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THERMODYNAMICS of FORMATION LIQUID INTERLAYERS in COMPOSITE MATERIALS

Composite materials consisting of refractory particles and a low-melting binder have been studied. In a composite body the process of the liquid outflow from a capillary into the body bulk have been described in terms of thermodynamics. An equation for the variation of the Helmholtz free energy of a microdispersed system during this process has been derived and the conditions, under which the liquid interlayers are either stable or unstable in the bulk of a composite body, have been established.

Key words: composite material, liquid interlayer, thermodynamics

1. Introduction

The object of the present investigation is composite materials consisting of refractory particles and metallic binder. They include cemented carbides, composite ceramics [1], contact materials [2], structural materials [3], etc. The structure of these materials forms during the liquid phase sintering, after which they present solid–liquid structured dispersed systems. The stability of liquid interlayers in such systems is of great importance for the development of advanced technologies like the capillary welding, formation of mesostructures [4], reinforcing of composite materials with metallic fibers, etc. For these processes to be effective, it is necessary to ensure stability of the liquid interlayer forming in a composite body during the liquid phase sintering. The problem can best be dealt with by first examining it from a thermodynamic standpoint and then explaining certain kinetic characteristics of the formation and disappearance of liquid metallic interlayers within a sintered composite body.

2. Thermodynamic investigation

The Gibbs thermodynamics was used for the study of the stability of liquid interlayers in composite materials [5]. The investigations were made on the model of a system containing a vapor phase v , n particles of a solid phase s , and a liquid l . The system contains region I filled by particles and a liquid (Fig. 1). Particles s formed a refractory skeleton that was saturated by the liquid l . In region I there was a capillary filled with the liquid l (Fig. 1 *a*). Region II of the system was filled solely by a vapor phase. In the final state of the system (Fig. 1 *b*) the liquid migrated from the capillary into the bulk of a composite body, the capillary became empty and was filled with the vapor phase. During the migration of the liquid, the particles in the refractory skeleton are regrouped, as a result of which the particle contact surface area A_{ss} decreases, the phase interface area A_{sl} in the composite material increases, and solid-vapor surface A_{sv} appears in the capillary. The process of the capillary emptiness proceeded at a constant temperature and volume of the system. Under these conditions the characteristic function that describes the state of the system is the Helmholtz free energy F .

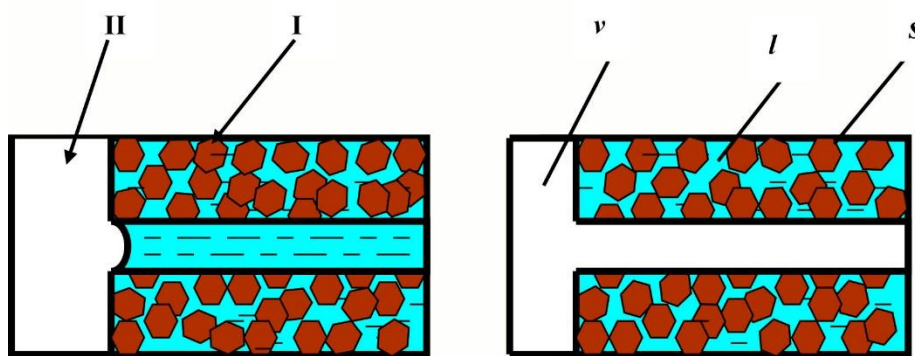


Fig. 1. Model of dispersed solid–liquid–vapor system with liquid interlayer: a – initial; b – final state

The following limitations are imposed on the system:

$$T_s = T_l = T_v = T_{ss} = T_{sl} = T_{sv} = T_{lv} = T = \text{const}, \quad (1a)$$

$$V_s + V_l + V_v = V = \text{const} \quad (1b)$$

$$m_i^{(s)} + m_i^{(l)} + m_i^{(v)} + m_i^{(ss)} + m_i^{(sl)} + m_i^{(sv)} + m_i^{(lv)} = m_i = \text{const}, \quad (1c)$$

$$\mu_i^{(s)} = \mu_i^{(l)} = \mu_i^{(v)} = \mu_i^{(ss)} = \mu_i^{(sl)} = \mu_i^{(sv)} = \mu_i^{(lv)} = \mu_i, \quad (1d)$$

where T is the temperature, V is the volume, m is the amount of the i -th component, μ is the chemical potential, i is the number of components, indices s, l, v, ss, lv, sv, lv indicate that the values they define refer to the corresponding phase, contact surface, or interface.

