Thermodynamics of the Formation of Mesostructures in Nanodispersed Composite Materials

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Abstract:
Two models of the formation of mesostructures in nanodispersed composite materials are considered. According to the first model, a mesoelement is formed of coarsely dispersed compositions as an inclusion in a nanodispersed composite body. The second model considers a mesoelement being formed from nanoparticles as an inclusion in the volume of a coarsely dispersed composite body. Depending on the class of composite materials used to produce mesoelements and a composite body, their composition and structure are defined by the liquid phase migration (or absence of the migration) as well as diffusion flows of the components.

Keywords: Thermodynamics; Mesostructure; Nanodispersed composite material

Introduction

One of the promising lines of increasing performance of composite material products is the formation of mesostructures in the product bulk [1 – 3]. As applied to composite materials, the mesostructure is a set of granules (aggregates) prepared from composite materials with a binder. Metals, e.g., Cu, Co, Ni, Fe, steels and special alloys can be used as a binder for the granules. The size of granules (mesoelements) varies from 20 to 500 μm.

At present the kinetics and mechanism of the mesostructure formation are understood as applied to coarsely dispersed composite materials (the refractory particle size is 0.5 – 10 μm), while the mesostructure formation in nanodispersed materials (the refractory particle size is 10 – 100 nm) remains poorly known. This problem may be successfully solved using results of thermodynamic studies of the processes proceeding in these materials.

Investigation procedure

Thermodynamic researches are executed on two models of the system. According to the first model (Fig.1), a mesoelement I is made from coarsely dispersed composite materials. It is in a nanodispersed material II which may be considered as a matrix for the mesoelement I. According to the second model (Fig. 2), a mesoelement I is made from nanoparticles, it is in a coarsely dispersed composite material. In coarsely dispersed composite materials the size of particles is 0.5 – 10 μm.
The initial material for the formation of a composition is powder mixtures with refractory particles of different sizes and mixtures containing refractory particles and a low-melting binder. From these mixtures products are formed mesostructure composite materials with variously sized particles. In this state the product is a porous briquette, which may be presented as a two-phase system that consists of refractory particles and a dispersion medium. A dispersion medium can be vapour, gas, liquid, which we will call a mobile phase. In sintering a briquette the consolidation of nano- and microparticles occurs. When forming a product from powdered mixtures that contain refractory particles and a low-melting binder, we obtain a briquette, which is a three-phase system. The system consists of nano- or microparticles of the refractory phase 1, binder particles 2, and dispersion medium 3. At the first stage this briquette is subjected to sintering in a vacuum or gaseous atmosphere and then as the melting temperature of the binder is attained, to the liquid-phase sintering. During the solid-phase sintering the particle consolidation takes place and the solid–solid contact surface forms. During the liquid-phase sintering the solid–gas phase interface disappears and the solid–liquid interface appears. After the completion of the liquid-phase sintering the body represents a two-phase composition consisting of a refractory skeleton and a liquid phase.

Based on the theoretical and experimental studies, these composite materials (from here on referred to as “the materials”) were divided into two classes [4]. Materials having $\gamma_{ss}/2\gamma_{sl} > 1$ were assigned to the first class and those having $\gamma_{ss}/2\gamma_{sl} \leq 1$ were assigned to the second class (where $\gamma_{ss}$ and $\gamma_{sl}$ are surface tensions on the contact surface of refractory particles and refractory particle–liquid interface, respectively; the $\gamma_{ss}$ and $\gamma_{sl}$ values are given for the temperature above the binder melting temperature). Materials of the WC–Co, WC–Ni, WC–Fe, TiC–Co, TiC–Ni, Cr$_2$C$_2$–Ni systems belong to the first class, materials of the WC–Cu, Cr$_2$C$_2$–Cu, Mo–Ag, W–Cu, Ni–Pb systems to the second class. Above the melting temperature of the binder the materials of the first class imbibe metal melts out of the medium surrounding them. Under these conditions in the materials of the first class there is the imbibition pressure, which is called the migration pressure $\Pi$ [5]. Under the action of the gradient of pressure $\Pi$ the migration of the liquid phase takes place in the volumes of a product formed from different mixtures with the result that the initial content of a binder changes and deconsolidation refractory skeleton occurs. In materials of the second class the migration pressure is absent and because of this the initially set binder content remains. Under the action of the gradient of pressure $\Pi$ the liquid phase migrates in the materials of the first class.

