The thermodynamics of the liquid phase migration in nanodispersed composite bodies

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ABSTRACT

The thermodynamics of the liquid phase migration in a nanodispersed composite body has been studied. An expression describing the variation of the Gibbs potential in the course of the above process has been derived. The notion "the migration pressure" has been introduced. The equation for the migration pressure has been derived, which includes size of nanoparticles, interphase and surface tensions and the variation of the area of contact and interphase surfaces in the course of migration.

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1. Introduction

The objects of this investigation are composite materials consisting of refractory particles and a binding metal, for instance, W–Ag, WC–Co, WC–Ni, TiC–Co, TiC–Ni, Cr_3C_2–Ni, Cr_3C_2–Cu, Fe–Cu and others. Above the melting point of the binding metal, particles in these materials form 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 the chemical equilibrium melts, for instance, the composite WC–Co imbibes cobalt melts saturated C and W.

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 composite body volume. This type of mass transport, called by the present author the migration of a liquid, occurs in a chemical equilibrium pore-free systems 'metal melts–composite body'. It cannot be described on the basis of the diffusion of components or capillary theory.

In the studies [2] was used the Gibbs method for the thermodynamics of the liquid phase migration in composite bodies. The method is applicable to objects, in which the surface layer volume is negligibly small as compared to the volume of the whole object. Thus, the results obtained in [2] are true only for coarse-dispersion composite materials and cannot be used for nanocomposites body.

Nanoparticles belong to small objects, which are characterized by a much curved surface and the volume of the surface layer is comparable to the volume of a whole particle. Because of this the use of the Gibbs thermodynamic method to study processes that proceed with the participation of such particles is incorrect. In our opinion to study the processes occurring in nanodispersed systems, the thermodynamic methods developed for small objects should be used [3].

2. Experimental procedure

One of the efficient thermodynamic methods to study small objects is Hill's method [4]. Hill [4] used the thermodynamics to describe the state not of an isolated particle, but of a great group consisting of n particles. Each particle contains m_i molecules of the ith sort. If we assume that the number of molecules in the system under consideration remains constant, then the energy of the group of particles changes with the variation of the particle size r and the number of them n. For this system the fundamental equation of state can be written [5]:

$$d(nu) = Td(n\eta) - Pd(n\nu) + \Sigma\mu_i d(nm_i) + \Lambda dn, \tag{1}$$

The u and η magnitudes refer to the same particle, Λ is the new potential, which shows how the energy of the particle group changes with variation of the particle sizes. Rusanov [5] showed that potential Λ equaled the work of the small object formation:

$$\Lambda = \frac{1}{3}\gamma s, \tag{2}$$

where γ is the surface tension, s is the particle surface area.

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Nomenclature

A	work		v	particle volume
F	free energy		w	volumetric fraction of liquid
G	Gibbs potential			
g	coefficient of particle geometry		*Greek symbols*	
i	sort of component		γ	surface tension
K	coefficient		η	entropy
k	number of components		Λ	potential of system
m	mass of component		μ	chemical potential
n	number of particles		Π	migration pressure
P	pressure			
r	particle radius		*Subscripts*	
S	system surface area		α	particle
s	particle surface area		β	liquid
T	temperature		$\alpha\beta$	solid–liquid interface
U	internal energy of system		$\alpha\alpha$	solid–solid interface
u	internal energy of particle			
V	volume of system			

By integrating Eq. (1), we obtain equation for the whole system

$$U = T\eta - PV + \Sigma m_i \mu_i + \Lambda n. \tag{3}$$

For other thermodynamic functions we have

$$F = -PV + \Sigma m_i \mu_i + \Lambda n,$$
$$G = \Sigma m_i \mu_i + \Lambda n.$$

In the present paper, to describe the thermodynamics of the liquid migration in the solid–liquid nanodispersed system, the Hill method was used.