Limitation (1 a) indicates that there are no temperature gradients in the system. The system consists of independent components, which can pass from one phase into the other (1 c). Limitation (1 d) indicates that there are no chemical gradients in the system. Moreover, we assume that the system is a monodisperse one; the size of particles s remains constant, in the course of the liquid migration a change of the particle shape is possible, while the capillary size and shape do not change.

A change in Helmholtz free energy ΔF in passing of the system from the initial to the final state may be represented as a sum of the variation of Helmholtz free energy ΔF_m of the liquid migration from capillary into the composite body and the variation of Helmholtz free energy ΔF_c of the capillary emptying $\Delta F = \Delta F_m + \Delta F_c$. The change in the free energy of the system, with allowance for conditions (1a–1d), is described by the expression

$$\Delta F = -V_s \Delta P_s - V_l \Delta P_l - V_v \Delta P_v - \gamma_{ss} \Delta A_{ss} + \gamma_{sl} \Delta A_{sl} + \gamma_{lv} \Delta A_c^{lv} + (\gamma_{sv} - \gamma_{sl}) \Delta A_c^{sv}, \quad (2)$$

where P is the pressure, γ is the surface tension, A_c^{lv} and A_c^{sv} are the areas of the capillary surface occupied by the liquid and solid phases, respectively.

To transform Eq. (2), we use the relationships

$$\Delta A_{sl} = 2g \Delta A_{ss} \quad A_c^{lv} = u A_c \quad A_c^{sv} = (1-u) A_c \quad A_c = k_c \frac{V_c}{d_c} \quad \gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \Theta \quad (3)$$

where A_c is the total surface area of the capillary; u is the fraction of the capillary surface occupied by the liquid phase (according to a fundamental theorem of stereology, the fraction of a surface occupied by a phase is equal to the volume fraction of this phase, and hence u is the volume fraction of the liquid phase in the composite body); V_c is the volume of the capillary; d_c is the size of the capillary; k_c is the coefficient allowing for the geometric shape of the capillary; θ is the angle of contact; and g is the coefficient allowing for the change in the geometric shape of the particles.

As the volume of the composite body into which the liquid migrates is many times larger than the volume of the capillary, it is possible, without significantly affecting subsequent derivations, to ignore the effect of the geometric particle shape on the quantity ΔA_{ss} and use the relationship $\Delta A_{sl} = 2\Delta A_{ss}$.

In Eq. (2), $\Delta P_l = 0$ and $\Delta P_v = 0$, since the liquid and the vapor in the system possess the properties of unbounded phases. The refractory particles are a typical example of a phase bounded by an interface, and for them therefore $\Delta P_s \neq 0$. When the liquid penetrates into the interparticle surface in the skeleton, the contact surface becomes replaced by a solid-liquid phase interface. This changes the surface tension of the particles, which brings about a change in their phase pressure. In [6] it is demonstrated that the change in the phase pressure of an assembly of particles induced by their contact surface being replaced by a solid-liquid phase interface is described by the expression

$$\Delta P_s = \frac{2}{3} \frac{\Delta A_{ss}}{V_s} (2\gamma_{sl} - \gamma_{ss})$$

from which we have

$$V_s \Delta P_s = -\frac{2}{3} (\gamma_{ss} - 2\gamma_{sl}) \Delta A_{ss} \quad (4)$$

Taking into account Eqs. (3) and (4), we obtain

$$\Delta F = -\frac{1}{3} (\gamma_{ss} - 2\gamma_{sl}) \Delta A_{ss} + k_c \frac{V_c}{d_c} \gamma_{lv} \cos \Theta_1, \quad (5)$$

where Θ_1 is the angle of contact of the surface containing portions of the solid and liquid phases, with $\cos \Theta_1 = u + (1-u) \cos \Theta$.

In Eq. (5), the first term describes the energetic changes within the composite body brought about by migration of the liquid phase, while the second term describes the energetic change in the capillary. According to the conditions adopted, the liquid in the capillary is identical in composition to the liquid in the composite body. This liquid wets well the capillary walls, so that $\cos \Theta_1 > 0$, and the second term is always positive. At $\gamma_{ss} < 2\gamma_{sl}$, the first term, too, is positive. This means that in Eq. (5) $\Delta F > 0$, and the capillary cannot be denuded, i.e., the liquid interlayers are stable, and can be preserved within a sintered composite body. If in a composite material $\gamma_{ss} > 2\gamma_{sl}$, the first term is negative, and the stability of the interlayers in the composite body is determined by the relative magnitudes of the first and second terms of Eq. (5). In such a composite body, the liquid interlayers will be stable when

$$k_c \frac{V_c}{d_c} \gamma_{lv} \cos \Theta_1 > \frac{1}{3} (\gamma_{ss} - 2\gamma_{sl}) \Delta A_{ss} \quad (6)$$

