THERMODYNAMICS OF METAL MELT MIGRATION IN THREE-PHASE SINTERED COMPOSITION MATERIALS

A. F. Lisovskii and T. É. Gracheva

UDC 620.22:669.018.25

We have derived the thermodynamic functions describing the change in the energy of a system on penetration of a liquid into three-phase sintered compositions, and we offer a prediction with respect to the structures which will develop as a result, in addition to examining the moving forces of this process.

A significant increase in the physicomechanical and operational properties of sintered composition materials can be attained through the predictable formation of structures within the volume of sintered items. An effective method of actively affecting the structure of composition materials involves their treatment with metal melts. In the case of high-temperature interaction with metallic melts a number of processes are generated within sintered materials: the absorption of the liquid phase by nonporous compositions, the penetration of the liquid through the contact boundaries of the particles, a restructuring of the high-melting skeleton, etc. [1]. In order to be able to predict within these compositions the formation of various structures, it is necessary that we study the thermodynamics involved in the migration process of the liquid phase in sintered materials. Such studies are available with respect to two-phase systems [1]. Questions related to the thermodynamics of migration for metallic melts in multiphase sintered composition materials have not been adequately studied.

The migrational thermodynamics of molten metal in three-phase compositions has been studied on a model consisting of n particles in phase 1, the particles of phase 2, and the liquid phase 3. There was a region I within the system, containing the particles in solid phases 1 and 2 and liquid 3, as well as a region II which consisted entirely of liquid (see Fig. 1). Particles 1 and 2 in region I were in contact with each other, with neighboring particles, and with the liquid, i.e., they formed two interpenetrating skeletal structures, which corresponds to the real structures of compositions based on high-melting phases. We will assume that the liquid provides good wetting for the high-melting particles. This condition is necessary for the existence of composition material as a physical object.

The regions are separated by a diaphragm which is permeable to the liquid phase. We made the assumption that some volume ΔV_3 of liquid penetrated through the diaphragm out of regions II into I, as a result of which the system made a transition from its initial state a to the final state b. On transition of the liquid ΔV_3 out of region II into I the following changes occurred within the system: the volume of region II diminished and the volume of region I increased,

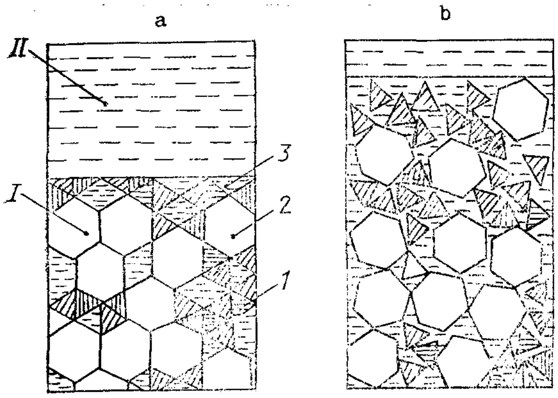

Fig. 1. Diagram of the liquid-phase migration in a triple-phase composition made up of a solid and a liquid: 1, 2) the solid phase; 3) liquid.

Institute of Supersolid Materials, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 59, No. 2, pp. 243-247, August, 1990. Original article submitted July 7, 1989.

0022-0841/90/5902-1006$12.50

the surface contact area of phases 11, 22 and the interphase surface 12 decreased in size, while the area of the interphase surfaces 13 and 23 increased.

