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A. F. Lisovsky (Kiev)
lisovsky@ism.kiev.ua

Thermodynamics of the formation of composite material structures. A review

Composite material structures at nano-, micro-, and meso- levels have been examined. The application of the Gibbs and Hill thermodynamics has allowed researchers to give the physical interpretation of the Laplace pressure for composite materials; to derive the thermodynamic functions describing the particles consolidation; to establish the new phenomenon, namely, metal melt imbibition (MMI), and to define its acting forces, to establish the criterion that allows to determine a direction of a liquid phase migration in a composite body, as well as to predict the final structure of composite materials. For the description of composite material structure, which forms under extreme conditions, it has been necessary to use the nonequilibrium thermodynamics. At the extreme conditions the Prigogine concept of local equilibrium is promising.

Keywords*: composite material, structure, thermodynamics.*

INTRODUCTION

The subject of the present study is composite materials consisting of refractory particles and low-melting point binders; for example, WC–Co, Diamond–WC–Co, Cr_3C_2–Ni cemented carbides, Ti (C, N)–(Ni, Mo) cermets, W–(Ni, Fe) heavy alloys, W–Cu, Fe–Cu, Ni–Pb, Cu–(Sn, Pb) constructional materials, etc. These materials are produced by powder metallurgy. The final structures of composite materials are formed in the course of sintering. Researchers have well studied the kinetics and mechanism of sintering at molecular [1–7], micro-, and macrolevels [8–12], developed mathematical models of sintering powders [13–20]. The authors of [21–23] described the driving forces of sintering, and proposed the concepts of the Laplace effective pressure, sintering stress, and sintering potential. The phenomenology, kinetics, driving forces, and mechanism of powder sintering are analyzed in [24].

The development of the thermodynamic theory of the formation of composite materials structures at nano- and micro- levels has started only recently and in my opinion demands further investigation.

Chemical thermodynamics and phase equilibria are widely used at the development of composite materials. These areas of thermodynamics are well described in [25, 26], therefore, in the present review they are not examined.

The aim of the present review is to generalize the results of thermodynamic studies of the formation of composite materials structures and define the ways for the subsequent development of this field of the material science.

INVESTIGATION PROCEDURE

The structure of a composite material is formed of particles. The particle consists of a core and surface layer. Particles, in which the volume of core V_c is larger than the volume of surface layer V_l ($V_c >> V_l$), are macroobjects. Particles, in which $V_c \approx V_l$, are small objects (nanoparticles). To describe thermodynamic state of the macro object, the Gibbs thermodynamics is used. To make thermodynamic studies, it is necessary to allocate a system and to determine parameters of its interaction with the environment. Independent thermodynamic parameters of a system are the volume, V, pressure, p, temperature, T, masses of components, m, chemical potential, μ, and entropy, η. To describe a thermodynamic state of the system, the following state functions are used: internal energy, U (η, V, m), enthalpy, H (η, p, m), Helmholtz free energy, F (T, V, m), and Gibbs free energy, G (T, p, m). The state functions are total differentials of independent parameters and supposes linear integration. Using this property, it is possible to determine independent parameters of a system from state functions, for example: $\mu_i = \left(\frac{\partial G}{\partial m}\right)_{T,P,m_j \neq m_i}$; $p = -\left(\frac{\partial F}{\partial V}\right)_{T,m}$, where i and j are the components. Let's note the important property of macroobject: its parameters and state functions do not depend on the particle size, r. Unlike a macroobject, the parameters and state functions of a small object depend on the size, r [27]. Thus, the particle size, r, is an independent parameter of a nanoparticle state. For nanoparticles a special method of thermodynamic research should be developed.

For nanoparticles, it is worthwhile to use the Hill thermodynamic method [28]. Hill suggested that the system should be considered as an ensemble consisting of a great number of small objects, n, each containing m_i molecules of the i-th kind. Providing that Σm_i = const, the state of this system can be described by any of the known thermodynamic potential, say, internal energy

$$d(nu) = Td(n\eta) - pd(nV_\alpha) + \Sigma\mu_i d(nm_i) + \Lambda dn,$$

here u, η, V_α, and m belong to a small object α, p is the external pressure, the Λ magnitude allows for variations of the system energy as the small object sizes vary.

Upon integration and some simplifications of this equation Hill derived an expression for the internal energy of a small object:

$$u = T\eta - pV_\alpha + \Sigma\mu_i m_i + \Lambda. \quad (1)$$

Attention should be drawn to the fact that the surface area, s, and surface tension, γ, values of a small object are absent in Eq. (1). These values are indirectly allowed for by the Λ magnitude, which is equal to the work of the small object formation $\Lambda = \gamma s/3$ [29]. For the whole system Hill has derived the equation

$$U = T\eta - pV + \Sigma\mu_i m_i + \Lambda n.$$

The Helmholtz free energy, F, and Gibbs free energy, G, are

$$F = -pV + \Sigma\mu_i m_i + \Lambda n; \quad G = \Sigma\mu_i m_i + \Lambda n.$$

Hill's method correctly describes the consolidation of nanoparticles.

So, a technique of a thermodynamic research is simple: we allocate a system, then define the interface parameters, choose a state function, then determine its change at transition of the system from the initial into final state. The ignoring of this technique does not allow one to obtain correct results of thermodynamic studies.