It is convenient to transform this expression bearing in mind that, when a liquid penetrates into a composite body, the change in the contact surface ΔA_{ss} can be calculated, with an error 5 — 9%, using the expression [7]

$$\Delta A_{ss} = \frac{K}{d_s} \left(\frac{1-u}{u} \right)^{\frac{1}{3}} \Delta V_l \quad (7)$$

where u is the volume fraction of the liquid phase in the composite body, d_s is the particle size, K is the coefficient allowing for the geometric shape of the particles and the voids formed by them; and ΔV_l is the volume of the liquid which has penetrated into the composite body (and, of course, $\Delta V_l = V_c$).

Substituting Eq. (7) in Eq. (6) for composite materials having $\gamma_{ss} > 2\gamma_{sl}$, we find the condition of stability of the liquid interlayers as a function of composition of the material and size of the refractory particles. Allowing for what has been said above, we obtain

$$d_c < K_1 d_s \left(\frac{u}{1-u} \right)^{\frac{1}{3}} \frac{\gamma_{lv} \cos \Theta_1}{(\gamma_{ss} - 2\gamma_{sl})}, \quad (8)$$

where $K_1 = 3 k_c / K$.

Depending on the relative magnitude of the surface energies, two-phase composite materials may be divided into two classes. Composite materials of the first class are characterized by $\gamma_{ss} > 2\gamma_{sl}$, and those of the second class by $\gamma_{ss} \leq 2\gamma_{sl}$. A characteristic feature of composite materials of the first class is that the refractory particles in them form nonequilibrium dihedral angles [8]. The interphase surface forces acting on the solid-liquid and solid-solid boundaries are unbalanced. Such composite materials have the ability to imbibe liquid metals, and a migration pressure exists in them which has the physical meaning of suction pressure [9]. Under the action of this pressure, the liquid migrates from the capillary into the composite body. When the capillary pressure P_c in the capillary exceeds the migration pressure Π , a liquid interlayer is stable, while at $\Pi > P_c$ it is unstable. For each composite materials of the first class, there exists a critical capillary size above which an interlayer is unstable, while below it is stable.

3. Experiment

In composite materials of the second class ($\gamma_{ss} \leq 2\gamma_{sl}$), the refractory particles form equilibrium dihedral angles, the liquid phase is in mechanical equilibrium with the solid, there is no migration pressure ($\Delta F > 0$) and liquid interlayers are always stable. According to investigations [8], WC-Co, WC-Ni, TiC-Co, TiC-Ni, and Cr₃C₂-Ni composite materials are of the first class, while WC-Cu, Cr₃C₂-Cu, and Ni-Pb materials are of the second class. A study was made of the stability of liquid interlayers in some of these materials. Specimens 5 x 5 x 35 mm in size were sintered from the materials listed in Table.

Compositions and characteristics of specimens

Spec. No.	Designation of materials	Composition, mas. %					Liquid phase cont. at 1370°C vol. %	Particle size, d_s , μm	Critical capillary size, d_c , μm
		Co	Ni	Cu	WC	Cr ₃ C ₂			
1	WC-6Co fine	5.90	0	0	94.10	0	13.8	2.5	5
2	WC-6Co	5.90	0	0	94.10	0	13.8	3.0	6
3	WC-6Co coarse	5.90	0	0	94.10	0	13.8	4.5	10
4	WC-10Co	9.65	0	0	90.35	0	21.8	3.1	12
5	WC-15Co	14.3	0	0	85.70	0	31.1	3.4	15
6	WC-20Co	20.1	0	0	79.90	0	41.9	9.9	18
7	WC-6Ni	0	6.00	0	94.00	0	13.9	2.5	6
8	WC-15Ni	0	13.80	0	86.20	0	30.8	2.5	16
9	WC-20Ni	0	20.12	0	79.88	0	41.7	2.5	20
10	Cr ₃ C ₂ -20Ni	0	21.20	0	0	78.8	-	11.3	40
11	WC-12Cu	0	0	12.3	87.70	0	21.0	3.0	-
12	Cr ₃ C ₂ -25Cu	0	0	24.9	0	75.1	20.8	15.0	-