Let us impose the following limitations on the system:

$$m_i^1 + m_i^2 + m_i^3 + m_i^{11} + m_i^{22} + m_i^{12} + m_i^{13} + m_i^{23} = m_i = \text{const}, \qquad (1)$$

$$\mu_i^1 = \mu_i^2 = \mu_i^3 = \mu_i^{11} = \mu_i^{22} = \mu_i^{12} = \mu_i^{13} = \mu_i^{23}.$$

In the final state the system undergoes total replacement of the solid-to-solid surfaces 11, 22, 12 by the interphase surfaces solid liquid 13 and 23. In order to describe the thermodynamics of this process we will use the expression for the change in the Helmholtz function which describes the process of altering the interphase surface of the particle as it makes its transition from one medium to another [2]. With respect to the problem being solved we found

$$\Delta F = -V_3\Delta P_3 + \frac{1}{3}\left(2g_1\overline{\gamma}_{13} - \overline{\gamma}_{11}\right)\Delta S_{11} + \frac{1}{3}\left(2g_2\overline{\gamma}_{23} - \overline{\gamma}_{22}\right)\Delta S_{22} + \frac{1}{3}\left(g_{12}\overline{\gamma}_{13} + g_{12}\overline{\gamma}_{23} - \overline{\gamma}_{12}\right)\Delta S_{12}. \qquad (2)$$

The averaged surface tension $\overline{\gamma}$ in expression (2) is taken from the expression $\overline{\gamma} = \Sigma s_j\gamma_j/\Sigma s_j$ [3].

In the system under consideration the liquid phase exhibits the properties of an unbounded phase and according to the results of the research in [4] we therefore have: $\Delta P_3 = 0$, and consequently, in expression (2), we have the term $V_3\Delta P_3 = 0$.

The liquid migration process in region I will proceed in arbitrary fashion, provided that $\Delta F < 0$, i.e., on satisfaction of the following conditions:

$$\overline{\gamma}_{11} > 2g_1\overline{\gamma}_{13}; \quad \overline{\gamma}_{22} > 2g_2\overline{\gamma}_{23}; \quad \overline{\gamma}_{12} > g_{12}\overline{\gamma}_{13} + g_{12}\overline{\gamma}_{23}. \qquad (3)$$

This inequality, as is well known, serves as the condition for the penetration of the liquid at the contact and interphase surfaces.

If any inequality such as, for example, $\overline{\gamma}_{11} < 2g_2\overline{\gamma}_{13}$, is violated, the liquid will not penetrate through contact surfaces 11 and after the liquid has penetrated through surfaces 22 and 12 into the structure of the composition particle concretions 1 are preserved. Despite the presence in the system of phase I, the term $(1/3)(2g_1\overline{\gamma}_{13} - \overline{\gamma}_{11})\Delta S_{11}$ disappears in expression (2) because under these conditions $\Delta S_{11} = 0$. Having analyzed the process of liquid penetration through the contact surfaces, it must be kept in mind that when $\overline{\gamma}_{11} > 2g_1\overline{\gamma}_{13}$ surface 11 is unstable and its replacement by surface 13 is more advantageous from the standpoint of energy. If $\overline{\gamma}_{11} \le 2g_1\overline{\gamma}_{13}$, equilibrium bilateral angles may arise within the system, and the existence of these will ensure the mechanical equilibrium of the liquid and the solid phases in contact with each other [1].

In the case of a sintered composition, at the point of contact between two particles and the liquid at the interphase and contact boundaries we note the effect of forces generated by the surface tensions γ_{11}, γ_{22}, γ_{12}, γ_{13}, and γ_{23}. It follows out of condition (3) that these forces have not been offset, and the resultant is directed along the contact surface. When subjected to this force the liquid penetrates into the zone of particle contact, as a result of which we have a change in the surface tension of the particle facets. According to the Yu. Vul'f theorem, extended by V. K. Semenchenko to multicomponent systems [5], the change in surface tension even for a single crystal face disrupts its equilibrium geometric shape. This leads to the activation of the process of particle recrystallization, and the particles thereupon seek to adopt a new geometric shape, i.e., we are confronted with the restructuring of the high-melting skeleton. As a result of this restructuring, the particles assume a new position in space and liquid-containing cavities expand within the composition. As a result the liquid is drawn out of region II into these cavities.