The author [30] used Gibbs thermodynamics to derive the expression of the Laplace pressure

$$\Delta p_L = p_2 - p_1 = \gamma_{12}\frac{\delta A_{12}}{\delta V_2},$$

where A is the surface area, indices 1, 2 , and 12 indicate that the values they define refer to the corresponding phase or interface.

It is known from differential geometry that $\frac{\delta A}{\delta V} = K = R_1^{-1} + R_2^{-1}$, where K is the surface curvature, R_1 and R_2 are the main radii of the curvature at the given point. Taking into account this dependence, the known expression of the Laplace pressure has been derived

$$\Delta p_L = \gamma_{12}\left(\frac{1}{R_1} + \frac{1}{R_2}\right). \qquad (2)$$

There is a contradiction in the expression of the Laplace pressure. Eq. (2) describes the pressure at a point of a curved surface, which contradicts the physical essence of the mere notion of the pressure, which is an integral characteristic and has the meaning only as applied to a certain surface area or to the bulk of the body. Because of this Eq. (2) may be correctly used only to describe a surface with a constant curvature, K, i.e., spherical, cylindrical, or plane. Eq. (2) cannot be used for the definition of the Laplace pressure in a crystal, which has a precise facet. Expression for the definition of the Laplace pressure in bodies of any geometrical shape is [30]

$$\Delta p_L = \frac{2}{3}\gamma\frac{s}{v},$$

where v is the volume of a body.

In [24, 31, 32] the Laplace pressure (Eq. (2)) is used to describe the motive force of the particle consolidation process. To apply the Laplace pressure for cavities of an arbitrary geometrical shape, the authors [24, 31, 32] introduced the so-called effective Laplace pressure and negative Laplace pressure. The authors of [24, 31, 32] think that at the consolidation of particles the Helmholtz free energy (F) changes only as a result of the reduction of the solid–gas interface. Thus, the changes of the Helmholtz free energy in volumetric phases and changes of the component chemical potentials are ignored. The authors [24, 31, 32] do not give a clear physical interpretation of the “effective Laplace pressure” and the “negative Laplace pressure” terms. The application of Eq. (2) gives erroneous results of research [32]. The Laplace pressure can be positive only.

THERMODYNAMICS OF STRUCTURE FORMATION IN TWO-PHASE COMPOSITE MATERIALS

To study the structure formation of microdispersed composite materials, the Gibbs thermodynamics was used [33]. The particles consolidation was studied using a model of a system that consists of n equidimensional particles of solid phase, α, and one moving phase, ε (a gas or liquid). In its initial state, the system consisted of region I filled with the phase ε and region II that contained n particles of the phase α and the phase ε. The particles were in point contacts and formed a regular structure. Regions I and II were separated by a surface III. The passing of the system from the initial to final state is shown in Fig. 1.

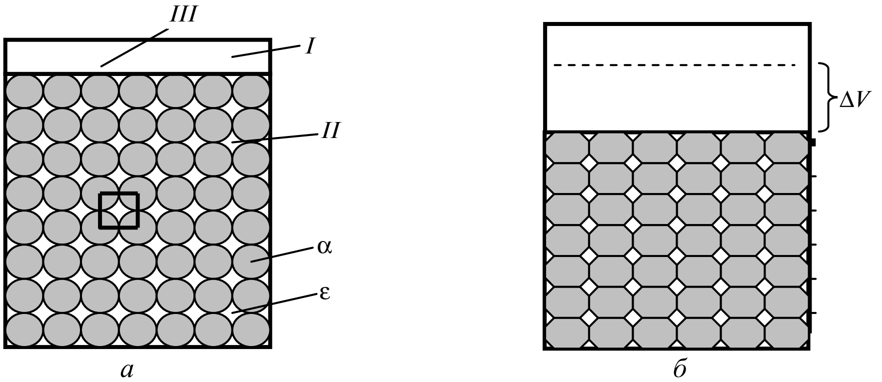


Fig. 1. A model of a two-phase dispersed system: α is a solid dispersed phase, ε is a moving phase (gas, liquid); initial (*a*) and final (*b*) states [33].

A change of the Helmholtz free energy (ΔF) of the particle consolidation is described by the expression

$$\Delta F = \frac{1}{3}(\gamma_{\alpha\alpha} - 2g\gamma_{\alpha\varepsilon})\Delta A_{\alpha\alpha}\,, \tag{3}$$

where A is the surface area, g is the coefficient, which allows for the variation of the particle geometry, indices αα and αε show that the indicated values belong to the appropriate interface.

Thus, the consolidation process proceeds spontaneously when $\gamma_{\alpha\alpha} < 2g\gamma_{\alpha\varepsilon}$.

Equation (3) is the thermodynamic potential of the system under consideration. From this reason, the pressure of the system can be defined from $p = -(\partial F/\partial V)_{T,m}$. This pressure will be further referred to as the shrinkage pressure p_{sh}.

$$p_{sh} = \frac{1}{3}(2g\gamma_{\alpha\varepsilon} - \gamma_{\alpha\alpha})\frac{\partial A_{\alpha\alpha}}{\partial V} \tag{4}$$

Equation (4) is basic, using Eq. (4) the author [33] has obtained

$$p_{sh} = K_{sh}\frac{1}{r}\left(\frac{1-u}{u}\right)^{\frac{1}{3}}\Phi(u),$$

where $K_{sh} = k(2g\gamma_{\alpha\varepsilon} - \gamma_{\alpha\alpha})$, k is the coefficients, r is the size of a particle α, u is the phase ε volume content of region *II* (in volume fractions), $\Phi(u)$ is a dimensionless parameter, which takes into account changes in the cavity geometry in the course of the particles consolidation.