The face 5x35 mm of the specimens was ground to a level $h = 1.0, 1.5, 2.0, 2.5, 3.0, 3.6, 4.4, 5.0, 5.6, 6.2, 7.0, 8.1, 9.2, 10.0, 12.0, 15.3, \text{ and } 20.5 \mu\text{m}$ (h is the height of irregularities between upper and lower points). When the ground faces were placed together, a capillary was formed whose maximum size was $2h$. By varying the height of the irregularities, capillaries were obtained ranging in sizes from 2 to $41 \mu\text{m}$. Specimens from composite materials of the first class (Nos. 1-10 in Table

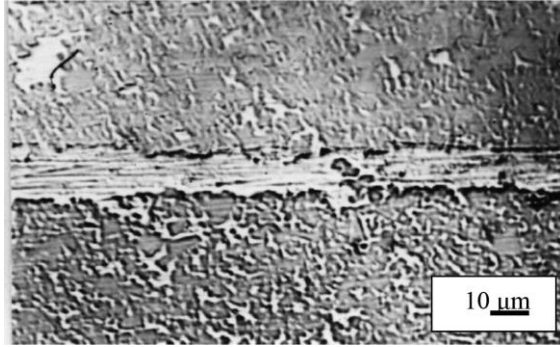


Fig. 2. Microstructure of WC-20Ni composite with nickel interlayer

the structure of the interlayer after annealing. After the liquid interlayer had formed spontaneously, chromium carbide particles began to grow inside it. The process was particularly vigorous in WC-Ni composites.

1) were heated in a vacuum at a residual pressure of $1.0-0.1 \text{ Pa}$ to a temperature of 1370°C and held at that temperature for between 1 and 60 min. After cooling, on the faces $5 \times 5 \text{ mm}$ the capillaries were examined by optical metallography methods. A study was made of the structures of capillaries of various sizes, and determinations were made of the critical capillary size d_{cr} , below which liquid metallic interlayers formed spontaneously (Figs. 2 and 3) and above which we have the capillaries without the liquid, empty.

Fig. 3 *a* depicts the process of filling of a capillary with molten nickel, while Fig. 3 *b* shows

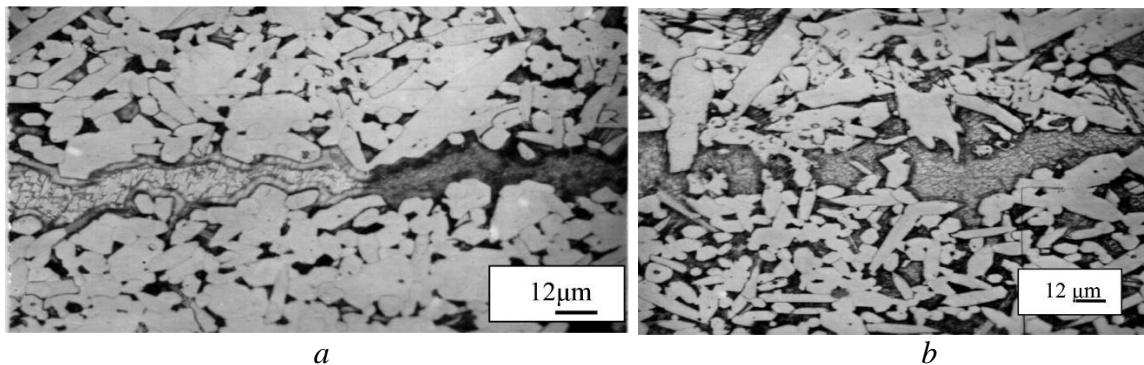


Fig. 3. Microstructures of joint zones of $\text{Cr}_3\text{C}_2\text{-}20\text{Ni}$ specimen *s* during filling of the capillary (*a*) and after 60-min annealing (*b*)

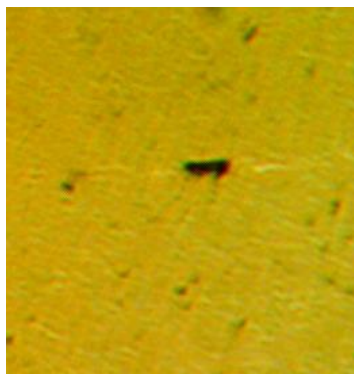


Fig.4. The empty capillary in joint zone of WC-6Co specimens of $3.6 \mu\text{m}$ surface roughness

For a WC-20Ni specimen, containing 20 mas. % Ni, it took 10 min to fill a $10 \mu\text{m}$ size of the interlayer (Fig. 2). In WC-6Co specimens ground to levels $h < 3 \mu\text{m}$, the capillaries filled up with molten cobalt, while at $h > 3.6 \mu\text{m}$ the capillaries were empty (Fig. 4).