Pressures generated as a result of the restructuring of the high-melting skeleton in region I, and particles with a specific force act on the diaphragm (see Fig. 1). The diaphragm is displaced under the action of this pressure Π and the system performs work W. In this model of the system work W is defined by the change in the volume of region I. This change in volume is equal to the quantity of liquid ΔV_3 which has penetrated into region I. Thus, work W performed by the system is equal to

$$W = \Pi\Delta V_3. \qquad (4)$$

TABLE 1. Classification of Composition Materials Based on Their Ability to Absorb the Liquid Phase

Structure type	Conditions of liquid penetration	Final structure composition
I	$\gamma_{11} > 2g_1\gamma_{13}$ $\gamma_{22} > 2g_2\gamma_{23}$ $\gamma_{12} > g_{12}\gamma_{13} + g_{12}\gamma_{23}$	All particles separated by the liquid
II	$\gamma_{11} > 2g_1\gamma_{13}$ $\gamma_{22} \leqslant 2g_2\gamma_{23}$ $\gamma_{12} > g_{12}\gamma_{13} + g_{12}\gamma_{23}$	Concretions and conglomerates of particles 22 preserved in the structure
III	$\gamma_{11} > 2g_1\gamma_{13}$ $\gamma_{22} \leqslant 2g_2\gamma_{23}$ $\gamma_{12} \leqslant g_{12}\gamma_{13} + g_{12}\gamma_{23}$	Concretions of particles 22 and 12 preseved in the structure
IV	$\gamma_{11} > 2g_1\gamma_{13}$ $\gamma_{22} > 2g_1\gamma_{23}$ $\gamma_{12} \leqslant g_{12}\gamma_{13} + g_{12}\gamma_{23}$	Concretions of particles 12 preserved in the structure
V	$\gamma_{11} \leqslant 2g_1\gamma_{13}$ $\gamma_{22} \leqslant 2g_2\gamma_{23}$ $\gamma_{12} > g_{12}\gamma_{13} + g_{12}\gamma_{23}$	Concretions of particles 11 and 22 preserved in the structure
VI	$\gamma_{11} \leqslant 2g_1\gamma_{13}$ $\gamma_{22} \leqslant 2g_2\gamma_{23}$ $\gamma_{12} \leqslant g_{12} + g_{12}\gamma_{23}$	The liquid in region I does not penetrate and the process of liquid migration out of regions I into II is possible

Work W, performed by the system, is equal to the Helmholtz energy loss, i.e., W = $-\Delta F$. Having substituted this equality into expressions (2) and (4), we find that:

$$\Pi = \frac{1}{3}\left[(\bar{\gamma}_{11} - 2g_1\bar{\gamma}_{13})\frac{\Delta S_{11}}{\Delta V_3} + (\bar{\gamma}_{22} - 2g_2\bar{\gamma}_{23})\frac{\Delta S_{22}}{\Delta V_3} + (\bar{\gamma}_{12} - g_{12}\bar{\gamma}_{13} - g_{12}\bar{\gamma}_{23})\frac{\Delta S_{12}}{\Delta V_3}\right].$$

We will designate pressure Π as the migration pressure. The conclusion drawn above is extremely clear and exposes the physical essence of migration pressure. A more rigorous expression for the pressure Π can be found from the relationship $(\partial F/\partial V)_T = -\Pi$ from which we find

$$\Pi = b_1\frac{\partial S_{11}}{\partial V_3} + b_2\frac{\partial S_{22}}{\partial V_3} + b_{12}\frac{\partial S_{12}}{\partial V_3}, \tag{5}$$

where $b_1 = (1/3)(\bar{\gamma}_{11} - 2g_1\bar{\gamma}_{13})$, $b_2 = (1/3)(\bar{\gamma}_{22} - 2g_2\bar{\gamma}_{23})$, $b_{12} = (1/3)(\bar{\gamma}_{12} - g_{12}\bar{\gamma}_{13} - g_{12}\bar{\gamma}_{23})$. The derivatives $\partial S/\partial V$ in expression (5) reflect the capability of the particles to undergo restructuring as a result of the penetration of the liquid into the contact zone, and the coefficients b_1, b_2, b_{12} make provision for the action of the uncompensated forces at the point of contact between the solid and liquid phases.

