neglect energy dissipation and to assume that the work done by the system under isochoric–isothermal conditions is equal to the change in the Helmholtz energy, i.e. $W = -\Delta\mathscr{F}$. Substituting equations (5) and (6) into this expression gives

$$\Pi = b\frac{1}{d}\left(\frac{1-u}{u}\right)^{1/3} \qquad (7)$$

where

$$b = \tfrac{1}{3}K(\bar{\gamma}_{ss} - 2k\bar{\gamma}_{sl}), \quad \Pi = P'' - P'.$$

The pressure Π, hereafter referred to as the migration pressure, is the motive force for the mass transport in the system. The physical meaning of the migration pressure Π can be understood from Fig. 2. The surface tensions operating within the region of the contact of particles and at the phase interfaces 'solid–liquid' bring about unbalanced forces $F_{ss} > F_{sl}$, the action of which causes the suction of a metal melt into a sintered body.

From equation (7) it follows that for a certain liquid phase content in the system there uniquely corresponds a certain migration pressure, with the increase in the liquid content entailing a decrease in the pressure Π. This conclusion was verified experimentally using samples of sintered carbides WC—Co with different cobalt contents (Table 1). The averaged size of WC particles was 2.3 μm. The pressure Π was measured by the technique of fixing of the liquid phase equilibrium state in a wedge-shaped capillary [3].

It was established by the investigations that when two samples with different migration pressures Π are in contact, the liquid phase will migrate into the sample with a higher pressure, resulting in the equalization of migration pressure within the contacting samples (Table 2). From the data given in Table 2 it follows that in the process of metal melt migration under the pressure a liquid flows from the volume with a lower pressure Π into the volume with a higher migration pressure; that is, the directions of the flow vector and of the pressure Π gradient vector coincide. This is one of the differences between liquid phase migration and filtration when the directions of the liquid flow vector and the gradient vector are opposite.

THE KINETICS OF MIGRATION OF METAL MELTS

The migration was investigated on 5 × 8 × 70 mm samples prepared from sintered carbides WC—Co (Table 1). The samples were heated in a vacuum to 1640 K at the residual pressure of 0.1 Pa and then by their 5 × 8 mm face the samples were brought into contact with the cobalt melt saturated with carbon and tungsten. At 1640 K the binding metal of the samples—a cobalt melt saturated with tungsten and carbon—was in the liquid state. The identity of compositions of the liquid phase in the samples and of the melt interacting with this phase made it possible to achieve equality of the chemical potentials of the components at constant temperature and pressure and to exclude any influence of diffusion on the process of cobalt melt migration. The time of contact was chosen so as to preclude the penetration of the melt to the opposite face of a sample. This corresponded to the condition of liquid phase migration in a semi-finite bar. The holding times were selected to be 300, 600, 900, 1200 and 1500 s. The depth of melt penetration into the samples and the binding metal distribution over their length were determined by X-ray spectral analysis. The investigations established a linear dependence of the melt penetration depth on time $\sqrt{\tau}$ (Fig.

Table 1. The composition and characteristics of samples under study

Sample labelling	Co† (mass %)	Liquid content at 1640 K (vol. %)	Migration pressure (MPa)	
			Experimental	Calculated
Co4	3.85	9.10	0.76	0.73
Co6	5.90	13.75	0.61	0.61
Co8	7.60	17.51	0.56	0.52
Co10	9.65	21.83	0.42	0.45
Co15	14.30	31.10	0.27	0.29
Co20	20.10	41.90	0.20	0.19

† The balance was tungsten carbide.

Table 2. Migration of Co melt in sintered carbide WC—Co

Characteristics of samples	Samples in contact		
	Co4–Co20	Co6–Co15	Co8–Co15
Content of cobalt melt (% by volume)			
(a) in initial state	9.10–41.90	13.75–31.10	17.51–31.10
(b) after 4800 s at 1640 K	24.51–27.78	22.6–23.5	23.8–24.4
Migration pressure in samples (MPa)			
(a) in initial state	0.76–0.20	0.61–0.27	0.56–0.27
(b) after 4800 s at 1640 K	0.32–0.30	0.42–0.40	0.38–0.36

3) as well as the direct dependence of the liquid flow, q, on the migration pressure gradient, $\Delta\Pi/l$ (Fig. 4).