It is necessary to note, that the expression of shrinkage pressure p_{sh} (4) is an integral characteristic of the whole group of sintering particles and it is devoid of contradictions inherent in Eq. (2).

According to Fig. 1, the transformation of the system from state (*b*) into state (*a*) results in the deconsolidation of a refractory skeleton into an ensemble of particles. Having fulfilled the above requirements for this process, author [33] obtained the following expression for the change of Helmholtz free energy for this system:

$$\Delta F = \frac{1}{3}(2g\gamma_{\alpha\varepsilon} - \gamma_{\alpha\alpha})\Delta A_{\alpha\alpha}.$$

Thus, deconsolidation of a refractory skeleton occurs when $\gamma_{\alpha\alpha} > 2g\gamma_{\alpha\varepsilon}$. During the deconsolidation of a refractory skeleton a pressure, Π, generates in region *II*. The pressure, Π, has the physical sense of the imbibition pressure. The expression for the Π pressure is [33]:

$$\Pi = \frac{1}{3}(\gamma_{\alpha\alpha} - 2g\gamma_{\alpha\varepsilon})\frac{\partial A_{\alpha\alpha}}{\partial V}; \; \Pi = K_{\Pi}\frac{1}{r}\left(\frac{1-u}{u}\right)^{\frac{1}{3}}\Phi(u), \tag{5}$$

where $K_{\Pi} = k(\gamma_{\alpha\alpha} - 2g\gamma_{\alpha\varepsilon})$.

In gas medium, the condition $\gamma_{\alpha\alpha} < 2g\gamma_{\alpha\varepsilon}$ is fulfilled and the consolidation of particles proceeds spontaneously. When a liquid is a moving phase, the condition $\gamma_{\alpha\alpha} > 2g\gamma_{\alpha\varepsilon}$ arises. In these systems the deconsolidation of refractory skeletons into ensembles of particles takes place. This phenomenon was observed in WC–Co, WC–Ni, TiC–Ni, Cr_3C_2–Ni composite materials [34, 35]. In the composite material having a refractory skeleton, there is a metal melt imbibition by pore-free composite body (MMI-phenomenon) [36]. The mathematical model of the MMI-phenomenon is described in [37], where the new law of the mass transfer of a liquid phase in the dispersed structured systems is given. The MMI-phenomenon takes place only in composite materials, in which refractory particles form non-equilibrium dihedral angles [38]. According to experimental data [38], composite materials consisting of refractory particles and a binder can be conventionally divided into two classes. Composites with $\gamma_{\alpha\alpha} > 2g\gamma_{\alpha\varepsilon}$ form the first class, while the second class includes those with $\gamma_{\alpha\alpha} < 2g\gamma_{\alpha\varepsilon}$. The characteristic feature of the first class of composites is their ability to imbibe metal melts. In the second class of composites, equilibrium dihedral angles are formed, and liquid and solid phases are in mechanical equilibrium. These composites have no pressure, Π (Eq. (5)) and do not imbibe metal melts.

The Hill thermodynamics was used to study the formation of structures of nanodisperse composite materials [39]. According to [40], the chemical potential of a particle component, *i*, under the equilibrium conditions is not equal to the chemical potential of a component, *i*, in the dispersion medium, their interrelation is described by $\mu_r = \mu_\infty + 2\gamma\Omega/3r$, where μ_r and μ_∞ are the chemical potentials of a component in a particle of radius *r* and in an unlimited volume (gas, vapor, liquid), respectively, Ω is the atomic volume. This expression has been used in thermodynamic investigations [39].

A change of the Helmholtz free energy (ΔF) of nanodispersed system is described by the expression [39]:

$$\Delta F = \frac{1}{3}(\gamma_{\alpha\alpha} - 2g\gamma_{\alpha\varepsilon})\Delta A_{\alpha\alpha} + \frac{2}{3r}(\gamma_{\alpha\alpha} - \gamma_{\alpha\varepsilon})\sum_{i=1}^{k} m_i^{\alpha} v_i^{m}, \tag{6}$$

where v_i^m is the molar volume.

The shrinkage pressure, p_{sh}, of the nanodispersed composite material is [39]

$$p_{sh} = \frac{1}{3}(2g\gamma_{\alpha\varepsilon} - \gamma_{\alpha\alpha})\frac{\Delta A_{\alpha\alpha}}{\Delta V_{sh}} + \frac{1}{\Delta V_{sh}}\frac{2}{3r}(\gamma_{\alpha\varepsilon} - \gamma_{\alpha\alpha})\sum_{i=1}^{k} m_i^{\alpha} v_i^{m}. \tag{7}$$

A comparison of Eqs. (3) and (4) with (6) and (7) for nanoparticles allows a conclusion that the additional items $\frac{2}{3r}(\gamma_{\alpha\alpha}-\gamma_{\alpha\varepsilon})\sum_{i=1}^{k} m_i^{\alpha} v_i^{m}$ in (6) and $\frac{2}{3r}(\gamma_{\alpha\varepsilon}-\gamma_{\alpha\alpha})\sum_{i=1}^{k} m_i^{\alpha} v_i^{m}$ in (7) are due to the effect of size of a small object (nanoparticle).

