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Современные направления развития теории сдвигово-диффузионной перекристаллизации аустенита в железоуглеродистых сплавах

Резюме

Представлены фундаментальные положения теории сдвигово-диффузионного превращения аустенита в железоуглеродистых сплавах при формировании бейнитной структуры. Приведены результаты экспериментальных и промышленных исследований термической кинетики структурообразования матрицы чугунов с шаровидным графитом и высокопрочных колесно-бандажных сталей при бейнитной реакции. Рассмотрены современные направления развития теории изотермического и термокинетического упрочнений железоуглеродистых сплавов.

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Modern trends of development of displacing-diffusion theory of austenite recrystallization in iron-carbon alloys

Summary

Fundamentals of the theory of displacing-diffusive transformation of austenite in iron-carbon alloys at bainite structure formation have been presented. Results of experimental and industrial studies of kinetics of structure formation of thermal in nodular cast iron matrix and high-strength wheel-steels at bainite reactions have been shown. Modern trends of development of displacing-diffusion theory of iron-carbon alloys isothermal and thermal kinetic strengthening have been observed.

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The features of phase equilibrium in the system Al-Si with microheterogeneous liquid phase

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It is revealed that at isothermal holding of Al-21,5Si alloy at 610 °C into semi-liquid alloy except equilibrium liquid and β -Si phases there are two more phases: α -Al and L2a. Emergence of two last is explained on the basis of thermodynamics of irreversible processes. The modified Gibbs phases rule for system with a microheterogeneous liquid phase is offered.

Introduction The Gibbs's thermodynamics of equilibrium state operates within the parameters describing macroscopic characteristics of system.

Usually it is accepted that equilibrium in thermodynamic system comes after more or less long exposure in the state of invariable independent intensive parameters.

The second assumption presumes that all phases have homogeneous composition. In the equilibrium the equality of chemical potentials of the atoms of a given component in any point of the given phase is established that excludes both possibility directed diffused transfer of substance and spontaneous infringement of the phase equilibrium at the state of invariable equilibrium parameters.

It is known however that the homogeneous liquid or solid solutions under certain conditions can become unstable. It leads to occurrence of ascending diffusion. As a result in originally homogeneous solution the micro-areas enriched by one or several components are spontaneously formed. The thermodynamic aspect of this phenomenon is developed by Borelius [1]. In the systems containing clusters the assumption about chemical uniformity of equilibrium phases is not confirmed which inevitably should entail certain complication of thermodynamics of this system in an equilibrium state.

The thermodynamics of metallurgical systems with micro-heterogeneous phases is developed insufficiently. It makes research of features of an equilibrium state of these systems as topical.

The results and discussion It has previously been shown that the Al-21.5 Si alloy, chilled after heating up to 610 °C (i.e., according to the phase diagram of Al-Si, after heating up in two-phase region L+ α -Al), contains in microstructure not only the primary Si crystals and the eutectic (Si+ α -Al), but also the large primary crystals α -Al (Fig. 1 a) [2]. Latest structural constituent according to the phase diagram can not exist in the biphasic (Si+L) field of this diagram.

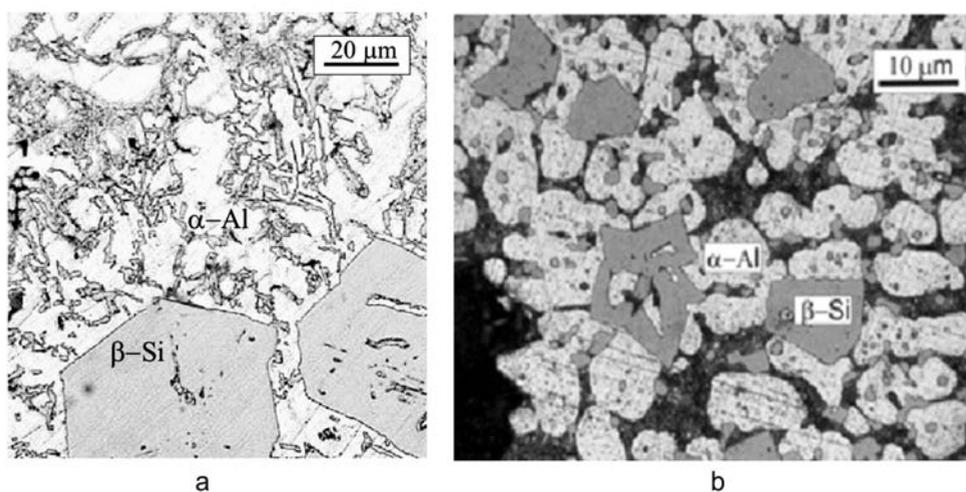


Fig. 1. Microstructure of Al-21 Si alloy. a – as cast; b – as cast + holding at 610 °C, 5 hrs + quenching in water. Note coalescence of α -Al. Black areas symbolize quenched liquid phase.

