MATHEMATICAL METHOD OF PHASE EQUILIBRIUM OF BINARY SYSTEM Cr-Si BASED ON BJERRUM GUGGENHEIM CONCEPT

The procedure to study the phase equilibrium lines "solid - liquid" was developed for the binary systems with using a coefficient of Bjerrum Guggenheim. The universality of this procedure to solve a mathematical problem of phase diagrams and its efficiency to find the behavioristic characteristics of a solvent and the dissolved components in the equilibrium phases were demonstrated. Two types of the generalized mathematical expression as the modified Le Chatelier-Shreder equation were proposed to describe analytically the liquidus and solidus lines of phase diagrams of the whole class of systems.

Key words: Cr-Si system, mathematical method, phase diagrams, Le Chatelier-Shreder equation, coefficient of Bjerrum Guggenheim.

INTRODUCTION

No universal solution have yet been found for a problem of a heterogeneous phase equilibrium which results might be suitable to calculate and construct the phase diagrams and phase constitution of various system types.

Thereby each system requires the individual solution that is accompanied by considerable labor inputs especially in case of studying the multicomponent systems.

The heart of the theory of regular and subregular solutions, the surrounded atom theory [1] and the cluster theory of solutions suppose that properties and structure of melts are defined generally with sizes of particles and forces of interparticle interaction.

All listed directions have one common fault, namely, require preliminary determination of the conditional interaction parameters and enthalpies of mixture of melts that provide the special researches [1].

Besides the mathematical apparatus of each direction and their versions is only used for the certain groups of systems [2-4], and for others is needed the development of aspecial mathematical apparatus or introduction of complex correction factors.

WAYS OF STUDY

Solution to inverse problems under Gibbs is connected with decoding the phase diagrams with the obtaining of its thermodynamic information, namely relative and excess functions of mixture of components in melt.

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In fact the problem consists of two parts: development of the correct mathematical models of phase diagrams in an analytical form, and further, based on the fundamental laws of thermodynamics, their transformation to the thermodynamic functions of equilibrium phases [5,6].

The analysis of some phase diagrams of binary metal and oxide systems found the general regularity consisting in a deviation of energy parameters of components of a real system from ideal one.

For the real system the monovariant phase equilibrium lines are calculated with Le Chatelier-Shreder equation:

$$\ln \frac{a_{id}^L}{a_{id}^S} = \frac{\Delta H_{m,i}}{R}\left(\frac{1}{T_{m,i}} - \frac{1}{T}\right) + \int_T^{T_{m,i}}\left[\frac{1}{RT^2}\int_T^{T_{m,i}}\Delta C_p, dT\right]dT \quad (1)$$

where, $\Delta H_{m,i}$, $T_{m,i}$ – enthalpy and temperature of melting i – components; R – universal gas constant; ΔC_p – change of heat capacity during melting of components; T – the melting point of the components and the crystallization of melts.

A measure of deviation was used as coefficient of Bjerrum Guggenheim known in paper [7], (Φ_i), which for "solid-liquid" equilibrium is written in the following form of:

$$\Phi_i = \frac{\Delta G_{m,i}^{S\to L}}{\Delta G_{m,i}^{id}} = \frac{\Delta \mu_i^L - \Delta \mu_i^S}{\Delta \mu_{i,id}^L - \Delta \mu_{i,id}^S} =$$

$$= \frac{\ln(a_i^L/a_i^S)}{\ln(x_i^L/x_i^S)} = 1 + \frac{\ln \gamma_i^L/\ln \gamma_i^S}{\ln x_i^L/\ln x_i^S} \quad (2)$$

where, $\Delta G_{m\,i}^{S\to L}$ – Gibbs energy of melting component to its ideal component $\Delta G_{m,i}^{id}$.

The liquidus and solidus lines on the phase diagrams in generalized form are represented as:

$$\ln x_i^L / x_i^S = (\ln a_i^L / a_i^S) / \Phi_i'$$

The coefficient of Bjerrum Guggenheim (2) characterizes a range of deviation of the energy condition of this component from ideality in equilibrium conditions. Thus when this deviation is more might be observed a strong interparticle interaction of this component with other components. This interaction might be divided into two constituents: the Van der Waals (interatomic or intermolecular interaction in the melt of any system) and directed (connected with directed hetero- and homeopolar bonds between components in the melt). Moreover, in both cases the interacting force and range of deviation of component property from ideality will depend on the particle quantity which is in other states.