Features of the deconsolidation of a refractory skeleton in nanodispersed composite materials are described in [41].

THERMODYNAMICS OF THE STRUCTURE FORMATION IN THREE-PHASE COMPOSITE MATERIALS

The formation of the structure in a three-phase composite material is a complex process. A simplified model and the following expression of a change of the free energy (ΔF) were proposed in [42].

$$\Delta F=\frac{1}{3}(\gamma_{\alpha\alpha}-2g_{\alpha}\gamma_{\alpha\varepsilon})\Delta A_{\alpha\alpha}+\frac{1}{3}(\gamma_{\beta\beta}-2g_{\beta}\gamma_{\beta\varepsilon})\Delta A_{\beta\beta}+\frac{1}{3}(\gamma_{\alpha\beta}-g_{\alpha\beta}\gamma_{\alpha\varepsilon}-g_{\alpha\beta}\gamma_{\beta\varepsilon})\Delta A_{\alpha\beta}, \quad (8)$$

where α and β are the particles, ε is the moving phase (gas, liquid).

The particle consolidation process will be spontaneous, if $\Delta F < 0$, i.e., if the following conditions are met:

$$2g_{\alpha}\gamma_{\alpha\varepsilon} > \gamma_{\alpha\alpha},\ 2g_{\beta}\gamma_{\beta\varepsilon} > \gamma_{\beta\beta},\ g_{\alpha\beta}\gamma_{\alpha\varepsilon} + g_{\alpha\beta}\gamma_{\beta\varepsilon} > \gamma_{\alpha\beta}. \quad (9)$$

In the gaseous phase these inequalities are always met, in the liquid phase some of the inequalities (9) may not be met. For instance, if $2g_{\alpha}\gamma_{\alpha\varepsilon} < \gamma_{\alpha\alpha}$ contacts between particles of the phase α do not form in such a system. Similarly, if $2g_{\beta}\gamma_{\beta\varepsilon} < \gamma_{\beta\beta}$ and $g_{\alpha\beta}\gamma_{\alpha\varepsilon} + g_{\alpha\beta}\gamma_{\beta\varepsilon} < \gamma_{\alpha\beta}$ contacts β–β and α–β do not form.

Thus, if the inequalities (9) are met, during the particle consolidation a structure of two interpenetrating skeletons forms from particles of the α and β phases in the system. If any of the inequalities (9) is not met, aggregates and intergrowths of several particles form in the system. If all three inequalities are not fulfilled, the consolidation process does not occur. From Eq. (8) the expression describing shrinkage pressure in three-phase composite materials have been obtained [42]:

$$p_{sh}=\frac{1}{3}\left[\left(2g_{\alpha}\gamma_{\alpha\varepsilon}-\gamma_{\alpha\alpha}\right)\frac{\partial A_{\alpha\alpha}}{\partial V_{sh}}+\left(2g_{\beta}\gamma_{\beta\varepsilon}-\gamma_{\beta\beta}\right)\frac{\partial A_{\beta\beta}}{\partial V_{sh}}+\left(g_{\alpha\beta}\gamma_{\alpha\varepsilon}+g_{\alpha\beta}\gamma_{\beta\varepsilon}-\gamma_{\alpha\beta}\right)\frac{\partial A_{\alpha\beta}}{\partial V_{sh}}\right].$$

The final structures of composite materials are formed during the liquid-phase sintering. The analysis of physicochemical processes occurring in composite bodies during the liquid-phase sintering, motive forces, and process mechanisms is given by German [43]. Thermodynamic studies of sintering of composite materials with the liquid phase present are described in [44]. The author [44] has investigated a system, which contained particles α, liquid β, and gas ε in the initial state. In the final state the particles have formed a refractory skeleton penetrated by a liquid phase. The change of the Helmholtz free energy in the system transition from the initial state into the final state is

$$\Delta F=-\frac{1}{3}\left(A_{\alpha\varepsilon}\cos\theta+A_{\beta\varepsilon}\right)\gamma_{\beta\varepsilon}+\frac{1}{3}\left(\gamma_{\alpha\alpha}-2g\gamma_{\alpha\beta}\right)\Delta A_{\alpha\alpha}+\frac{1}{3}\gamma_{\alpha\beta}\Delta A_{\alpha\beta}+\frac{1}{3}\gamma_{\alpha\alpha}\Delta A_{\alpha\alpha}+\sum_{i} m_i\Delta\mu_i, \quad (10)$$

where θ is the wetting angle.

During liquid phase sintering a number of complex processes take place; however the thermodynamics does not consider the kinetics and mechanism of these processes. Equation (10) describes only a change of the Helmholtz free energy of the system.

In Eq. (10) the $\frac{1}{3}\left(A_{\alpha\varepsilon}\cos\theta + A_{\beta\varepsilon}\right)\gamma_{\beta\varepsilon}$ term describes the change of the Helmholtz free energy at the first stage of sintering, in the course of which a complete removal of the gaseous phase from the sintered compact takes place. The main driving force of this stage is a decrease of the solid–gas and liquid–gas interfaces. The first term is always below 0, i.e., this process proceeds spontaneously. The second term of Eq. (10) describes the process of the formation of a skeleton from particles α. The main driving force of this process is the variation of the particle contact surfaces, $\Delta A_{\alpha\alpha}$. It follows from Eq. (3) that the formation of the refractory skeleton is possible with the following relation of surface tensions: $\gamma_{\alpha\alpha} < 2g\gamma_{\alpha\beta}$. Under these conditions the equilibrium dihedral angles form in the composite material. If the liquid volume in the composite material is inadequate, the particles cannot take the equilibrium form and form nonequilibrium dihedral angles. The structure of such a composite material is also nonequilibrium and as the composite body contacts the liquid phase, the latter is imbibed to the instant of the formation of equilibrium dihedral angles and separation of particles by the liquid [35, 36]. The third and fourth terms describe growth of particles during sintering a composite material.