2.1. The liquid phase migration in nanodispersed composite bodies

Let us consider a system consisting of n nanoparticles, which we denote by phase α, and the liquid β (Fig. 1). In the initial state (see Fig. 1a) the liquid is in region I and nanoparticles are concentrated in region II of the system. The regions I and II are separated by diaphragm III that is permeable for phase β. Because of the liquid migration from region I to region II, the system has passed into the final stage (see Fig. 1b), in which region II consists of particles α and the liquid β, and diaphragm III displaced to a new position. We impose the following limitations on the system:
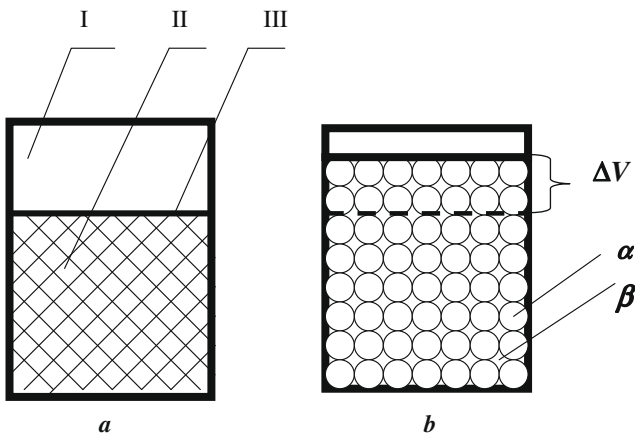

Fig. 1. Model of the liquid phase migration in the solid–liquid two-phase system: *a* and *b*, the initial and final states of the system; α, nanoparticles; β, liquid; I, region filled by the liquid only; II, region occupied by particles; III, diaphragm.

$$V_\alpha + V_\beta = V, \tag{3a}$$
$$T_\alpha = T_\beta = T_{\alpha\beta} = T_{\alpha\alpha} = T = \text{const}, \tag{3b}$$
$$m_i^\alpha + m_i^\beta + m^{\alpha\beta} + m_i^{\alpha\alpha} = m_i = \text{const}, \tag{3c}$$
$$r_\alpha = \text{const}, \tag{3d}$$

where V_α and V_β are the volumes of phases α and β, respectively, the α, β, $\alpha\beta$, $\alpha\alpha$ indices indicate that the denoted values refer to the corresponding phase or interphase.

Limitation (3a) allows a change of the V_α and V_β values, limitations (3c) indicate that the system consists of independent components. In the initial state of the system the Gibbs thermodynamic potential for the α phase is described by the following equation:

$$G'_\alpha = \sum_{i=1}^{k} (m_i^\alpha)'(\mu_i^\alpha)' + \Lambda'n',$$

where the sign ($'$) indicates that the designated values refer to the initial state of the system, k is the number of the system components.

Using dependence (2) and taking into account that $sn = S_{\alpha\alpha}$, we have

$$G'_\alpha = \frac{1}{3}\gamma_{\alpha\alpha}S_{\alpha\alpha} + \sum_{i=1}^{k} (m_i^\alpha)'(\mu_i^\alpha)'.$$

For the β phase

$$G'_\beta = \sum_{i=1}^{k} (m_i^\beta)'(\mu_i^\beta)'.$$

According to [6], under the equilibrium conditions the chemical potential of the ith particle component is not equal to that of the ith component in the particle surroundings. Their interrelation is described by the expression

$$\mu_r = \mu_\infty + \frac{2\gamma}{3r}v_m,$$

where μ_r and μ_∞ are the chemical potentials of component i in a particle of radius r and in the surroundings, respectively, v_m is the volume of a molecule of component i.

