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GIBBS PHASE RULE FOR THERMODYNAMIC SYSTEM WITH MICRO-HETEROGENOUS PHASE

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Обнаружено, что при изотермической выдержке сплава Al-21,5Si при 610 °C 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 для системы с микрогетерогенной жидкой фазой.

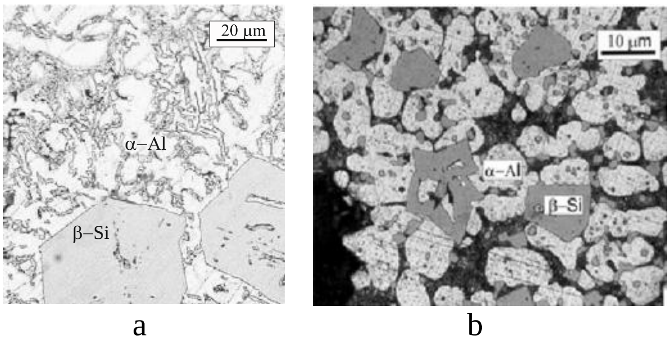
Introduction. The Gibbs's thermodynamics of equilibrium state operates within the parameters describing only macroscopic characteristics of system, such as quantity and volume fractions of phases, their equilibrium concentration. Usually it is accepted that equilibrium in thermodynamic system comes after more or less long holding at the state of invariable independent intensive parameters.

The second assumption presumes that all phases have homogeneous composition. In the conditions of 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 instabile. 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 carried out 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 which makes research of features of an equilibrium state of these systems as topical.

The results and discussion. The microscopic analysis indicates that the Al- 21.5 Si alloy, quenched 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), included in its microstructure not only the primary Si crystals and the eutectic (Si+ α-Al), but also the large primary crystals α-Al (fig. 1, a). Latest structural constituent according to the phase diagram can not exist in the biphasic (Si+L) field of this diagram.



a b

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 exposure 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 thermodynamic equilibrium phase. It look 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 [2, 3]. By results of these works the polystructural model of hypereutectic melt is offered [3]. It includes two zone that are differ by degree of heterodesmicity 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 overheat rising 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 [4] the results of XRD in situ analysis of alloy Al-21,5Si 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=4.1981Å and c=4.4352Å. The tetragonal elementary cell has atoms of aluminum in the apexes of a tetragon with probability of 0.85 (in the others of 15 % of cases some probable atoms of silicon are present in the apexes) and the central atom of silicon with probability 0.5, in others of 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 ($10^o<2\Theta<14^o$) 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 $2\Theta_{exp}=12.54°$. 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 1.

Table 1.

A parity of some interplane distances in phases L2a, α-Alandβ-Si

L2a		β-Si			α-Al			d_{HKL}, %
HKL	d_{HKL}, Å	HKL	d_{HKL}, Å	Δ,Å	HKL	d_{HKL}, Å	Δ,Å	
(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

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.

On the other hand the L2a phase can carry out a role of a buffer phase between α-Al and β-Si at growth of crystals of silicon in α-Al shell (see fig. 2, in [4]). The layer of this phase between silicon and aluminum 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-phasic transformation *L+ (β-Si) → (α-Al) + (β-Si) of* eutectic type in hypereutectic alloy Al-Si.

As the L2a phase is formed on base of silicide clusters which are not Gibbs phase, it is necessary to consider it as metastable one in the given conditions.**microstr**

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.

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

and besides

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

$$\varepsilon_{Al\text{-}Si}>>kT \qquad (3)$$

where

$\varepsilon_{Al\text{-}Si}$- 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 convexity fases the axis of concentration, in some concentration interval the local maximum is formed. 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 energy of thermal movement kT surrounding atoms, thermal degradation of clusters Al-Si 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 individual.

The arrangement of curves of specific free energies G of equilibrium phases at T=610 °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 the pieces cut on axis G by these tangents, give value of chemical potentials of atoms Al and Si in corresponding local equilibria.

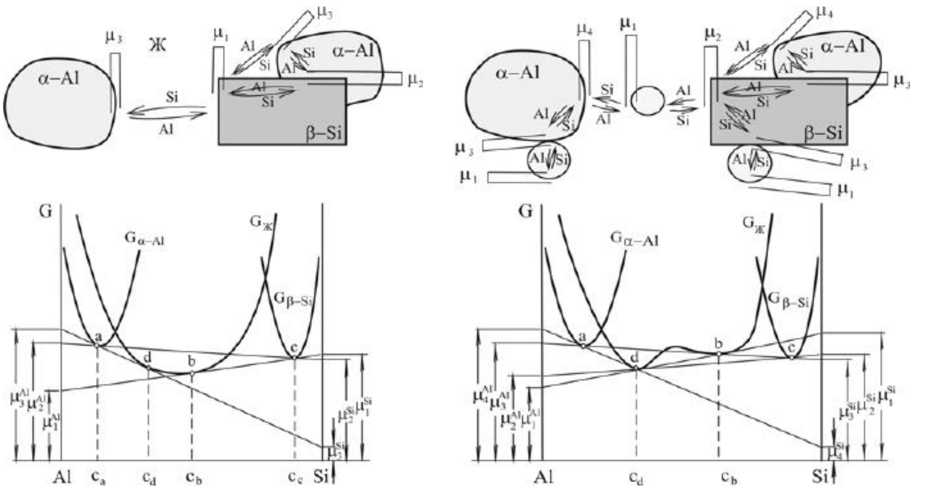
Without pressing in the detailed analysis of growth of eutectic phases crystals we will note only influence of cluster formation on feature of local equilibria on borders of phases.