Furthermore, upon prolonged holding of the alloy in the semi-liquid state at 610 °C, the α -Al crystals do not dissolve, which they are expected to do as an unstable phase, but, on the contrary, they coalesce and coarsen (Fig.1 b). In other words, α -Al behaves like the thermodynamically equilibrium phase. It looks like a thermodynamic paradox.

The micro-heterogeneous structure of a liquid phase is revealed in alloys Al-Si with the help of both micro-structural analysis of quenched semi-liquid alloy and XRD in situ analysis [3, 4]. By results of these works the polystructural model of hypereutectic Al-Si melt is offered [4]. It includes two zones that are differ by degree of hetero-desmicity of inter-atomic bonds and parameters of short-range order. At small overheat over liquidus the metallized zone of a liquid phase is formed on the basis of liquid aluminum. The second structural constituent of a liquid phase represented by clusters of FCC coordination. They have close to silicide Al_3Si concentration and occupy 36 % of volume of a liquid phase. During the rising of overheat the silicide clusters decrease and then disappear.

These features of a structure of liquid hypereutectic silumines make them a convenient object for studying the phase equilibria in systems with a micro-heterogeneous liquid phase. In the previous work [2] the results of XRD in situ analysis of alloy Al-21,5 Si was performed for semi-solid state. In the present work the results of the specified phase analysis of alloy are discussed.

By the way of calculation combined with the modeling, using the help software CaRIne 3.1 it is established that among crystal phases in an investigated alloy at 610 °C, together with α -Al and β -Si, the volume-aligned tetragonal L2a is present also. The D14h-P4/mmm (type δ -TiCu) phase has the lattice parameters $a=b=4.1981\text{\AA}$ and $c=4.4352\text{\AA}$. The tetragonal elementary cell has atoms of aluminum in the apexes of a tetragon with probability of 0.85 (in the other 15 % of cases there is likely presence of Si atoms) and the central atom of silicon with probability 0.5, in others 50 % of cases the atom of silicon is replaced by vacancy. Such high density of vacancies causes occurrence of super-structural lines on the diffraction pattern in area of small angles ($10^\circ < 2\Theta < 14^\circ$) where these lines are well identified due to the absence of reflexes from α -Al and β -Si, with an exception of β -Si (111) on $2\Theta_{exp} = 12.54^\circ$. The intensity of some interference maxims at relatively high temperatures of research can change under influence so-called «fuzzy»-effect [5].

The distinctive feature of a crystal lattice of a L2a-phase is good conformity of some of its interplane distances with those for two other equilibrium phases – α -Al and β -Si, namely: (102) L2a and (200) β -Si; (103) L2a and (400) β -Si, as well as (220) L2a and (220) β -Si; (222) L2a and (222) β -Si (Table).

From the table follows that parameters of crystal lattice of L2a phase satisfy to Dankov's principle of orientation and dimensional conformity and this phase can serve as a good substrate for nucleation of crystals both α -Al and β -Si.

Фазові перетворення

A parity of some interplane distances in phases L2a, α -Al and β -Si

L2a		β -Si			α -Al			$\Delta d_{\text{HKL}}, \%$
HKL	$d_{\text{HKL}}, \text{\AA}$	HKL	$d_{\text{HKL}}, \text{\AA}$	$\Delta, \text{\AA}$	HKL	$d_{\text{HKL}}, \text{\AA}$	$\Delta, \text{\AA}$	\AA
(102)	1.961	(200)	1.965	+0.004				0.20
(220)	1.484				(220)	1.498	+0.014	0.94
(103)	1.394	(400)	1.389	+0.005				0.36
(222)	1.233				(222)	1.223	-0.010	0.08
(321)	1.126	(422)	1.134	+0.008				0.71
(400)	1.050				(400)	1.060	+0.010	0.09

On the other hand the L2a phase can carry out a role of a buffer phase between α -Al and β -Si during growth of crystals Si in α -Al shell (Fig. 2, in [2]). The layer of this phase between Si and Al crystals provides coherence of inter-phase borders β -Si/L2a and L2a/ α -Al and it reduces inter-phase tension. For these reasons the L2a phase can be considered as a transitive phase (“transient phase” [5]) in multi-phase transformation $L + (\beta\text{-Si}) \rightarrow (\alpha\text{-Al}) + L2a + (\beta\text{-Si})$ of eutectic type in hypereutectic alloy Al-Si.