Thus, two basic processes (the consolidation of particles and migration of the liquid phase) take place in the formation of mesostructures in nanodispersed materials. The processes essentially affect the structure formation. The thermodynamics of these processes at the nano- and macrolevel is described in [5–10].

A variation of Helmholtz free energy ($\Delta F$) in the process of the consolidation of nanoparticles in a two-phase system is described by the equation [7]:

$$\Delta F = \frac{1}{3} (\gamma_{ss} - 2\gamma_{sl}) \Delta S_{ss} + \sum_{i=1}^{k} m_i \Delta \mu_i ,$$

where $\gamma$ is the surface tension, $\Delta S$ is the variation of the contact surface of refractory particles, $m$ is the amount of the i component, $k$ is the number of components, $\Delta \mu$ is the variation of the chemical potential, $g$ is the coefficient that allows for the variation of the geometrical shape of particles in the consolidation process, indices 11 and 13 indicate that these magnitudes refer to the contact surface of particles 1 or to the interface, respectively, and index 3 refers to the dispersion medium.

In Eq. (1) a change of the chemical potential $\Delta \mu$ is caused by the effect of the nanoparticle size. According to [11], under the equilibrium conditions the chemical potential of component i of a nanoparticle is not equal to the chemical potential of the i component of the medium surrounding the nanoparticle and their interrelation is described by the equation...
\[ \mu_r = \mu_\infty + \frac{2\gamma}{3r} v_m \]

where \( \mu_r \) and \( \mu_\infty \) are chemical potentials of the i components of a particle of radius r and of the medium surrounding the particle, respectively, \( v_m \) is the volume of a molecule of the i component.

With allowance made for this dependence and some limitations, Eq. (1) takes the form [6]

\[ \Delta F = \frac{1}{3}(\gamma_{11} - 2g_{13})\Delta S_{11} + \frac{2}{3r}(\gamma_{11} - \gamma_{13}) \sum_{i=1}^{k} m_iv_i^m, \]  

(2)

The last term of Eq. (2) allows for the effect of nanoparticle size on the variation of the system free energy.

In the course of the consolidation of nanoparticles in the bulk of a product a shrinkage pressure, \( p_{sh} \), originates [7]:

\[ p_{sh} = \frac{1}{3}(2g_{13} - \gamma_{11}) \frac{\Delta S_{11}}{\Delta V_{sh}} - \frac{1}{\Delta V_{sh}} \sum_{i=1}^{k} m_i \Delta \mu_i. \]  

(3)

Here \( \Delta V_{sh} \) is the variation of the volume of the composite body (hereinafter is referred as “body”) being sintered.

Equations for the free energy and shrinkage pressure variation for a coarsely dispersed system are of the form [8]

\[ \Delta F = \frac{1}{3}(\gamma_{11} - 2g_{13})\Delta S_{11} \]  

(4)

\[ \Delta P_{sh} = \frac{1}{3}(2g_{13} - \gamma_{11}) \frac{\Delta S_{11}}{\Delta V_{sh}} \]  

(5)

For a three-phase system that consists of nanoparticles of phase 1, nanoparticles of phase 2, and dispersion medium 3 the variation of the system free energy in the consolidation of particles in a vacuum is described by equation [9]

\[ \Delta F = \frac{1}{3}[ (\gamma_{11} - 2g_{13})\Delta S_{11} + (\gamma_{22} - 2g_{23})\Delta S_{22} + (\gamma_{12} - g_{12}\gamma_{13} - g_{12}\gamma_{23})\Delta S_{12} ] + \sum_{i=1}^{k} m_i \Delta \mu_i. \]  

(6a)

Using \( \mu_r = \mu_\infty + \frac{2\gamma}{3r} v_m \) this expression may be written as follows:

\[ \Delta F = \frac{1}{3}(\gamma_{11} - 2g_{13})\Delta S_{11} + \frac{2}{r}(\gamma_{11} - \gamma_{13}) \sum_{i=1}^{k} m_i^1 v_i^m + \frac{1}{3}(\gamma_{22} - 2g_{23})\Delta S_{22} + \frac{2}{r}(\gamma_{22} - \gamma_{12}) \sum_{i=1}^{k} m_i^{22} v_i^m + \frac{1}{3}(\gamma_{12} - g_{12}\gamma_{13} - g_{12}\gamma_{23})\Delta S_{12} + \frac{2}{r}(\gamma_{12} - \gamma_{13} - \gamma_{23}) \sum_{i=1}^{k} m_i^{12} v_i^m. \]  

(6b)