4. Discussion

The analysis data of Table 1 shows that for WC-6Co fine (1), WC-6Co (2), and WC-6Co coarse (3) composites the d_{cr} proved to be directly proportional to particle size d_s , while for WC-6Co, WC-10Co, WC-15, and WC-20Co composites and also for WC-6Ni, WC-

15Ni, and WC-20Ni composites, it was – in good accord with Eq. (8) – proportional to $\left(\frac{1-u}{u}\right)^{\frac{1}{3}}$. This means that Eq.(8) can be employed for calculating the stable interlayers for various composite materials.

A quantitative characteristic of the filling phenomenon may be provided by the rate of displacement of the refractory particle front into a liquid interlayer. For WC-6Co, WC-10Co, and WC-20Co composites, these rates were 1.0, 0.7, and 0.5 $\mu\text{m}/\text{min}$, respectively. Similar results were obtained for WC-Ni materials.

The filling of an interlayer with refractory particles takes place as follows. During the liquid phase sintering of a composite material of the first class a structure with nonequilibrium refractory particles forms in the material. During contact with an interlayer, refractory particles tend to assume an equilibrium shape by recrystallization through the liquid phase, using an additional volume of the liquid interlayer, as a result of which they grow into it layer by layer. The rate of filling of an interlayer is determined by the rate of recrystallization of the particles and also by the degree of their initial unequilibrium. As the volume fraction of the liquid phase grows in WC-6Co, WC-10Co, and WC-20Co composites (Table 1), the tungsten carbide particles approach an equilibrium shape, and the rate of filling of the void accordingly diminishes. Thus, in composite materials of the first class and under conditions determined by expression (8), liquid interlayers at first appear spontaneously and then become filled by growing refractory particles, as a result of which they vanish. This means that in fact liquid interlayers in composite materials of the first class are metastable, so that, to preserve them, it is necessary to take into account the rate at which they become filled by growing refractory particles. In composite materials of the second class (WC-Cu and $\text{Cr}_3\text{C}_2\text{-Cu}$), stable liquid interlayers were found to form. In addition, 40- to 200 μm size of the interlayers were produced by electrodeposition; these interlayers withstood 100 min. annealing in a hydrogen atmosphere at 1300°C. We have not observed displacement of the refractory particles front into a liquid interlayer. In opinion of the author of the article, it is caused by that in WC-Cu and $\text{Cr}_3\text{C}_2\text{-Cu}$ composites refractory particles form equilibrium dihedral angles, W, Cr, C are not dissolved in copper, therefore recrystallisation of particles through a liquid phase do not occur.

5. Conclusions

For composite materials of the first class ($\gamma_{ss} > 2\gamma_{sl}$) there exists a critical liquid interlayer size above which they do not form. They are unstable. At a capillary size smaller than the critical, liquid interlayers at first form spontaneously by migration of liquid from within the composite body into the capillary, and subsequently they become filled by growing refractory particles. In composite materials of the second class ($\gamma_{ss} \leq 2\gamma_{sl}$), liquid interlayers of all sizes are stable.

Изучены композиционные материалы, состоящие из тугоплавких частиц и легкоплавкой связки. Процесс обнажения жидкого капилляра путем миграции жидкости из капилляра в объем тела описан в терминах термодинамики. Получено выражение для изменения свободной энергии Гельмгольца микродисперсной системы при протекании этого процесса и определены условия, при которых жидкая прослойка является устойчивой или нестабильной в объеме композиционного тела.

Ключевые слова: композиционный материал, жидкая прослойка, термодинамика

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Термодинаміка формування рідких прошарків в композиційних матеріалах

Вивчені композиційні матеріали, які складаються з тугоплавких частинок і легкоплавкої зв'язки. Процес оголення рідкого капіляра шляхом міграції рідини з капіляра в об'єм тіла описаний у термінах термодинаміки. Отримано вираз для зміни вільної енергії Гельмгольца микродисперсної

системи при протіканні цього процесу і визначені умови, при яких рідкий прошарок є стійким або нестабільним в об'ємі композиційного тіла.

Ключові слова: композиційний матеріал, рідкий прошарок, термодинаміка

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