If clusters are absence 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 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 $\mu^{Al}_3> \mu^{Al}_2> \mu^{Al}_1$ and $\mu^{Si}_3<\mu^{Si}_2<\mu^{Si}_1$ – fig. 2, a.

Under influence of chemical potential gradients, the local diffusion flows arise in all three phases. On border *L/α-Al* in a liquid phase atoms of silicon go to α-Al, and atoms of aluminium in the opposite direction – fig. 2, a. It will lead to liquid depletion with Al atoms on border of aluminium and to enrichment with atoms of silicon. According to Le Chatelier’s – Brown’s principle for maintenance of local balance Al atoms should pass from α-Al in a liquid and it will cause local dissolution of this phase. As a result α–Al crystal, independently existing in a liquid, will be dissolved. Consideration 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 atoms of silicon are directed in the opposite direction. It leads to dissolution α-phase and to establishment of diphasic equilibrium as it is provided by the Al – Si phase diagram.

The occurrence in a liquid phase of a new disperse phase - clusters with stoichiometry Al_3Si [3] – make enter three more types of inter-phase border into system.

When triple equilibrium of *cluster↔(α-Al)↔(β-Si)* chemical potentials of atoms of the given component are equal μ_3 by definition in all phase.. On interfaces of the metallized zone of L_{met} with (α-Al) and (β-Si) value of chemical potentials will make μ_4 and μ_2, and on border with кластерами μ_1 accordingly. Thus it is important to note inequalities $\mu^{Al}_4> \mu^{Al}_3> \mu^{Al}_2> \mu^{Al}_1$ and $\mu^{Si}_4<\mu^{Si}_3<\mu^{Si}_2<\mu^{Si}_1$, defining a direction of local diffusion flows of atoms of components in phases between diphasic borders (fig. 2, b). Crystals α-Al, independently existing in a liquid phase, as well as in the previous analysis, are doomed to dissolution as the liquid phase on their border is enriched with Si and depleted with Al.



a b

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 phases.

When silicide cluster approaches to Si crystal on the interfaces of *cluster/β-Si* the localized phase equilibrium [4] with chemical potential μ_3 is established and on interface *cluster/*L_{met} localized phase equilibrium with chemical potential μ_1 is also established. Due to $\mu^{Al}_3 > \mu^{Al}_1$, $\mu^{Si}_3 < \mu^{Si}_1$, inside of cluster diffusion flow of Si atoms arises to a surface of Si crystal and thatof the Al atoms arises in the opposite direction. The first flow causes local growth of Si crystal, the second one leads to enrichment cluster with Al and its transformation (after achieving necessary super-saturation with Al) in a α-Al phase.

In a β-Si crystal two diffusion flows of Si atoms are established: from border *β-Si/*L_{met} to border *β-Si/α-Al* and from border *β-Si/*L_{met} to border *β-Si/cluster*, caused by an inequality $\mu^{Si}_3 < \mu^{Si}_2$. Al atoms are transferred in opposite direction.

Arguing analogically we will obtain that in crystals (α-Al) local diffusion flows of Si atoms arise from border *(α-Al)/β-Si* to border *(α-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 β-Si crystals on this border.

Because of the fact that in crystal phases Al atoms are connected by the metal bond, and Si atoms by the covalent one the 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 flow of vacancies will arise. The raised concentration of vacancies explains the super-structure lines on XRD, fixed in the previous work [4]. The diffusion porosity of silicon crystals in the samples heated after isothermal endurance in a semi-fluid condition (fig. 3), also forms due to the coalescence of vacancies.

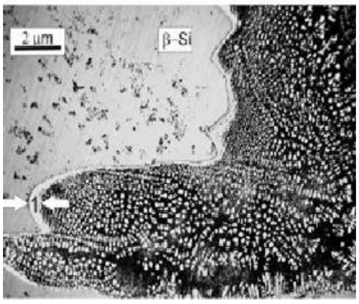


Fig. 3. Diffusion porosity in a primary crystal of the silicon, generated during isothermal endurance at 610 °C. White arrows indicate thin layer of L2a phase.

Thus, genesis of α-Al crystals as equilibrium phase (for a micro-heterogeneous condition) is caused by the diffusion flows in a liquid phase between borders L_{met}*/(β-Si)* and L_{met}*/cluster*. As appears from fig. 1 suppression of the cluster forming leads to dissolution of the third equilibrium phase and to transition to classical Gibbs diphasic equilibrium.

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

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

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

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

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

In other words, *in micro-heterogeneous system, the quantity of the phases which are in equilibrium in given phase diagram area, raises by the number of clusters types which are present in this system.*

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

L2a phase, whose genesis is connected with relative, instead of the absolute minimum of Gibbs free energy 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

1. The microscopic and specified computer modeling of the XRD phase analysis result of alloy Al-21,5 Si at 610 °C has shown that at equilibrium conditions there are three stable phases: liquid and solid solutions: β-Si and α-Al. Besides these one more the metastable (or transitive) L2a phase was defined.
2. It is established that in the system with a micro-heterogeneous liquid phase in equilibrium condition, the local diffusive flows take place caused by an inequality of chemical potentials of atoms of components on inter-phase borders.
3. The modified Gibbs rule phases is offered, considering quantity of the cluster types in the given phase area in the equilibrium condition.

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