Regularities of phase equilibria based on the Bjerrum-Guggenheim concept for the Fe-Al binary system

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A theoretically justified method of mathematical description of phase equilibrium lines based on the regularity of the behavior of components along the phase crystallization line has been developed. When analyzing the state diagrams of various systems, a regularity was found in the formation of crystallization fields of phases in the form of a correlation dependence between the osmotic coefficient of the crystallizing component and the ratio of its activity in the liquid and solid phases. The Bjerrum-Guggenheim osmotic coefficient can serve as a measure of the deviation of the energy properties of a real system from the ideal one described by the Schroeder-Le Chatelier equation.

Two types of generalized mathematical expression in the form of a modified Schroeder-Le Chatelier equation are proposed for the analytical description of the liquidus and solidus lines of state diagrams of a whole class of systems. These types make it possible to calculate the dependence between the composition and the temperature. Mathematical expressions describing the lines of monovariant phase equilibria are presented on a single analytical basis.

Mathematical expressions represent the liquidus and solidus lines of the Fe-Al system for the corresponding elements and compounds using the Schroeder-Le Chatelier equation and the Bjerrum-Guggenheim coefficient (Φ_i). The linear nature of the change in the osmotic coefficient of crystallizing phases (Φ_i) on the ratio of the activity of the components in the ideal liquid and solid phases under the boundary conditions of the formation of crystallization fields of the phases was revealed. The type of change in the Bjerrum-Guggenheim osmotic coefficient depends on the intermolecular interaction of the components in the melt. If only van der Waals forces of interaction between the structural units of the considered component with the second prevail, then a linear relationship is observed. When the formation of various groups from the initial components or the dissociation of a chemical compound takes place in the melt, the osmotic coefficient has a curved dependence.

Keywords: iron, aluminum, Bjerrum-Guggenheim coefficient, state diagram, phases, mathematical model.
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Introduction

Development of the scientific grounds for creation of new materials with preset properties, as well as development of the technology for manufacture of these materials, are connected with inauguration and putting into practice of the new and more economically efficient and methods of building of state diagrams of multi-component systems. The state diagrams are very important not only for study of the theoretical scientific problems, but also for solving of many practical tasks. Based on the last years publications, it can be seen that especial attention was paid just to building and research of state diagrams [1-13]. Investigation of phase equilibria and experimental building the state diagrams for various systems is achieved via significant material and temporal expenses. The time urged to use more complicated compositions of alloys with paying much attention of the scientists on the complex alloys; at the same time the range of their operational conditions is widening. So the further theoretical and experimental investigations of various phase transitions in liquid and solid metals and alloys are required for searching the ways for scientifically substantiated managing by phase composition as well as structure and properties of alloys. Calculation methods allow to attract the achievements of theoretical physics, calculation facilities and successes in research of thermodynamic and physical properties of the alloys to building the state diagrams. Combination of theory and experience makes it possible to determine analytical form of dependencies between thermodynamic properties of phases (from one side) and temperature and composition (from other side).

At present time, thermodynamic methods are mainly applied for calculation of the state diagrams; various models of liquid and solid solutions are used in these methods. It is testified that no one method from the total variety of calculation techniques for solving the direct Gibbs problem is considered as the universal one [10]. It can be suggested with assurance that today there is no common theory of phase transformations, because the nature of origination of phases is not clear, thereby possibility of management by phase composition of the alloys is absent. The aim of this work is concluded in examination of regularities of phase transformations in metals and alloys on the base of the technique of mathematical description of lines in multi-variant phase equilibria, using osmotic Bjerrum-Guggenheim coefficient.

Methods and materials

Self developments, such as the technique, mathematical tools and the main thermodynamic and concentration relations on the lines of phase equilibrium “solidus – liquidus” were used in this work [11, 12]. The developed method of mathematical description of the lines in mono-variant equilibria in the state diagram has the common analytical base and presents semi-empiric dependence in the form of the modified Schroeder-Le Chatelier equation [13, 14]:

$$\ln X_i^L = \frac{\Delta H_{m,i}}{R}\left(\frac{1}{T_{m,i}} - \frac{1}{T}\right)\cdot \Phi_i'', \tag{1}$$

$$\ln X_i^S = \frac{\Delta H_{m,i}}{R}\left(\frac{1}{T_{m,i}} - \frac{1}{T}\right)\cdot\left(\frac{1}{\Phi_i''} - \frac{1}{\Phi_i'}\right), \tag{2}$$

where $\Delta H_{m,1(2)}$ – melting enthalpy of the 1st and 2nd components at melting temperature, J/mol;