In composite materials, in which nonequilibrium dihedral angles formed, there is pressure, Π, which has the physical sense of the imbibition pressure [38]. Under certain conditions stable pores form in these composite materials, which are not filled by the liquid [45]. The thermodynamics of the filling of isolated pores in such materials is discussed in [46]. The change of the free energy, F, is described by the following expression [46]:

$$\Delta F = \frac{K}{3d}\left(\gamma_{\alpha\alpha} - 2g\gamma_{\alpha\beta}\right)\left(\frac{1-u}{u}\right)^{\frac{1}{3}}\Delta V_{\beta} - \frac{k^{c}}{3}\frac{V^{c}}{r}\gamma_{\alpha\varepsilon}\cos\Theta, \tag{11}$$

where K is the coefficient allows for geometrical parameters of a composite body, k^c is the coefficient of the geometric form of a pore, d is the particle size, V^c is the volume of a pore, r is the radius of a pore.

It follows from Eq. (11) that when $\gamma_{\alpha\alpha} < 2g\gamma_{\alpha\beta}$ the $\Delta F < 0$ and hence, an isolated pore is spontaneously filled with liquid. In composite materials, in which $\gamma_{\alpha\alpha} > 2g\gamma_{\alpha\beta}$ a spontaneous pore filling with liquid ($\Delta F < 0$) is possible when

$$\frac{K}{d}\left(\gamma_{\alpha\alpha} - 2g\gamma_{\alpha\beta}\right)\left(\frac{1-u}{u}\right)^{\frac{1}{3}} < k^{c}\frac{\gamma_{\alpha\varepsilon}}{r}\cos\Theta.$$

If $\frac{K}{d}\left(\gamma_{\alpha\alpha} - 2g\gamma_{\alpha\beta}\right)\left(\frac{1-u}{u}\right)^{\frac{1}{3}} > k^{c}\frac{\gamma_{\alpha\varepsilon}}{r}\cos\Theta$ the pore is not filled with liquid. It follows from these inequalities that depending on the radius, r, the pore can or cannot be filled with the liquid. The critical pore radius, r_{cr}, below which the pore is filled with the liquid and above which it is not filled, was derived in [46]:

$$r_{cr}=\frac{k^c}{K}d\left(\frac{u}{1-u}\right)^{\frac{1}{3}}\frac{\gamma_{\beta\varepsilon}\cos\Theta}{\left(\gamma_{\alpha\alpha}-2g\gamma_{\alpha\beta}\right)}.$$

The filling of a pore in a solid–liquid nanodisperced system is described in [47], where the following expression for the thermodynamic function was suggested:

$$\Delta F=\frac{K}{3d}\left(\gamma_{\alpha\alpha}-2g\gamma_{\alpha\beta}\right)\left(\frac{1-u}{u}\right)^{\frac{1}{3}}\Delta V_{\beta}-\frac{k^c}{3}\frac{V^c}{r}\gamma_{\alpha\varepsilon}\cos\Theta+\frac{2}{3r}(\gamma_{\alpha\beta}-\gamma_{\alpha\alpha})\sum_{i=1}^{k}m_i^{\alpha}v_i^{m}.$$

To study the thermodynamics of the nanoparticles consolidation in three-phase composite materials, a system consisting of n_α nanoparticles of phase α, n_β nanoparticles of phase β, and medium ε was used [39]. In the initial state of the system the particles are separated by phase ε. In the final state the consolidation of the particles of phases α and β occurred and the particles formed two mutually penetrating skeletons.The change of the Gibbs free energy in the system transition from the initial into the final state can be described as the sum of changes of the Gibbs free energies of two-phase subsystems $\Delta G=\Delta G_{\alpha\alpha}+\Delta G_{\beta\beta}+\Delta G_{\alpha\beta}+$ $+\Delta G_{\beta\alpha}+\Delta G_{\varepsilon}$ [39].

After sintering in three-phase composite materials refractory skeletons are formed. Features of the formation of refractory skeletons are given in [48].

The structure of a refractory skeleton is described by a contiguity, *C*, [49] and a dihedral angle, φ, $\cos(\varphi/2)=\gamma_{ss}/2\gamma_{sl}$ [50]. By the thermodynamic investigations [51] it is established, that dihedral angle, φ, suggested by Smith [50], can be used only for unbounded contacting surfaces. In composite materials particles are limited by the closed surfaces which, as has shown by Gibbs [52], influence a state of a thermodynamic object (a liquid drop, a particle). Considering this position, expression for a dihedral angle, which is formed by particles, looks like [51]

$$\cos\frac{\varphi}{2}=\frac{\gamma_{ss}}{2\left(\gamma_{sl}+K_1\bar{\gamma}\right)},$$

where K_1 is the coefficient, $\bar{\gamma}$ is the averaged surface tension.