An equation for the shrinkage pressure is as follows [9]

\[ p_{sh} = \frac{1}{3} \left[ (2g_{13} - \gamma_{11}) \frac{\partial S_{11}}{\partial V_{sh}} + (2g_{23} - \gamma_{22}) \frac{\partial S_{22}}{\partial V_{sh}} + (g_{12}\gamma_{13} + g_{12}\gamma_{23} - \gamma_{12}) \frac{\partial S_{12}}{\partial V_{sh}} \right]. \]  

(6c)

\[ \sum_{i=1}^{k} m_i \frac{\partial \mu_i}{\partial V_{sh}}. \]
After the completion of the liquid-phase sintering the body under consideration represents a solid–liquid two-phase system. In this state in nanodispersed materials of the first class there is migration pressure \( \Pi \), which is described by the following equation [10]

\[
\sum = \gamma - \gamma + \Delta \gamma - \gamma = \Pi \sum_i m_i \nu_i V_r V.
\]

This equation may be presented as follows:

\[
\Pi = \frac{1}{3} (\gamma_{11} - 2g\gamma_{12}) \frac{\Delta S_{11}}{\Delta V} - \frac{1}{ΔV} \sum_{i=1}^{k} m_i \Delta \mu_i.
\]  

(7)

For coarsely dispersed system the equation for the migration pressure is of the form [8]

\[
\Pi = \frac{1}{3} (\gamma_{11} - 2g\gamma_{12}) \frac{\Delta S_{11}}{\Delta V}.
\]

(8)

Under the action of the gradient of pressure \( \Pi \) the migration of a liquid phase occurs in bodies. In the case that the liquid phase is imbibed from the medium, the contact surface of particles decreases, i.e. deconsolidation of the refractory skeleton takes place. A change in the free energy of a nanodispersed system during this process is described by the expression [10]

\[
\Delta F = \frac{1}{3} (2g\gamma_{13} - \gamma_{11}) \Delta S_{11} + \frac{2}{3r} (\gamma_{13} - \gamma_{11}) \sum_{i=1}^{k} m_i \nu_i.
\]

This expression may be written as follows:

\[
\Delta F = \frac{1}{3} (2g\gamma_{13} - \gamma_{11}) \Delta S_{11} + \sum_{i=1}^{k} m_i \Delta \mu_i.
\]

(9)

For coarsely dispersed systems Eq. (9) takes the form

\[
\Delta F = \frac{1}{3} (2g\gamma_{13} - \gamma_{11}) \Delta S_{11}.
\]

(10)

To assess the shrinkage and migration pressures by Eqs. (3), (5), (7), and (8), we introduce contact surface variation \( \Delta S_{11} \) according to the dependence [12]

\[
\Delta S_{11} = K \left( \frac{1-u}{u} \right)^{\frac{1}{3}} \Phi(u) \Delta V,
\]

where \( K \) is the coefficient that allows for the geometric shape of particles and cavities formed by them, \( u \) is the volumetric portion of the mobile phase in the composition, \( \Phi(u) \) is the nondimensional parameter.

After corresponding transformations the following equation for the nanoparticle shrinkage pressure is obtained

\[
p_{sh} = \frac{K}{3r} (2g\gamma_{13} - \gamma_{11}) \left( \frac{1-u}{u} \right)^{\frac{1}{3}} - \frac{1}{ΔV_{sh}} \sum_{i=1}^{k} m_i \Delta \mu_i.
\]

(12)

The equation for the shrinkage pressure of macroparticles is

\[
p_{sh} = \frac{K}{3r} (2g\gamma_{13} - \gamma_{11}) \left( \frac{1-u}{u} \right)^{\frac{1}{3}}.
\]

(13)

The pressure of the liquid migration in a nanodispersed composition is described by the equation
\[ \Pi = \frac{K}{3r} (\gamma_{11} - 2g'_{12}) \left( \frac{1-u}{u} \right)^{1/3} - \frac{1}{\Delta V} \sum_{i=1}^{k} m_{i} \Delta \mu_{i} \quad (14) \]

For a macrosystem we have

\[ \Pi = \frac{K}{3r} (\gamma_{11} - 2g'_{12}) \left( \frac{1-u}{u} \right)^{1/3} \quad (15) \]

In Eqs. (12)–(15) nondimensional parameter \( \Phi(u) \), whose values are in the range from 1.0 to 1.2, is neglected. Eqs. (1)–(15) form the basis for a thermodynamic description of the processes of formation of mesostructures in nanodispersed materials.