R – universal gas constant, equal to 8.3144 J/mol·K;

$T_{m,1(2)}$ and T – the melting temperature of the 1st and 2nd components and crystallization of melts, K;

Φ_i' – the Bjerrum-Guggenheim coefficient for the 1st and 2nd components, which allows to find correlation dependence and to obtain mathematical expression for relation between activities of i-component in liquid and solid phases;

Φ_i'' – the Bjerrum-Guggenheim coefficient for the 1st and 2nd components, which allows to find correlation dependence and to obtain mathematical expression for the liquidus line of i-component.

All calculations were conducted using the programs in Delphi language.

Based on our multi-year operating experience in the field of mathematical description of the lines in mono-variant equilibria and solution of the reverse Gibbs task on the basis of the Bjerrum-Guggenheim concept, we have paid attention on energy of mixing of the components in the melt: the stronger is negative deviation of the properties of each component, the better is their mixing ability of this component together with other components. For example, there are pairs of Fe-Al, Cr-Al and Mn-Al systems in such complex alloys as ferrosilicoaluminium, alumosilicomanganese or alumosilicochromium; the components in these systems are not molten absolutely via conventional methods (e.g. via liquid mixing). However, during melting of these components with use of high-ash coal (not coke), it is possible to provide their melting; it is only required in this case to determine optimal relations of the elements in these alloys via thermodynamic methods, in order to achieve complete aluminium absorption by melt (this aluminium is added in melt with charge materials).

Aluminium alloys occupy especial place among other structural materials. It is connected with possibility of achievement of unique combination of their basic properties and operating parameters, while presentation of crystallization fields of phases in the Fe–Al state diagram in the form of mathematical expressions is the information of great interest.

Obtained results and their analysis

Despite the fact that Fe–Al state diagram is well examined [15], analysis of the literature data displayed contradictions in building crystallization fields of phases. The binary Fe–Al system is characterized by the wide α–Fe crystallization area (**Fig. 1**). The existence area of ordered α_2(FeAl) phase is divided by separate fields. The system includes five

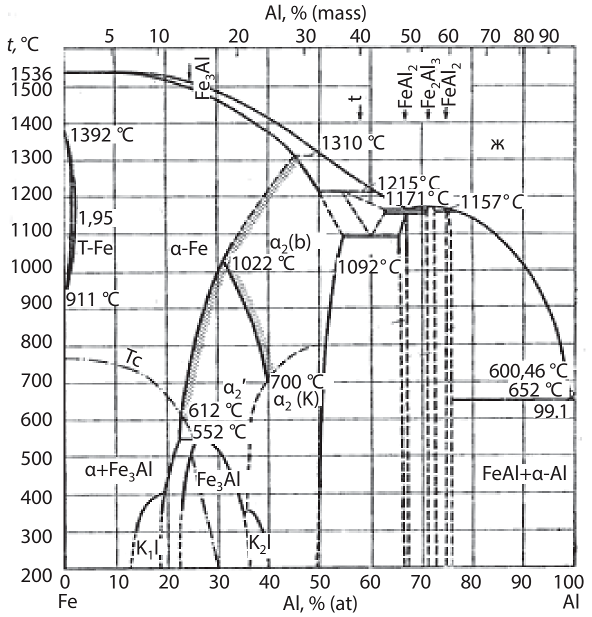

Fig. 1. Fe–Al system state diagram [18]

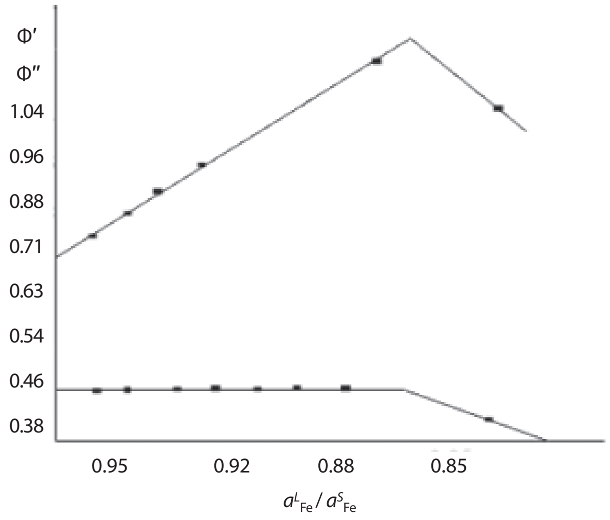

Fig. 2. Dependence between the Bjerrum-Guggenheim coefficients Φ_{Fe}' and Φ_{Fe}'' for α–Fe system and relation of activities of liquid and solid phases for Fe–Al system