As was stated above, liquid flows in the volume of a sintered body under the action of the migration pressure gradient Π. The flow velocity of the liquid was 5×10^{-6} m s^{-1}, and the radius of the channels through which the liquid moved in the volume of samples did not exceed 3×10^{-6} m.

On the basis of the above data and using the Reynolds number it was found that the flow of liquid is of laminar character. The flow of a viscous non-compressible liquid at constant temperature is described by the Navier–Stokes equation. Integration of the Navier–Stokes equation for a cylindrical capillary of radius r in the case of laminar horizontal flow gives the relation

$$\frac{8\eta}{r^2}\frac{dl}{dr}=\frac{\Delta\Pi}{l}.$$

This expression can be reduced to the form:

$$\bar{v}=\frac{dl}{d\tau}=\frac{r^2}{8\eta}\frac{\Delta\Pi}{l}. \tag{8}$$

The expression obtained is the Kozeny–Kármán equation, which in filtration theory is transformed to

$$\bar{v}=\frac{dl}{d\tau}=\frac{k_p}{\eta}\frac{\Delta\Pi}{l}. \tag{9}$$

Unlike equation (8), equation (9) describes the flow of liquid through a disperse system. The separation of variables and the integration of equation (9) yields:

$$l=\sqrt{\left(2\frac{k_p}{l}\Delta\Pi\tau\right)}. \tag{10}$$

The flow of liquid through a unit surface of a body at distance x is determined by:

$$q=\bar{v}Al=\frac{k_p}{\eta}\int_{r_0}^{r_{\max}}\pi r^2\frac{\partial n_r}{\partial r}\,dr\,\frac{\partial\Pi}{\partial x}. \tag{11}$$

The integral

$$\int_{r_0}^{r_{\max}}\pi r^2\frac{\partial n_r}{\partial r}\,dr$$

defines the surface area occupied by the liquid phase [4]. Equation (11) gives the basic law for the liquid phase migration:

$$q=k_m\,\mathrm{grad}\,\Pi \tag{12}$$

where

$$k_m=\frac{k_p}{\eta}\int_{r_0}^{r_{\max}}\pi r^2\frac{\partial n_r}{\partial r}\,dr.$$

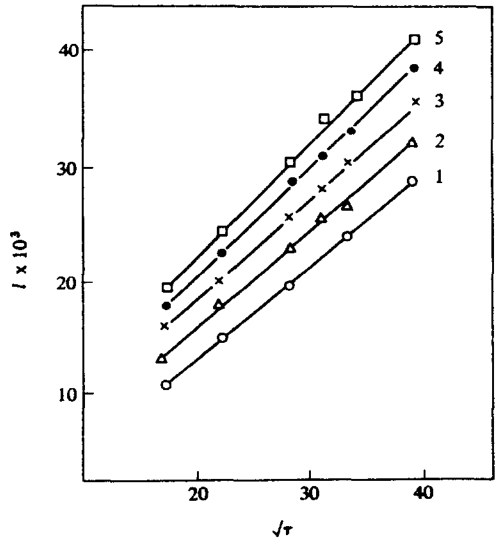


Fig. 3. The dependence of the Co melt penetration depth, l, on the time $\sqrt{\tau}$ of migration in samples of: (1) Co4; (2) Co6; (3) Co8; (4) Co10; (5) Co15.

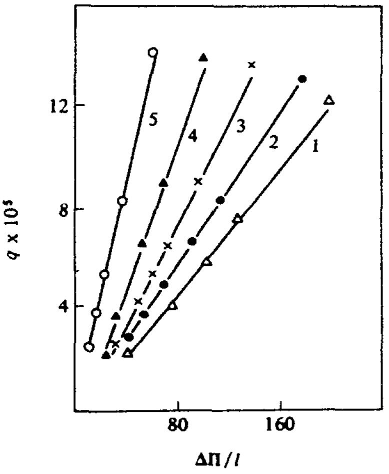


Fig. 4. The dependence of the Co melt flow, q, on the migration pressure gradient $\Delta\Pi/l$: (1) Co4; (2) Co6; (3) Co8; (4) Co10; (5) Co15.