**Thermodynamics of the formation of mesostructures in nanodispersed composite materials of the second class**

At the first stage we consider the mesostructure formation of nanodispersed materials consisting of refractory particles only. During a solid-phase sintering of composite materials according to the first model a consolidation of particles takes place in a nanodispersed matrix and in a mesoelement. A change of the Helmholtz free energy in the nanodispersed matrix and in the mesoelement are described by Eqs. (1 – 3) and (4, 5), respectively. In this case the nanodispersed matrix and the mesoelement exhibit different shrinkage pressures. The shrinkage pressure in a nanodispersed matrix is essentially higher than in a mesoelement. The calculation made for copper nanoparticles 10 nm in radius has shown that the shrinkage pressure in a nanodispersed matrix is 60000 Pa. Copper microparticles of 1 \( \mu \)m radius generate a shrinkage pressure of 560 Pa in a mesoelement (the calculation was made for a briquette with a porosity of 40% heated to a temperature of 1270 K). It follows from these data that in the course of the particle consolidation, a mesoelement undergoes the compression of a nanodispersed matrix. The compression stresses originate in a mesoelement and tensile stresses in a nanodispersed matrix.

At the second stage we consider the mesostructure formation of nanodispersed materials composed of refractory particles and a binder. During a solid-phase sintering of the composite materials according to the first and second models the thermodynamics of nanoparticle consolidation is described by Eqs. (6a – 6c). In the composite materials of the second class there is no migration pressure, therefore, during the liquid-phase sintering of a mesocomposition the liquid does not migrate between the matrix and mesoelement. At the formation of a mesocomposition according the second model (Fig. 2) the shrinkage pressure of the mesoelement is higher than that in the matrix; therefore, it is necessary that the shrinkage coefficients of the matrix and mesoelement should be close in value. This makes it possible for the matrix to make good contact with the mesoelement.

**Thermodynamics of the formation of mesostructures in nanodispersed composite materials of the first class**

A solid-phase sintering of mesostructural composite materials of the first class does not differ from the one considered above. In the formation of mesostructural composite materials of the first class with the liquid phase present it is necessary that the mass transfer of a liquid under the action of the migration pressure is taken into consideration. The approximate calculation of the migration pressure at a temperature of 1670 K using Eqs. (14) and (15) has shown that in the WC–6Co composition with WC particles 1 \( \mu \)m in radius the
Migration pressure is \( \Pi = 0.5 \) MPa, and in the WC–6Co composition with particles 10 nm in radius the migration pressure is 100 MPa. Thus, according the first model (Fig.1), the migration pressure in the matrix of a composite body exceeds that in the mesoelement by several orders of magnitude. Under the action of the migration pressure gradient the liquid migrates from the mesoelement to the matrix and the former becomes virtually deprived of the liquid phase. It means, that in the mesoelement the consolidation of particles occurs, while in the matrix the particle deconsolidation takes place.

![Fig.1](image)

**Fig.1.** Model of the mesostructure system: \( a \) is the initial and \( b \) is the final states of the system, I is the mesoelement, II is the nanodispersed composite body (matrix).

The change of Helmholtz’s free energy of this system is \( \Delta F = \Delta F_c + \Delta F_m \). Here \( \Delta F_c \) is the change of Helmholtz’s free energy of the system during the consolidation of microparticles, which is described by Eq. 4, \( \Delta F_m \) is the change of Helmholtz’s free energy during the liquid migration in the nanosturtrural composition, which is described by Eqs. (9 – 10).

The liquid migration is always accompanied by a rearrangement of a refractory skeleton and change of the volume of a composite body. In the system under consideration as a result of the liquid migration the mesoelement volume decreases, while that of the matrix increases. Therefore, the mesoelement–matrix separating surface moves to the mesoelement.
center. Thus, during the formation of mesostructures according the first model (Fig.1) low-binder mesoelements will be obtained in nanodispersed composite materials of the first class.

In the course of the formation of mesostructures according to the second model (Fig. 2) in composite materials of the first class the migration pressures in the nanodispersed mesoelement and microdispersed matrix differ. The migration pressure in the mesoelement essentially surpasses the migration pressure in the matrix, and hence, the liquid tends to leave the matrix and migrate to the mesoelement. As a result the volumes of the matrix and the mesoelement change, therefore, the bounding surface of the mesoelement moves into the matrix, and the bounding surface of the matrix moves into the mesoelement. Each of these surfaces hinders the movement of the other. Under these conditions the migration of a liquid does not affect the mesoelement and matrix structures.