Table 1. **Parameters of fields of phases crystallization in Fe–Al system state diagram**

System	Phase (Ф') or Ф'')	Coefficients			Correlation coefficient
		A	B	C	
Fe–Al ($T^{\alpha-\alpha 2}_{calc.}$ = 1584 K)	α–Fe (Ф')	9.80955	–9.74677	–	0.9999
	α–Fe (Ф'')	1.36057	–1.33189	–	0.9952
	α_2–Fe (Ф')	–3.9832	6.0297	–	0.9962
	α_2–Fe (Ф'')	0.5445	–0.3883	–	–0.9997
	ε–Fe (Ф')	–2.0783	3.6996	–	0.9999
	ε–Fe (Ф'')	0.4955	–0.3215	–	–0.9987
Fe_2Al_5–Fe	Fe_2Al_5 (Ф')	–3.9832	6.0297	–	09962
	Fe_2Al_5 (Ф'')	0.5445	–0.3883	–	–0.9997
Fe_2Al_5–Al	Fe_2Al_5 (Ф')	1.28	–1.27	–	–0.9980
	Fe_2Al_5 (Ф'')	0.84	–0.83	–	–0.9880
$FeAl_3$ (Al-Fe)	$FeAl_3$ (Ф')	0.42789	–0.39174	–	–0.9937
	$FeAl_3$ (Ф'')	0.3263	–0.3027	–	–0.9984

stable phases: Fe_3Al, $FeAl_2$, FeAl, Fe_2Al_5, $FeAl_3$, each of them has its own homogeneity area [16-18].

The graphs of curves variation for osmotic coefficients Φ'_{Fe} and Φ''_{Fe} for α–Fe, which were obtained on the base of the results [18], provides fracture at the temperature 1583 K; it suggests presence of ordering in the field of crystallization of ferrite solutions (not mentioned in [18]), see **Fig. 2**. Existence of this phase was firstly proven in the work [19].

The data for Φ'_{Fe} and Φ''_{Fe} obtained in [18] were processed separately for these two areas with obtaining of the coefficients A and B (see **Table 1**, equations 3-6). Then the temperature of phase transition (equal to 1584 K), was determined solving these two pairs of equations [20].

$$\Phi'_{Fe} = 9.8096 - 9.7468 \cdot a^L_{Fe} / a^S_{Fi} \qquad R_{xy} = -0.9999, \quad (3)$$

$$\Phi''_{Fe} = 1.3606 - 1.3319 \cdot a^L_{Fe} / a^S_{Fe} \qquad R_{xy} = -\ 0.9952. \quad (4)$$

Ordering area of α_2(FeAl) phase

$$\Phi'_{Fe} = -3.9832 - 6.0297 \cdot a^L_{Fe} / a^S_{Fi} \qquad R_{xy} = 0.9962, \quad (5)$$

$$\Phi''_{Fe} = 0.5445 - 0.3883 \cdot a^L_{Fe} / a^S_{Fe} \qquad R_{xy} = -\ 0.9997. \quad (6)$$

Mathematical expression of the liquidus and solidus lines in the crystallization area of α-Fe in Fe-Al system can be presented as the following equations (7), (8):

$$x^L_{Fe} = \exp\left[\frac{\frac{15190.384}{8.3144} \cdot \left(\frac{1}{1811} - \frac{1}{T}\right)}{1.3606 - 1.3319 \cdot a^L_{Fe}/a^S_{Fe}}\right], \quad (7)$$

$$x^S_{Fe} = \exp\left[\frac{15190.384}{8.3144} \cdot \left(\frac{1}{1811} - \frac{1}{T}\right) \cdot \left(\frac{1}{1.3606 - 1.3319 \cdot a^L_{Fe}/a^S_{Fe}} - \frac{1}{9.8096 - 9.7468 \cdot a^L_{Fe}/a^S_{Fe}}\right)\right]. \quad (8)$$

Thereby, the Fe–Al state diagram suggested in [18] without mentioning any phase transitions in the field of α–Fe crystallization, allows to suggest during its analysis from the point of view of the Bjerrum-Guggenheim concept that it probably exists with the following temperature of the ordering reaction of the 2nd order:

$Ж + \alpha_{Fe} \Leftrightarrow \alpha_2(FeAl) + Ж$,

What correlated well with the experimental data in more late work [19].