The infiltration of refractory skeletons with liquid metals is one of the efficient methods to produce composite materials with unique properties. During the infiltration of the nanodispersed composite materials the important problem is to chose the prerequisites to the stable existence of metal layers in nanodispersed bodies. The thermodynamics of the liquid interlayers in nanodispersed composite materials is described in [53]. The thermodynamic investigations were conducted on the model of a system shown in Fig. 2.

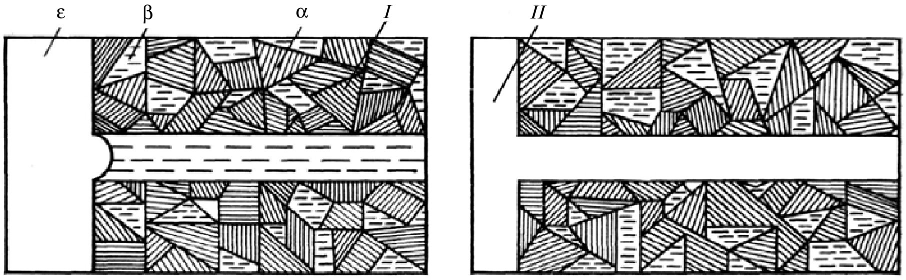
The change of the Gibbs free energy, Δ*G*, of the system during the capillary emptying is described by the equation [53]

$$\Delta G=\frac{1}{3}(2\gamma_{\alpha\beta}-\gamma_{\alpha\alpha})\Delta A_{\alpha\alpha}+\frac{2}{3r}(\gamma_{\alpha\beta}-\gamma_{\alpha\alpha})\sum_{i=1}^{k}m_i^{\alpha}v_i^{m}+\frac{V_c}{d_c}g_c\gamma_{\beta\varepsilon}\cos\Theta_1.$$

In this expression when $\gamma_{\alpha\alpha}>2\gamma_{\alpha\beta}$ the first and the second terms are negative and the Δ*G* value is defined by the following relations:

$$\frac{1}{3}(2\gamma_{\alpha\beta}-\gamma_{\alpha\alpha})\Delta A_{\alpha\alpha}+\frac{2}{3r}(\gamma_{\alpha\beta}-\gamma_{\alpha\alpha})\sum_{i=1}^{k} m_i^{\alpha} v_i^{m} > \frac{V_c}{d_c} g_c \gamma_{\beta\varepsilon}\cos\Theta_1,\ \Delta G<0; \quad (12)$$

$$\frac{1}{3}(2\gamma_{\alpha\beta}-\gamma_{\alpha\alpha})\Delta A_{\alpha\alpha}+\frac{2}{3r}(\gamma_{\alpha\beta}-\gamma_{\alpha\alpha})\sum_{i=1}^{k} m_i^{\alpha} v_i^{m} < \frac{V_c}{d_c} g_c \gamma_{\beta\varepsilon}\cos\Theta_1,\ \Delta G>0. \quad (13)$$



а *б*

Fig. 2. Model of a system in the initial (*a*) and in the final (*b*) states, α is a nanoparticle, β – liquid, ε – gas phase; *I* indicates a composite body consisting of nanoparticles α and liquid β, *II* is the region filled by a gas phase [53].

If Rel. (13) is fulfilled, liquid interlayers of any size are stable, while in Rel. (12) they are unstable. From Rel. (12) it follows that the capillary empties and the gas phase occupies the place of the liquid.

THERMODYNAMICS OF MESOSTRUCTURE FORMATION IN COMPOSITE MATERIALS

A mesostructure consists of a random ensemble of mesoelements (granules), which are bound by a metal or composite matrix. It is possible to consider the matrix as a binder phase. The mean sizes of the mesoelements are 30–500 μm. In [54] mesostructured composite materials have been divided into three types. The first type is the composites consisting of a metal matrix, for example, Co, Ni, special alloys, and mesoelements that are formed from composite materials. The second type includes the composites consisting of mesoelements and a matrix formed from composite materials. For example, the mesoelements are produced from WC–6Co cemented carbide and a matrix is formed from W–Fe–Ni heavy metal. The third type is represented with composites consisting of mesoelements that are produced from a single crystal and a matrix is made from a composite material, for example, a diamond mesoelement and a WC–Co composite. In the composite materials considered above the mesoelements can contact with each other, forming a three dimensional structure, or may be in regular intervals located in a matrix without contacts. The structure of a mesocomposite can be described by the stereology on metallographic specimens [55, 56].

The formation of the mesostructure allows one to produce composite materials with particular properties by varying sizes and compositions of mesoelements as well as the composition and properties of a matrix [57, 58].

The thermodynamics of solid–phase sintering of the first type of mesocomposite materials is described by the following expression

$$\Delta F=\frac{1}{3}(\gamma_{\alpha\alpha}-2g\gamma_{\alpha\varepsilon})\Delta A_{\alpha\alpha}+\frac{1}{3}(\gamma_{\beta\alpha}-\gamma_{\beta\varepsilon})A_{\beta}+\sum_{i} m_i\Delta\mu_i\,, \quad (14)$$

where α is the particles of mesoelement, β is the mesoelement, ε is the gas phase.