From the experimental results [3] and analysis of Borelius [1] follows that in a micro-heterogeneous liquid phase of alloy Al-21,5 Si energy of interaction of dissimilar atoms exceeds the same for the atoms with the same name, i.e.

$$\varepsilon_{\text{Al-Al}} < \varepsilon_{\text{Al-Si}} > \varepsilon_{\text{Si-Si}} \quad (1)$$

and besides

$$\partial_2^2 G / \partial x^2 < 0 \quad (2)$$

$$\varepsilon_{\text{Al-Si}} \gg kT \quad (3)$$

where: $\varepsilon_{\text{Al-Si}}$ – pair potential of interaction of dissimilar atoms;
 k – Boltzmann’s constant.

When plotting the curves of Gibbs free energy for a liquid phase of system, we will consider that according to (2) on the free energy curve of this phase which has a convexity to the axis of concentration, the local maximum is formed in some concentration interval. It means that in this interval the process of micro-stratification of originally micro-homogeneous phase is energetically profitable and consequently is spontaneous. The inequality (3) indicates that because energy of pair interaction Al-Si exceeds an energy of thermal movement kT of surrounding atoms, thermal degradation of Al-Si clusters is improbable. Therefore it is possible to tell about cluster stability not only in statistical sense, but also in sense of its stability as the individuals.

The arrangement of curves of specific free energies G of equilibrium phases at $T = 610 \text{ }^\circ\text{C}$ is shown on Fig. 2 a. The common tangents to minima of curves G show concentration of phases in a situations of local equilibria, and

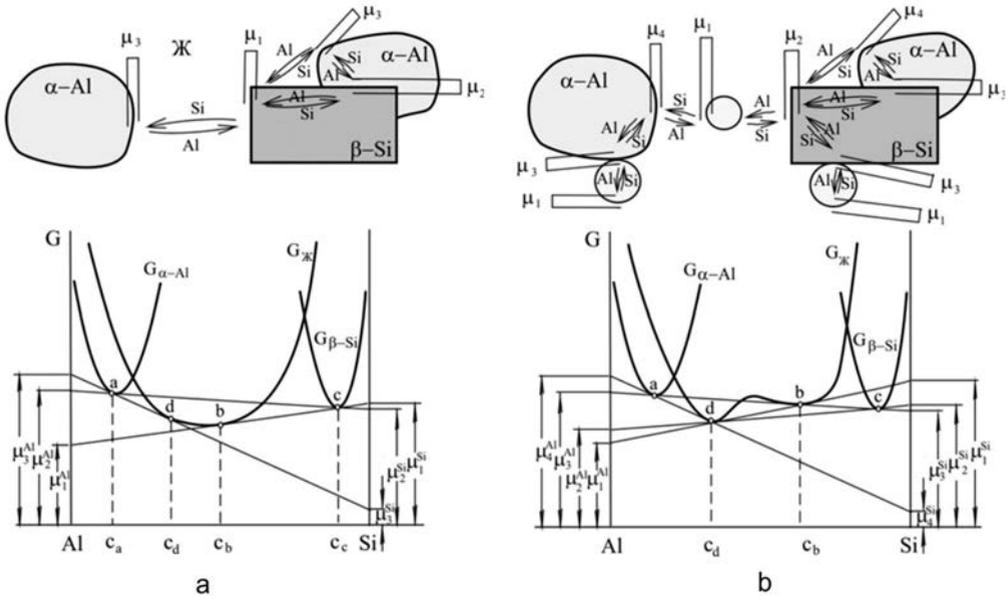


Fig. 2. Distribution of chemical potentials and diffusion flows at the local phase equilibria in alloy Al-21,5 Si with: a – micro-homogeneous, b – micro-heterogeneous liquid phase.

the pieces cut on axis G by these tangents, give value of chemical potentials of atoms Al and Si in corresponding local equilibria.

Without pressing in the detailed analysis of growth of eutectic phases crystals we will note only influence of cluster formation on a feature of local equilibria on borders of phases.