In the theory of the statistical thermodynamics the first is defined as $\exp\left(-\dfrac{\Delta G_{m,i}^0}{RT}\right)$, and the second as difference of quantity of the particles which are completely in the associated and free states. Thus, Φ_i change along the phase equilibrium line might be written as:

$$\Phi_i = A_i + B_i \cdot \exp\left(-\frac{\Delta G_{m,i}^0}{RT}\right) \qquad (3)$$

or

$$\Phi_i = A_i + B_i \cdot \exp\left(-\frac{\Delta G_{m,i}^0}{RT}\right) +$$

$$+ C \frac{1}{\exp\left(-\dfrac{\Delta G_{as,i}}{RT}\right) - \exp\left(-\dfrac{\Delta G_{m,i}^0}{RT}\right)}, \qquad (4)$$

where $\Delta G_{as,i}$ - Gibbs free energy of melting on reaching which transition of this component completely in the associated state is possible; A_i, B_i are empirical coefficients.

Therefore, the equations (3 and 4) permit under the statistical thermodynamics to explain the physical meaning of dependence of Φ_i on the crystallizing component activities.

It should be pointed out that in the depending on a character of interpartial interaction in melts for various systems will be observed a different type of Φ_i change along liquidus and solidus lines. If in the melt along a liquidus line the Van der Waals interaction forces (equation 3) are prevail between the elementary structural units of the studied component with the second, then the rectilinear dependence will be observed (the elementary structural units are meant as element atoms or molecules of compounds). At formation of associates from initial elements or dissociation of the studied compound in melt, the true amount of atoms or molecules of this phase will depend stronger (on very complex depend-

ences including dissociation rate of compounds) on temperature and composition of melt that must inevitably lead to a nonlinear dependence (equation 4).

Equations (1, 3, 4) permit to show out the semi-empirical dependences as the generalized Le Chatelier - Shreder equations to calculate liquidus and solidus lines for any real system in crystallization of a relevant phase on the following dependences:

$$\frac{x_1^L}{x_1^S} = \exp\left[\frac{\ln a_{id}^L / \ln a_{id}^S}{\Phi_1'}\right] = Mr,$$

$$\frac{x_2^L}{x_2^S} = \exp\left[\frac{\ln a_{id}^L / \ln a_{id}^S}{\Phi_2'}\right] = Nr. \qquad (5)$$

The solution of system of the equations (5) gives the mathematical expressions of solidus and liquidus lines for the real systems:

$$x_{1,r}^L = M_r \cdot \frac{N_r - 1}{N_r - M_r}; \; x_{1,r}^S = \frac{N_r - 1}{N_r - M_r}. \qquad (6)$$

Based on equations (4-6) the processing procedure of experimental data was developed. The open experimental results in binary phase diagrams contain two coordinates for each point of liquidus and solidus lines, namely: concentration of a crystallizing component $X_i^{L(S)}$ and temperature K. A key feature of various crystallization regions of binary systems is an existence of close correlations between the thermodynamic properties along curves of monovariant phase equilibrium. This correlation for the simple systems is observed as rectilinear dependence of osmotic coefficient of Bjerrum Guggenheim of the crystallizing component Φ_i on its activity a_i^L / a_i^S, in liquid and solid phases as:

$$\Phi_i = A_i + B_i \cdot a_i^L / a_i^S, \qquad (7)$$

Where coefficients A and B are constants determined with the nature of components and the interpartial interactions. The experimental data of various binary metal systems were used to receive these values at a concrete temperature T_m under equations:

$$\Phi_1' = \frac{\ln(a_1^L / a_1^S)}{\ln(x_1^L / x_1^S)} \text{ and } \Phi_2' = \frac{\ln(a_2^L / a_2^S)}{\ln(x_2^L / x_2^S)}, \qquad (8)$$

where $x_i^{L(S)}$ is concentration of a crystallizing component at this temperature; $a_i^{L(S)}$ – activity of a crystallizing component for ideal solution calculated under Le Chatelier - Shreder equation (1).

Processing of the received results with the least-squares method permits to find values of constants and coefficients of correlation for various systems under equations 3 and 4, and to show the analytical expressions of surfaces of fields of crystallization phases in any quasi-system found at setup of the phase diagram with the TDA method (equations 5 and 6).