Pressure Π is the moving force of liquid-phase migration in the sintered three-phase composition.

On the basis of expression (2) and condition (3) we can isolate several types of composition materials and prognosticate their structure after the penetration of the liquid. A classification of these composition materials is presented in Table 1.

The derived results from this investigation were utilized to determine the structural types of composition materials fabricated on the basis of carbides and nitrides of transition metals and a number of nonmetals.

Our research has established that materials produced as a consequence of various combinations of carbides of the transition metals TiC, ZrC, HfC, VC, NbC, TaC, Cr_3C_2, Mo_2C, WC, and one of the metals of the iron group (Fe, Co, Ni), used as binders, make up the compositions which form I-type structures.

The compositions forming II-type structures include primarily materials combining carbides and nitrides of transition metals and nonmetals. In these materials the molten metals penetrate along the contact boundaries of carbide particles 11, interphase boundaries between the carbide and nitride 12, and they do not penetrate through the contact boundaries of the nitride particles 22. An example of such a structure is the one attained on interaction in a vacuum between the composition WC–Si_3N_4–Co and a cobalt melt at 1610 K. Melted cobalt does not penetrate through the Si_3N_4–Si_3N_4 boundaries, as a result of which conglomerates of these particles exist within the structure.

Compositions that are based on the nitrides of high-melting metals as a rule do not interact with metallic melts in chemical equilibrium, retaining their original structure (a VI-type structure). It has been established through research that such compositions include materials based on nitrides of the metals AlN–TiN–NiTi, TiN–Si_3N_4–NiTi, as well as the carbonitrides of Ti(CN)–Zr(CN)–Ni.

Among these composition materials based on the carbides and nitrides of transition metals, we found no evidence of III-, IV-, and V-type structures. Apparently, such structures might appear in systems based on oxides, high-melting metals, and similar materials.

Results from studies into the thermodynamics of liquid-phase migration in three-phase systems enables us to determine the optimum means of controlling composition structure formation and to achieve high-efficiency composition products with a differentiated volume of physicomechanical properties.

In the present study we examined the thermodynamics of the liquid-phase migration in a system in chemical equilibrium, i.e., a metallic melt and a sintered material. The resulting data obtained from these studies serve as a basis for subsequent research into the process of liquid-phase migration in systems not in chemical equilibrium.

NOTATION

n, number of particles; V, volume; T, temperature; P, phase pressure; m, mass; μ, chemical potential; F, Helmholtz energy; γ, surface tension; S, interphase surface area; s, area of particle face surface; W, work; Π, migration pressure; b, coefficient; g, coefficient which takes into consideration the change in particle surface area, associated with the change in particle geometric shape. Subscripts: 1, 2, 3, 11, 22, 12, 13, 23 indicate that the quantities pertain to the corresponding phase or interphase surface; i, number of components in the system; j, number of particle faces.

LITERATURE CITED

1. A. F. Lisovskii, *Molten Metal Migration in Sintered Composition Materials* [in Russian], Kiev (1984).
2. Yu. Ya. Golger, A. I. Rusanov, and V. I. Klassen, *Dokl. Akad. Nauk SSSR*, **179**, No. 3, 617-620 (1968).
3. L. M. Shcherbakov, *Kolloid. Zh.*, **23**, No. 2, 215-220 (1961).
4. L. M. Shcherbakov, *Uch. zap. Kishinevskogo gosuniversiteta*, **1**, No. 2, 11-21 (1949).
5. V. K. Semenchenko, *Surface Phenomena in Metals and Alloys* [in Russian], , Moscow (1957).