According to the second model (Fig. 2), a product can be made by various combinations of composites of the first and second classes. We consider a combination, in which a mesoelement is presented by a composite material of the first class, and a matrix is presented by a composite material of the second class. Under these conditions there is migration pressure $\Pi$ in the mesoelement, which tends to imbibe a liquid from the matrix volume. There is no migration pressure $\Pi$ in the matrix. In the imbibition of a liquid by the mesoelement its volume increases, and the matrix volume decreases. As a result, here the conditions are arranged when counter motions of the mesoelement and matrix surfaces hinder the liquid migration as described above, hence, the liquid content of the mesoelement changes insignificantly.

![Fig.2. Model of the system consisting from the nanodispersed mesoelement and the coarsely dispersed matrix.](image)

Under the conditions when the mesoelement is formed from a composition of the second class and the matrix is formed from a composition of the first class under the action of the migration pressure a liquid flows from the mesoelement to the matrix. In this case, the mesoelement structure forms with the minimum binder content and the consolidation of particles takes place, which is described by Eqs. (4, 5). At the same time particles of the matrix deconsolidate, which is described by Eqs. (10, 14).

Particles of equilibrium shape but different in size exhibit different dissolution of components in the liquid phase or partial pressure in the gas phase. The dependence of the particle dissolution on the particle radius $r$ is described by the Gibbs–Thomson known equation

$$\ln \frac{C_0}{C_m} = \frac{2\gamma_m}{rRT},$$
where \( C_0 / C_\infty \) is the relation between the concentrations of components of particles having radius \( r \to 0 \) and of particles with radius \( r \to \infty \), respectively, \( R \) is the gas constant, \( T \) is the temperature.

It follows from this equality that in the neighborhood of a small crystal the concentration of \( \text{i} \) component is higher than above the surface of a large crystal. The difference of the component concentrations in the neighborhood of a nano- and macroparticle sets up a difference in chemical potential of the components, which gives rise to a diffusion flow of the substance from a nanoparticle to a macroparticle. As a result of the mass transfer the macroparticle sizes increase and nanoparticle sizes decrease. Moreover, a nanodispersed system is unstable by itself and diffusion flows that contribute to an increase of one particles and decrease of the others also initiate in its volume. These processes bring about the formation of a nonuniform structure of the material.

In the case that particles in a mesoelement and a matrix are of different compositions simultaneously with the above processes the mutual diffusions of components takes place. To describe the mass transfer of a substance in such a system, the apparatus of the thermodynamics of irreversible processes, which is elaborated on the basis of the Onzager theorems and thermodynamic principles developed by Prigozhin, is successfully used [13].

Conclusions

The formation of mesostructures in nanodispersed composite materials has been considered in terms of thermodynamics. It has been shown that in the course of the particle consolidation in single-phase materials with particles of different sizes different shrinkage pressures are generated in the product volume which affect the formation of the mesostructures.

During the formation of mesostructures in two-phase composite materials that consist of refractory particles and a binder, one should take into account the relation between energies at the contact surface of particles and at the solid–liquid interface. Composite materials having \( \gamma_{sl}/2\gamma_{dl} > 1 \) belong to the first class and materials with \( \gamma_{sl}/2\gamma_{dl} \leq 1 \) to the second class.

There is no migration pressure in composite materials of the second class. Therefore, mesostructures can be formed at any combination of particle sizes and binder concentration. In composite materials of the first class there is the migration pressure, which has a physical meaning of the imbibition pressure. Under the action of the migration pressure gradient the liquid phase migrates from the region with a lower migration pressure to the region with a higher migration pressure. In the course of the liquid migration particles consolidate in the product region, which the liquid leaves, and the refractory skeleton of the composite material deconsolidates in the region, to which the liquid comes. The migration of the liquid is accompanied by the variation in the product volumes. These features should be allowed for in the formation of mesostructures in nanodispersed materials of the first class and in the combination of materials of the first and second classes.

References


Садржај: Размотрена су два модела формирања мезоструктура у нанодисперзним композитним материјалима. На основу првог модела мезоелемент се формира од грубо диспергованих композиција као инклюзија у нанодисперзном композитном телу. Други модели разматра формирање мезоелемента од наночестице као инклюзије у запремину грубо диспергованог композитног тела. У зависности од класе композитног материјала коришћеног за добијање мезоелемената и композитног тела, састав и структура се дефинишу миграцијом теке фазе (или одсуством исте), као и дифузионим током компонената.

Кључне речи: термодинамика, мезоструктура, нанодисперзни композитни материјал