Taking into account this expression, the Gibbs potential of the system in the initial state is defined by

$$G' = \frac{1}{3}\gamma_{\alpha\alpha}S_{\alpha\alpha} + \sum_{i=1}^{k}(m_i^\alpha \mu_i^\beta)' + \frac{2}{3}\frac{\gamma_{\alpha\alpha}}{r}\sum_{i=1}^{k}(m_i^\alpha v_i^m)' + \sum_{i=1}^{k}(m_i^\beta \mu_i^\beta)'$$

and in the final state

$$G'' = \frac{1}{3}\gamma_{\alpha\beta}S_{\alpha\beta} + \sum_{i=1}^{k}(m_i^\alpha \mu_i^\beta)'' + \frac{2}{3}\frac{\gamma_{\alpha\beta}}{r}\sum_{i=1}^{k}(m_i^\alpha v_i^m)'' + \sum_{i=1}^{k}(m_i^\beta \mu_i^\beta)''.$$

A change in the Gibbs potential in passing of the system from the initial to the final state may be represented in the following way:

$$\Delta G = G'' - G'$$

$$= \frac{1}{3}\gamma_{\alpha\beta}S_{\alpha\beta} - \frac{1}{3}\gamma_{\alpha\alpha}S_{\alpha\alpha} + \frac{2}{3}\frac{\gamma_{\alpha\beta}}{r}\sum_{i=1}^{k}(m_i^\alpha v_i^m)'' - \frac{2}{3}\frac{\gamma_{\alpha\alpha}}{r}\sum_{i=1}^{k}(m_i^\alpha v_i^m)'$$

$$+ \sum_{i=1}^{k}(m_i^\alpha \mu_i^\beta)'' - \sum_{i=1}^{k}(m_i^\alpha \mu_i^\beta)' + \sum_{i=1}^{k}(m_i^\beta \mu_i^\beta)'' - \sum_{i=1}^{k}(m_i^\beta \mu_i^\beta)'.$$

If in passing of the system from the initial to the final state the variation of the component i concentration in the β phase can be neglected, then $(\mu_i^\beta)' \approx (\mu_i^\beta)''$ and in this case $(m_i^\alpha)' \approx (m_i^\alpha)''$, $(m_i^\beta)' \approx (m_i^\beta)''$. Besides, $S_{\alpha\beta} = 2gS_{\alpha\alpha}$, where g is the coefficient allowing for the variation of the particle geometry in passing of the system to the final state. With allowances made for the limitations and equalities (3), we obtain

$$\Delta G = \frac{1}{3}S_{\alpha\alpha}(2g\gamma_{\alpha\beta} - \gamma_{\alpha\alpha}) + \frac{2}{3r}(\gamma_{\alpha\beta} - \gamma_{\alpha\alpha})\sum_{i=1}^{k}m_i^\alpha v_i^m. \tag{4}$$

In Eq. (4) the sum $\sum_{i=1}^{k}m_i^\alpha v_i^m = V_\alpha$. If we assume that in the final state particles were of a spherical shape, then $\frac{V_\alpha}{r} = \frac{S_{\alpha\beta}}{3} = \frac{2}{3}gS_{\alpha\alpha}$. Taking into account this equality, we have

$$\Delta G = \frac{1}{9}[10g\gamma_{\alpha\beta} - (3+4g)\gamma_{\alpha\alpha}]S_{\alpha\alpha}. \tag{5}$$

For the simplicity of the description the final state of the system given in Fig. 1b is idealized. In real systems the α particles in the initial state may have contacts with the liquid phase and in the final state they form equilibrium dihedral angles. Under these conditions in the initial state the $S_{\alpha\alpha}$ contact surface exists and Eq. (5) takes the form

$$\Delta G = \frac{1}{9}[10g\gamma_{\alpha\beta} - (3+4g)\gamma_{\alpha\alpha}]\Delta S_{\alpha\alpha}. \tag{6}$$

It follows from Eq. (6) that the migration occurs spontaneously with $(3+4g)\gamma_{\alpha\alpha} > 10g\gamma_{\alpha\beta}$.