1. If **clusters absent**, occurrence of the third phase α -Al in diphasic area (L+Si) of a Al-Si phase diagram according to principles of thermodynamics of irreversible processes [6] will cause an establishment of local equilibria on interphase borders L/α -Al, L/β -Si and α -Al/ β -Si. Thus value of chemical potentials of component atoms in these local equilibria $\mu_3^{Al} > \mu_2^{Al} > \mu_1^{Al}$ and $\mu_3^{Si} < \mu_2^{Si} < \mu_1^{Si}$ – Fig. 2 a.

Under influence of gradients of chemical potential, the local diffusion flows arise in all three phases. In a liquid phase on the border L/α -Al, atoms Si are moving to α -Al, and atoms Al in the opposite direction – Fig. 2 a. It will lead to liquid depletion with Al atoms on border of α -Al and to enrichment with atoms of Si. In according to principle of Le Chatelier's – Brown's for maintenance of local balance, Al atoms should pass from α -Al to liquid and it will cause local dissolution of α -Al phase. Consideration of local diffusion flows arising at epitaxial contact of both solid phases, shows that in a liquid phase Al atoms are directed from α -Al to β -Si, and Si atoms are directed in the opposite course. It leads to dissolution of α -phase and to establishment of biphasic equilibrium as it is provided by the Al – Si phase diagram.

2. **The appearance in a liquid phase of a new dispersed phase - clusters** with stoichiometry Al_3Si [3] enters into system three more types of inter-phase borders.

When triple equilibrium of $cluster \leftrightarrow (\alpha-Al) \leftrightarrow (\beta-Si)$ chemical potentials of atoms of the given component are equal μ_3 in all phases by definition. On interfaces of the metallized zone of L_{met} with $(\alpha-Al)$ and $(\beta-Si)$, value of chemical potentials will make μ_4 and μ_2 , and on border with clusters μ_1 accordingly. Thus it is important to note inequalities $\mu_4^{Al} > \mu_3^{Al} > \mu_2^{Al} > \mu_1^{Al}$ and $\mu_4^{Si} < \mu_3^{Si} < \mu_2^{Si} < \mu_1^{Si}$, defining a direction of local diffusion flows of atoms of components in phases between diphasic borders (Fig. 2 b). Crystals $\alpha-Al$, independently existing in a liquid phase, as well as in the previous analysis, are doomed to dissolution because the liquid phase on their border is enriched with Si and depleted with Al.

When silicide cluster approaches to Si crystal, two local phase equilibria [4] are established: on the border $cluster/\beta-Si$ with chemical potential μ_3 and on the border $cluster/L_{met}$ with chemical potential μ_1 . Because $\mu_3^{Al} > \mu_1^{Al}$ and $\mu_3^{Si} < \mu_1^{Si}$, inside of cluster diffusion flow of Si atoms arises to a surface of Si crystals and the diffusion flow of Al atoms in the opposite direction. The first flow causes local growth of Si crystal, the second one leads to enrichment cluster with Al and to its transformation (after achieving necessary supersaturation with Al) into $\alpha-Al$ phase.

Inside of $\beta-Si$ crystal two diffusion flows of Si atoms are established: from border $\beta-Si/L_{met}$ to border $\beta-Si/\alpha-Al$ and from border $\beta-Si/L_{met}$ to border $\beta-Si/cluster$. They caused by an inequality $\mu_3^{Si} < \mu_2^{Si}$. Al atoms are transferred in the opposite direction.

Arguing analogically we will obtain that in crystals $(\alpha-Al)$ local diffusion flows of Si atoms arise from border $(\alpha-Al)/\beta-Si$ to border $(\alpha-Al)/L_{met}$, and Al atoms in opposite direction – Fig. 2 b. Enrichment with Al of frontier layers of α -phases raises its stability and simultaneously halts the growth of $\beta-Si$ crystals on this border.

Because of the fact that in crystal phases atoms Al are connected by the metal bond, and Si atoms by the covalent one the difference of diffusion mobility of Al and Si atoms will very essentially. The noncompensation of the diffusion flows of these two component atoms will cause Kirkendall – Frenkel effect. As a result of the latter, in crystals of both phases the diffusion flows of vacancies will arise. The increased concentration of vacancies explains the appearance of super-structure lines on XRD, fixed in the previous work [2]. The diffusion porosity of silicon crystals in the samples heated after isothermal endurance in a semi-fluid condition (Fig. 3), also is formed due to the coalescence of vacancies.