The obtained data for the α–Fe crystallization area allows to conclude that previous to eutectic composition (see Fig. 1) strong positive deviation (Φ'_{Fe} values are rather smaller than 1, see Fig. 2), what explains bad mixing ability of aluminium and liquid iron; that's why obtaining of Fe–Al alloys in metallurgical conditions is slightly difficult from thermodynamic point of view.

The graphs $\Phi'_{Fe_2Al_5}$ and $\Phi''_{Fe_2Al_5}$ are curvilinear on the state diagram (see Fig. 1) for the crystallization area of Fe_2Al_5 compound which is melting in congruent mode, so their linear features is restored only during recalculation of compositions of liquid phases for the partial systems Fe-Fe_2Al_5 and Fe_2Al_5-Fe according to the special formulas [13, 14].

After recalculation of gross concentrations to net ones, the graphs of dependence between the values $\Phi'_{Fe_2Al_5}$ and $\Phi''_{Fe_2Al_5}$ have strictly correlation character (**Fig. 3**).

The obtained data for $\Phi'_{Fe_2Al_5}$ and $\Phi''_{Fe_2Al_5}$ were processed via the least squares method and the equations (9) and (10) were obtained:

$$\Phi'_{forps.Fe-Fe_2Al_5} = 2.0732 - 1.8675 \cdot a^L_{Fe_2Al_5} / a^S_{Fe_2Al_5}$$

$$R_{xy} = -0.9971, \quad (9)$$

$$\Phi''_{forps.Fe-Fe_2Al_5} = 1.8553 - 1.6594 \cdot a^L_{Fe_2Al_5} / a^S_{Fe_2Al_5}$$

$$R_{xy} = -\ 0.9991. \quad (10)$$

Mathematical expression of the liquidus and solidus lines in the area of Fe_2Al_5 crystallization for the partial system Fe-Fe_2Al_5 is presented as dependence of the equations (11) and (12):

$$x^L_{\mathrm{Fe_2Al_5}} = \exp\left[\frac{\frac{18000}{8.3144}\cdot\left(\frac{1}{1683}-\frac{1}{T}\right)}{1.8553 - 1.6594 \cdot a^L_{\mathrm{Fe_2Al_5}}/a^S_{\mathrm{Fe_2Al_5}}}\right], \tag{11}$$

$$x^S_{\mathrm{Fe_2Al_5}} = \exp\left[\frac{68617}{8.3144}\cdot\left(\frac{1}{1683}-\frac{1}{T}\right)\cdot\right. \tag{12}$$

$$\left.\cdot\left(\frac{1}{1.8553 - 1.6594 \cdot a^L_{\mathrm{Fe}}/a^S_{\mathrm{Fe}}} - \frac{1}{2.0732 - 1.8575 \cdot a^L_{\mathrm{Fe}}/a^S_{\mathrm{Fe}}}\right)\right].$$

The comparative analysis of calculated (the equations (11) and (12)) and pilot data in the area of Fe_2Al_5 crystallization for the partial system Fe-Fe_2Al_5 are presented in the **Table 2**.

The values of $\Phi'_{\mathrm{Fe_2Al_5}}$, which are quoted to the partial systems Fe-Fe_2Al_5 and Fe_2Al_5-Fe within crystallization interval of a congruent-melting compound Fe_2Al_5, start practically from the zero point of the $\Phi'_i - a^L_i/a^S_i$ coordinate system from the both sides of this compound (Table 1). It shows on dissociation of this phase during melting; at the same time molecular generations Fe_2Al_5 in the melt demonstrate very strong positive deviation (Φ_i<1) relating to liquid Fe.

Φ_i display high degree of correlation with a^L_i/a^S_i (Table 1) in all these three areas, what allows to describe rather exactly the lines of phase equilibria "solidus – liquidus" in the examined part of the system.

It should be mentioned that mathematical models of the solidus and liquidus lines, which were obtained using the Bjerrum-Guggenheim coefficients, correlate with the experimental data.