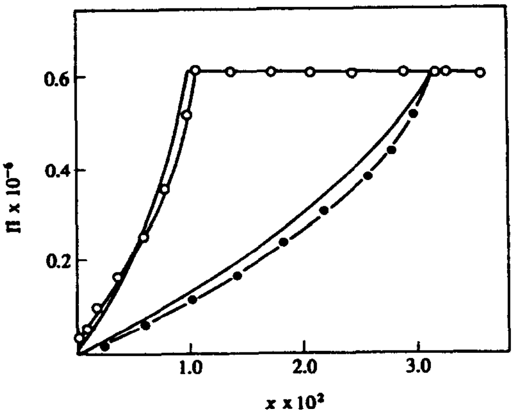


FIG. 5. The change of migration pressure along the length of samples after 180 s contact with the cobalt melt (left-hand side) and 1500 s contact (right-hand side) : ——, calculation ; O–O, experiment.

Based on equation (12), the mass equilibrium equation for a one-dimensional problem is obtained

$$-\frac{\partial q}{\partial x} = \Phi(\Pi)\frac{\partial \Pi}{\partial \tau}. \qquad (13)$$

The function $\Phi(\Pi)$ is a derivative of the function $u = f(\Pi)$ which is the inverse of function (7). The function $f(\Pi)$ is approximated well by the relation $f(\Pi) = u_0 \exp(-C\Pi)$, whence:

$$\Phi(\Pi) = -u_0 \exp(-C\Pi).$$

Taking into consideration equations (7), (9) and (12) as well as the mass conservation law, the following differential equation for migration is obtained

$$\Phi(\Pi)\frac{\partial \Pi}{\partial \tau} = -\frac{\partial(k_m \partial\Pi/\partial x)}{\partial x} - \frac{\partial(k_m \partial\Pi/\partial y)}{\partial y} - \frac{\partial(k_m \partial\Pi/\partial z)}{\partial z}.$$

If the process of migration occurs in such a manner that the coefficient k_m does not influence the flow of liquid, it is possible to write that k_m = const., and then the process is described by the equation:

$$\Phi(\Pi)\frac{\partial \Pi}{\partial \tau} = -k_m \nabla^2 \Pi.$$

The equation obtained was used to describe the flow of liquid into a semi-infinite bar. For the composition Co6 the following coefficients were determined: $k_m = 3.9 \times 10^{-13}$ m^4 N^{-1} s^{-1}; $u_0 = 0.6$; $C = 2.5 \times 10^{-6}$ m^2 N^{-1}; and $\Pi_0 = 0.61$ MPa. The calculated results agree well with experimental data (Fig. 5).

The results obtained can be used for theoretical calculations as well as for solving practical problems in developing composite articles with a phase content varying throughout their volume.

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LA MIGRATION DES METAUX FONDUS DANS DES MATERIAUX FRITTES COMPOSITES

Résumé—On décrit à partir d'un point de vue thermodynamique l'imbibition de métal fondu par un milieu fritté à pores libres composé de particules réfractaires et d'un liant. Les résultats expérimentaux sur la migration d'un métal fondu dans le volume de matériaux frittés sont présentés et on donne une analyse phénoménologique du mécanisme.

DIE WANDERUNG VON METALLSCHMELZEN IN GESINTERTEN VERBUNDWERKSTOFFEN

Zusammenfassung—Das Phänomen der Durchdringung von gesinterten, porenfreien Verbundmaterialien aus Feuerfestwerkstoffen und Binder durch Metallschmelzen wird aus thermodynamischer Sicht betrachtet. Die experimentellen Ergebnisse der Metallschmelzen-Wanderung im Innern von gesinterten Körpern werden dargestellt, und eine phänomenologische Analyse des Vorgangs wird beschrieben.

МИГРАЦИЯ МЕТАЛЛИЧЕСКИХ РАСПЛАВОВ В СПЕЧЕННЫХ КОМПОЗИЦИОННЫХ МАТЕРИАЛАХ

Аннотация—С позиций термодинамики описано явление поглощения металлических расплавов спеченными беспористыми композициями, состоящими из тугоплавких частиц и связующего металла. Приведены результаты экспериментальных исследований, кинетики миграции металлических расплавов в объеме спеченных тел, дано феноменологическое описание этого процесса.