Thus, genesis of $\alpha-Al$ crystals as equilibrium phase (for a micro-heterogeneous condition) is caused by the diffusion flows in a liquid phase between borders $L_{met}/(\beta-Si)$ and $L_{met}/cluster$. As appears from Fig. 1 suppression of the cluster formation leads to dissolution of the third equilibrium phase and to transition to classical Gibbs biphasic equilibrium.

As the third equilibrium $\alpha-Al$ phase (in the given conditions) is genetically connected with clusters in a liquid phase, then the phenomenon of formation of the clusters of the given type can be qualified as addition of one more degree of freedom.

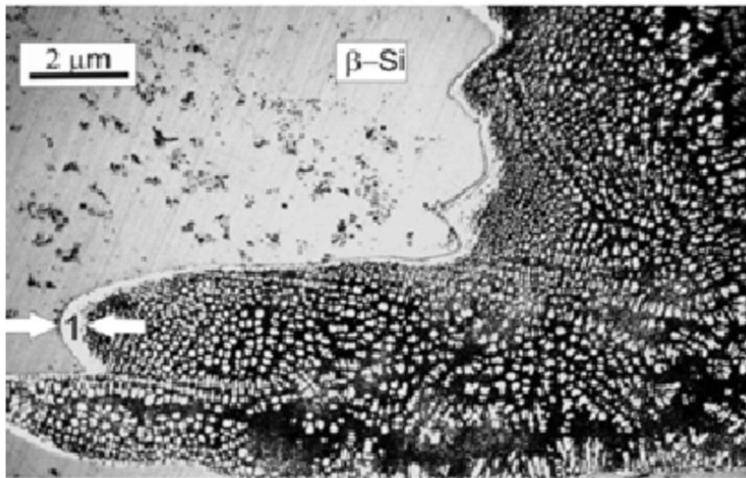


Fig. 3. Diffusion porosity in a primary crystal of the silicon, generated during isothermal endurance at 610 °C. White arrows indicate thin layer of L2a phase.

From here the Gibbs phases rule for the system with micro-heterogeneous phases is put in the following form:

$$C=K+N-\Phi+n$$

where: K – number of components; N – number of independent parameters; Φ – number Gibbs phases in the given phase diagram area; n – number of clusters types,
whence

$$\Phi = K+N-C+n$$

In other words, in system with micro-heterogeneous phase, the quantity of the phases which are in equilibrium in given phase diagram area that includes the micro-heterogeneous phase raises on the number of clusters types which are present in the given area.

In the specific case of alloy Al-21,5Si for 610 °C: $\Phi = K+N+n-C = 2+1+1-1 = 3$ and the micro-heterogeneous system in equilibrium condition includes three phases: L+Si+ α .

L2a phase, whose genesis is connected with relative, instead of the absolute minimum of Gibbs free energy curve for a micro-heterogeneous liquid phase, is a metastable phase and as usually, it is not considered in a rule of phases for stable equilibrium.

Conclusions Results of both the microscopic and specified computer modeling of the XRD phase analysis of alloy Al-21,5 Si at 610 °C show that at equilibrium conditions there are three stable phases: liquid and solid solutions: β -Si and α -Al. Besides one more the metastable (or transitive) L2a phase was defined.

It is shown that in the system with a micro-heterogeneous liquid phase in equilibrium condition, the local diffusive flows take place. They caused by an inequality of chemical potentials of components on inter-phase borders.

The modified Gibbs phases rule is offered, considering quantity of the cluster types in the given phase area in the equilibrium condition.

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Особенности фазовой равновесия в системе Al-Si з микрогетерогенною рідкою фазою

Резюме

Виявлено, що при ізотермічній витримці сплаву Al-21,5Si при 610 °С в напіврідкому сплаві крім рівноважних рідкої та β -Si були присутні ще 2 фази: α -Al і L2a. Появу двох останніх пояснено на основі термодинаміки необоротних процесів. Запропоновано модифіковане правило фаз Гіббса для системи з микрогетерогенною рідкою фазою.

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Особенности фазового равновесия в системе Al-Si с микрогетерогенной жидкой фазой

Резюме

Обнаружено, что при изотермической выдержке сплава Al-21,5Si при 610 °С в полужидком сплаве кроме равновесных жидкой и β -Si присутствуют еще 2 фазы: α -Al и L2a. Появление двух последних объяснено на основе термодинамики необратимых процессов. Предложено модифицированное правило фаз Гиббса для системы с микрогетерогенной жидкой фазой.