A change in the F free energy is described by

$$\Delta F = -P\Delta V + \frac{1}{9}[10g\gamma_{\alpha\beta} - (3+4g)\gamma_{\alpha\alpha}]\Delta S_{\alpha\alpha}.$$

The term $P\Delta V$ of this equation allows for the work done by the system against the external pressure P in changing the system volume ΔV. In the particular case that the dispersion medium is a liquid, $\Delta V \approx 0$, ΔG and ΔF coincide, and the variation of the F free energy is

$$\Delta F = \frac{1}{9}[10g\gamma_{\alpha\beta} - (3+4g)\gamma_{\alpha\alpha}]\Delta S_{\alpha\alpha}. \tag{7}$$

Eq. (7) defines the thermodynamic potential of the system under study, therefore, the system pressure may be found according to the $P = -(\partial F/\partial V)_{T,m}$ relation. Let us designate this pressure as migration pressure Π. To understand the physical meaning of pressure Π, we consider the migration process in the context of the work done by the system. When the system passed to the final state, diaphragm III displaced, as a result of which work $A = \Pi\Delta V$ (where Π is the pressure in region II, ΔV is the change of the volume in this region) was done. At the same time, a change in the system free energy equals the work, which was done under isochoric and isothermal conditions. Thus, $A = -\Delta F$. After corresponding substitutions and transformations we have

$$\Pi = \frac{1}{9}[(3+4g)\gamma_{\alpha\alpha} - 10g\gamma_{\alpha\beta}]\frac{\Delta S_{\alpha\alpha}}{\Delta V_\beta}. \tag{8}$$

Variation of the contact surface ($\Delta S_{\alpha\alpha}$) can be expressed in terms of the volume of liquid ΔV penetrated into region II, the particles size r and the volumetric fraction of the liquid w in region II [7]:

$$\Delta S_{\alpha\alpha} = \frac{K}{r}\left(\frac{1-w}{w}\right)^{\frac{1}{3}}\Delta V_\beta. \tag{9}$$

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 Eq. (9) into Eq. (8) yields

$$\Pi = \frac{K}{9r}[(3+4g)\gamma_{\alpha\alpha} - 10g\gamma_{\alpha\beta}]\left(\frac{1-w}{w}\right)^{\frac{1}{3}}. \tag{10}$$

3. Discussion

According to our researches spontaneous migration of a liquid phase in nanocompositions takes place under condition

$$(3+4g)\gamma_{\alpha\alpha} > 10g\gamma_{\alpha\beta}. \tag{11}$$

If during migration of a liquid phase change of the geometrical form of nanoparticles insignificant, $g \approx 1$ and Eq. (11) takes the form $\gamma_{\alpha\alpha}/\gamma_{\alpha\beta} > 1.43$.

Our researches have shown, that nanocompositions WC–Co, WC–Ni, TiC–Co, TiC–Ni, Cr_3C_2–Ni, Fe–Cu imbibe the chemical equilibrium melts. During immersion of WC–Co, WC–Ni, TiC–Co, TiC–Ni, Cr_3C_2–Ni, Fe–Cu specimens into metal melts the solid–solid contact surface is changed for the solid–liquid interface. From a thermodynamic standpoint, this process proceeds spontaneously when $\gamma_{\alpha\alpha}/\gamma_{\alpha\beta} > 1.43$. Nanocompositions W–Ag, WC–Cu, Cr_3C_2–Cu, Ni–Pb, Cu–Pb do not imbibe metal melts (Ag, Cu, Pb), in these nanocomposite specimens the liquid phase migration is absent. It means, that in these compositions $\gamma_{\alpha\alpha}/\gamma_{\alpha\beta} \leqslant 1.43$. Thus, using the experimental data obtained, nanocomposite materials consisting of high-melting particles and a bond can be conventionally divided into two classes. Composites with $\gamma_{\alpha\alpha}/\gamma_{\alpha\beta} > 1.43$ are considered to form the first class, while the second class includes those with $\gamma_{\alpha\alpha}/\gamma_{\alpha\beta} \leqslant 1.43$.

The characteristic feature of the first class of nanocomposites is their ability to imbibe metal melts. The second class of nanocomposites does not imbibe metal melts.

The pressure Π is the motive force for the mass transport in the composite body. From Eq. (10) it follows that for a certain size r of particles in the body there uniquely corresponds a certain migration pressure, with the decrease in the size r of particles entailing an increase in the pressure Π. 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.

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