However the simple analysis of crystallization fields in various systems [8] on a relative position of liquidus

Table 1 **Comparative experimental and calculated data for Cr – Si system**

$\Phi''_{Si,cal.}$	$\Phi''_{Si,exp.}$	$X^L_{Si,\,cal.}$	$X^L_{Si,exp.}$	$\Phi''_{Cr,cal.}$	$\Phi''_{Cr,exp.}$	$X^L_{Cr,cal.}$	$X^L_{Cr,\,exp.}$
0,8990	0,9002	0,9770	0,9770	0,0801	0,0744	0,0301	0,0230
0,9562	0,9588	0,9569	0,9570	0,0921	0,0917	0,0435	0,0430
1,0128	1,0277	0,9391	0,9400	0,1041	0,1055	0,0577	0,0600
1,0689	1,0645	0,9233	0,9230	0,1161	0,1190	0,0722	0,0770
1,1245	1,1114	0,9090	0,9080	0,1282	0,1314	0,0867	0,0920
1,1795	1,1674	0,8960	0,8950	0,1404	0,1429	0,1008	0,1050
1,2339	1,2328	0,8841	0,8840	0,1526	0,1535	0,1144	0,1160
1,2878	1,2869	0,8731	0,8730	0,1648	0,1645	0,1275	0,1270
1,3411	1,3429	0,8628	0,8630	0,1771	0,1752	0,1399	0,1370
1,3675	1,3784	0,8580	0,8590	0,1832	0,1801	0,1458	0,1410

lines does not practically present a structure of melt and authenticity of the experimental data except weak or strong decrease in melting temperature of the studied phase with the second components. The studying of phase diagrams of systems based on iron under Bjerrum Guggenheim concept was made according to the well-known classification [5] to show analytically the phase equilibrium lines "solid - liquid" and define behavior of components in melts of metal systems [9,10,11].

Cr – Si system.

As demonstration material of the developed procedure of the mathematical description of the phase equilibrium lines based on Bjerrum Guggenheim concept, the formation of crystallization fields of phases in Cr–Si system was studied.

For this system the following compounds: Cr_3Si, Cr_5Si_3, $CrSi$ and $CrSi_2$ were determined.

In order to calculate the mathematical expressions of the liquidus and solidus lines under specially made program, values of enthalpy and temperature of melting of silicium and chrome were used. $\Delta H_{m,Si} = 50\ 210 J / mol$, $T_{m,Si} = 1\ 703\ K$, $\Delta H_{m,Cr} = 19\ 246,4\ J / mol$, $T_{m,Cr} = 2\ 130\ K$ [9,12].

The basic data for crystallization of silicium and chrome were taken from the phase diagram as data array [13], each temperature (from chrome melting temperature) which relevant a structure to the eutectic temperature.

The equations of dependence of Bjerrum Guggenheim's coefficient from activities in liquid and solid phases with correlation coefficient were received.

$$\Phi''_{Si} = 3,6254 - 2,7841 \cdot a^L_{Si} / a^S_{Si}\quad R_{xy} = -0,9986 \quad (9)$$

$$\Phi''_{Cr} = 1,5593 - 1,9582 \cdot a^L_{Cr} / a^S_{Cr}\quad R_{xy} = -0,9969 \quad (10)$$

Table 1 demonstrates the comparative analysis of the experimental and calculated data for crystallization of silicium and chrome from melting temperature 1 420 K to 1 335 K which shows good repeatability of experimental and calculated data, thus the received mathematical expressions of liquidus and solidus lines describe ideally a line of crystallization of phases.

Figure 1 illustrates the diagrammatic curves for the first and second component, and they are rectilinear. It suggests that presence of particles of two types in melt that is Si and Cr, and of the Van der Waals interaction forces between them.
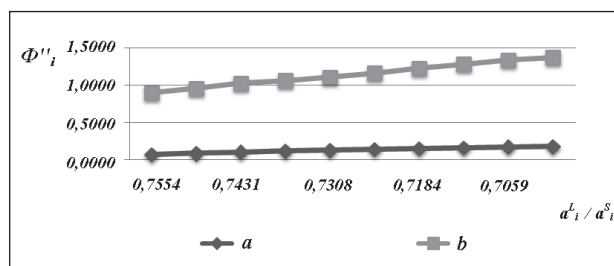

Figure 1 Dependences Φ''_{Cr} and Φ'_{Cr} of Bjerrum Guggenheim's coefficients from activities for system Cr–Si, where
a) $-\Phi''_{Cr} = f(a^L_{Cr} / a^S_{Cr})$;
b) $-\Phi'_{Si} = f(a^L_{Si} / a^S_{Si})$

CONCLUSIONS

Based on the above it can be concluded that for the analytical description of the liquidus and solidus lines of the phase diagrams of the whole class of systems were proposed two types of the generalized mathematical expression as modified Le Chatelier-Shreder equation (equation 6). The main correlations of thermodynamic properties and structures of phases along phase equilibrium lines "solid - liquid" permitting to set up the melt diagrams of the unstudied systems based on limited quantity of experimental data were also determined.

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