If solubility of components in phases is insignificant, expression (14) becomes

$$\Delta F = \frac{1}{3}(\gamma_{\alpha\alpha} - 2g\gamma_{\alpha\varepsilon})\Delta A_{\alpha\alpha} + \frac{1}{3}(\gamma_{\beta\alpha} - \gamma_{\beta\varepsilon})A_{\beta}. \tag{15}$$

From Eq. (15) the following relationships among the surface tensions are obtained:

$$2g\gamma_{\alpha\varepsilon} > \gamma_{\alpha\alpha};\ \gamma_{\beta\varepsilon} > \gamma_{\beta\alpha}, \tag{16}$$

$$2g\gamma_{\alpha\varepsilon} > \gamma_{\alpha\alpha};\ \gamma_{\beta\varepsilon} < \gamma_{\beta\alpha}, \tag{17}$$

$$2g\gamma_{\alpha\varepsilon} < \gamma_{\alpha\alpha};\ \gamma_{\beta\varepsilon} > \gamma_{\beta\alpha}, \tag{18}$$

$$2g\gamma_{\alpha\varepsilon} < \gamma_{\alpha\alpha};\ \gamma_{\beta\varepsilon} < \gamma_{\beta\alpha}. \tag{19}$$

If Rel. (16) is met, a compact composite material forms. From Rel. (17) it follows that the consolidation of only particles α occurs; according to Rel. (18) the consolidation of particles α does not occur; according to Rel. (19) the structure does not form. Liquid phase sintering of the first type mesocomposite is described by Eq. (10). During liquid phase sintering in mesostructure composite of the first class mesoelements imbibe a matrix liquid [38]. In mesostructure composite of the second class [38] the imbibition of a liquid phase by mesoelements is not observed. The thermodynamics of the mesostructure formation in a mesocomposite material of the second type is described by Eq. (10). During the liquid phase sintering in a mesostructure composite of the first class [38] the mass transfer of the liquid phase from mesoelements to the matrix is observed. The moving force of this process is a matrix-to mesoelement pressure gradient, Π, [59]. A special feature of the formation of the third type mesostructure is the absence of a liquid phase migration from a matrix into mesoelements. To attain high physico-mechanical properties of a measocomposition, one should gain a good a matrix-to-mesoelements adhesion [60]. To achieve this result, it is necessary to study the interaction of phases at the mesoelement–matrix interface. In some composite materials the mesoelements and matrix are thermodynamically incompatible; therefore, at the mesoelement–matrix interface new phases form. In a composite material consisting of WC–Co mesoelements and W–Fe–Cu matrix at the WC–Co/W–Fe–Cu interface a dense carbide layer forms (Fig. 3). This layer interferes with a liquid phase penetration from the W–Fe–Cu matrix into the WC–Co mesoelement [54].

Thermodynamics of the mesostructures formation in nanodispersed composite materials is given in [61, 62]. In nanodispersed mesostructured composite materials the consolidation of the nanoparticles is described by Eqs. (6) and (7). In these materials the nanoparticles dissolve in a dispersion medium and large particles grow. Large particles destabilize nanodispersed composite materials [62]. Using composite materials of the first class [38] for the formation of mesostructures in nanodisperced materials, it is necessary to consider transfer of a liquid phase in bulks of mesoelements and matrix [63].

From the considered above papers follows, that the surface energies ($\gamma_{\alpha\alpha}$, $\gamma_{\beta\beta}$, $\gamma_{\alpha\beta}$, $\gamma_{\alpha\varepsilon}$, $\gamma_{\beta\varepsilon}$) affect the formation of composite material structure. To form the required structure of a composite material, it is necessary to know the values of the surface energy. At present, there are good methods of research of the structure and composition of contact and interphase surfaces. They are high resolution transmission electron microscope equipped with an energy dispersive analyzers of X-rays (TEM-EDX) and the atom probe tomography (APT) in combination with TEM [64–67]. Methods of the definition of the surface energy at the liquid/gas interface are developed, but there are no reliable methods to define the surface energy at the solid/solid and solid/liquid interface. The last circumstance slows down the development of new effective composite materials.

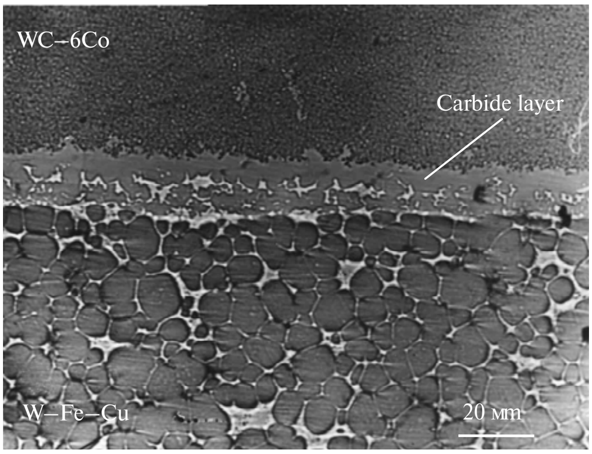


Fig. 3. Structure of the WC–6Co/W–Fe–Cu interface [54].

ON THE THERMODYNAMICS OF STRUCTURE FORMATION UNDER CONDITIONS OF INTENSIVE TECHNOLOGIES

The structures produced by traditional technologies of the powder metallurgy are described above. At present new methods of the composite material structure formation are developed: hot pressing (HP), hot isostatic pressing (HIP) [68], intensive electric sintering (IES) [69], spark plasma sintering (SPS) [70], high frequency induction heated sintering (HFIHS) [71], rapid omni compaction (ROC) [72], pulse plasma sintering (PPS) [73], and ultrahigh pressure rapid hot consolidation (UPRC) [74]. The sintering of WC–Co composites using intensive technologies is given in the table.