Besides that, the features of variation of this value along the lines of monovariant phase equilibria display that presence of groups of Fe_2Al_5 type are revealed practically countrywide in the whole area of the system compositions in melts, which make equilibrium with corresponding solid phases. It is confirmed by practically linear graphs of $\Phi_{\mathrm{Fe_2Al_5}}$ with correlation coefficients close to 1; these correlation coefficients were obtained during recalculation of compositions of melts for possible presence of mentioned groups (Fig. 3) [24-27].

Conclusion

Theoretically substantiated calculating and experimental method for mathematical description of the state diagrams using the Bjerrum-Guggenheim coefficient is developed. Universal features of this technique in solving the mathematical problem of state diagrams, as well as its efficiency for revealing the features of behaviour of solvent and dissolved components in equilibrium phases are shown. Two types of generalized mathematical expression in the form of semi-empiric Schroeder-Le Chatelier equation are suggested for analytical description of the liquidus and solidus lines in the Fe—Al state diagram.

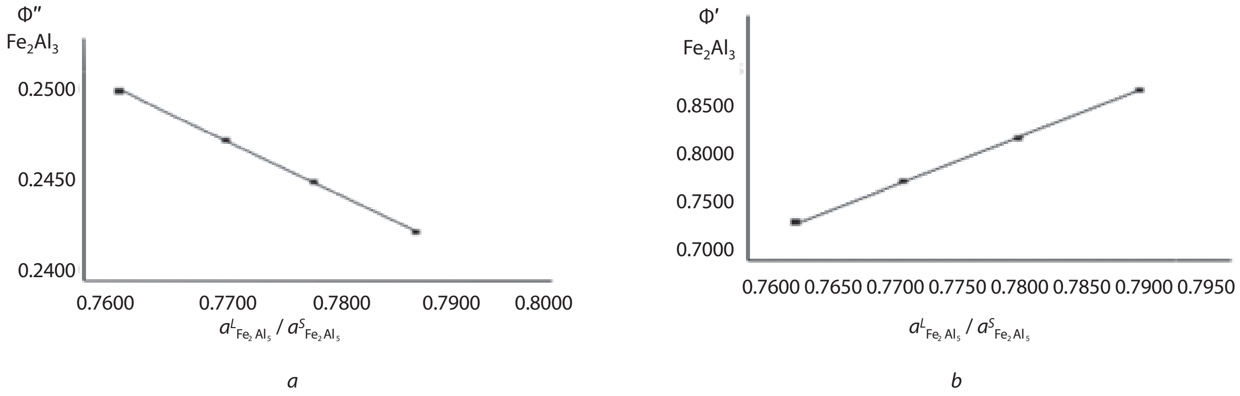

Fig. 3. Dependence between the Bjerrum-Guggenheim coefficients Φ''_{Fe2Al5} and Φ'_{Fe2Al5} and activity relation for the Fe-Fe_2Al_5 system

Table 2. **Comparative pilot and calculated data in the area of Fe2Al5 crystallization for the partial system Fe-Fe_2Al_5**

T, K	$\Phi''_{\mathrm{Fe, pil.}}$	$\Phi''_{\mathrm{Fe, calc.}}$	$X^L_{\mathrm{Fe, pil.}}$	$X^L_{\mathrm{Fe, calc.}}$	$\Phi'_{\mathrm{Fe, pilot}}$	$\Phi'_{\mathrm{Fe, calc.}}$	$X^S_{\mathrm{Fe, pil.}}$	$X^S_{\mathrm{Fe, calc.}}$
1444	0.2066	0.246	0.2810	0.3441	–2.9339	0.65581	0.547	0.5132
1443	0.2187	0.246	0.299	0.3424	–3.7547	0.64751	0.53	0.5147
1441	0.2294	0.247	0.314	0.3407	–2.2421	0.63920	0.514	0.5163
1439	0.2381	0.247	0.325	0.3390	–1.7954	0.63089	0.505	0.5181

Obtained theoretical results concerning the properties of the Bjerrum-Guggenheim coefficient (Φ_i< >1) for the systems Fe-Al, Fe-Si, Al-Mn, Al-Cr, Al-Si allow to determine the conditions providing maximal aluminium absorption by the melts FeSiAl, AlSiMn, AlSiCr; this aluminium appears from high-ash coals during melting of the a.m. metals in ore smelting furnaces.

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