Sintering of WC–Co mixtures on intensive technologies [75]

Sintering technology	Sintering temperature, °C	Holding time, s	Heating rate deg/min	Pressure, MPa	Compositions of the initial powders, wt %	Size of WC initial particles, nm	Relative density, %
HP	1300	5400	–	25	WC–11Co	80	100
HIP	1000	3600	–	150	WC–10Co	–	100
SPS	1100	600	150	60	WC–12Co–1VC	40–250	95.94
HFIHS	1200	55	1400	60	WC–10Co	100	99.4
ROC	1000	10	–	830	WC–8Co	~ 100	–
UPRC	1200	900	200	1000	WC–10Co	50	99.4
PPS	1100	300	1200	60	WC–12Co	60	98
IES [47]	1300	10	5000	300	WC–10Co	100–150	98

According to HP and HIP technologies, the final structure of a composite material is formed at high temperatures for long holding times. Under these conditions the system achieves an equilibrium state, therefore, for the description of a composite material structure the Gibbs thermodynamics can be used. The SPS, HFIHS, ROC, UPRC, PPS, IES technologies use high heating rate and short holding times. During heating of a powder compact in its volume a temperature gradient appears, which causes heat streams. Under these conditions the powder compact is a nonequilibrium system. For the description of the structure formation by these technologies it is necessary to use nonequilibrium thermodynamics. The Prigogine concept [76] of local equilibrium is promising in the description of the structure formation in these powder compacts. According to this concept, equilibrium thermodynamic relations are true for each small volume, thus intensive thermodynamic parameters T, p, μ are functions of coordinates and time, t. In a powder compact the particles are small volumes and thus it is supposed, that the Gibbs relations are working for each particle.

The local equilibrium theory is applied for an object, which is statistical ensemble, for example, a micro particle. This theory cannot be used for a nanoparticle, which is not a statistical ensemble and its parameters are influenced with fluctuations. In the nonequilibrium thermodynamic theory [76, 77] the fundamental expressions describing a local production entropy, the equations of material balance and balance entropy, and conservation of the energy are developed. This theory can be used for the description of the structure formation of composite materials produced by intensive technologies.

CONCLUSIONS

The use of the Gibbs and Hill thermodynamics has allowed to describe a formation of structures in composite materials at nano-, micro-, and meso- levels; to give a strict conclusion and physical interpretation of the Laplace pressure; to derive the thermodynamic functions describing process of the particle consolidation; to prove the MMI phenomenon and to define its moving forces; to establish the shrinkage pressure, p_{sh}, arising during the particles consolidation and the pressure, Π, arising during the deconsolidation of a refractory skeleton; to prove the existence of the first class of composite materials, in which there is a pressure, Π, and the second class, in which there is no pressure, Π, and MMI phenomenon; to prove the criterion allowing us to determine a direction of the liquid phase migration in composite materials. These results of thermodynamic investigations have been achieved for composite materials, whose structure is formed by traditional methods of the powder metallurgy.

At present, intensive thechnologies of the formation of composite material structure have been developed. It has been defined that the use of the Gibbs and Hill thermodynamics for these technologies is incorrect. To describe the structure formation of composite materials, which are produced by these technologies, it is necessary to apply the nonequilibrium thermodynamics. The existing theory of nonequilibrium thermodynamics requires further development for its practical use.

Изучена структура композиционных материалов на нано-, микро- и мезоуровнях. Используя термодинамику Гиббса и Хилла, исследователи дали физическую интерпретацию давления Лапласа для композиционных материалов; получили термодинамические функции, описывающие процесс консолидации частиц; установили новое явление – поглощение металлических расплавов спеченными композиционными телами (phenomen MMI), определили его движущие силы; обосновали критерий, который позволяет определить направление миграции жидкой фазы в композиционных телах; предсказать окончательную структуру композиционных материалов. Для описания структуры *композиционных материалов, которые формируются в экстремальных условиях, предложено применять неравновесную термодинамику. Для этих условий перспективной является концепция локального равновесия, разработанная И. Пригожиным.*

***Ключевые слова**: композиционные материалы, структура, термодинамика.*

Вивчено структуру композиційних матеріалів на нано-, мікро- і мезорівнях. Використовуючи термодинаміку Гіббса і Хілла, дослідники дали фізичну інтерпретацію тиску Лапласа для композиційних матеріалів; одержали термодинамічні функції, що описують процес консолідації часточок; виявили нове явище – поглинання металевих розплавів спеченими композиційними тілами (phenomenon MMI) та визначили його рушійні сили; обґрунтували критерій, який дозволяє визначити напрямок міграції рідкої фази в композиційних матеріалах та прогнозувати кінцеву їх структуру. Для опису структури композиційних матеріалів, яка формується в екстремальних умовах, запропоновано застосовувати нерівноважну термодинаміку. Для цих умов перспективною є концепція локальної рівноваги, яка розроблена І. Пригожиним.

***Ключові слова**: композиційні матеріали, структура, термодинаміка.*

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V. Bakul Institute for Superhard Materials,
National Academy of Sciences of Ukraine

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