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ASSESSMENT OF DISSOCIATION RATE OF $FeCr_2O_4$ USING THE BJERRUM-GUGGENHEIM COEFFICIENT

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Preliminary Note – Prethodno priopćenje

A calculation procedure of line positions of the monovariant phase equilibrium for the crystallization regions of a congruent compound using the osmotic coefficient of Bjerrum-Guggenheim $\left(\Phi'_{A_m B_n}\right)$ was developed. The relevant mathematical apparatus for an analytical description of lines and surfaces of the phase crystallization was recommended. As an example of FeO-Cr_2O_3 oxide system, the assessment of dissociation rate of congruent compound of $FeCr_2O_4$ was performed. The demonstration material of behavior of the osmotic coefficient of Bjerrum-Guggenheim under boundary conditions as assessment criterion of melt structurewas presented.

Keywords: FeO-Cr_2O_3 system, phase diagrams, crystallization, dissociation rate, Bjerrum-Guggenheim coefficient.

INTRODUCTION

In the theory of the physicochemical analysis, a question about the monovariant equilibrium curves near a composition of a chemical compound is of the great interest, but until recently it was not given enough attention. Up till nowthere is no general thermodynamic justification for the existence of a singular maximum [1-5].

Some phase diagrams of the metal and oxide systems were analyzedusing the concept of the osmotic coefficient of Bjerrum-Guggenheim $\left(\Phi'_{A_m B_n}\right)$, thus a general pattern [6] was discovered (where: A_m,B_n – stoichiometric connection coefficients).The value Φ_i fully corresponds to the boundary conditions of almost all types of phase diagrams found in nature and predicted by N. S. Kurnakov [7].

The preconceptual study on some systems of Fe-Ti, Fe-Si, Mn-Si, and also oxide systems of CaO-SiO_2, MgO-SiO_2, CaO-P_2O_5 [8,9], etc. demonstrated that if the liquidus line continues above a meltingpoint, it makes a loop and returns to unity (Figure 1a).

Figure 1b demonstrates a dependence diagram of $\left(\Phi'_{A_m B_n}\right)$ on activity. If the liquidus line is continued at $T > T_{m,A_m B_n}$, where: T - current temperature, $T_{m,A_m B_n}$ - melting point of the compound then there will be $\Phi'_{A_m B_n} \to \infty$, $\ln x_{A_m B_n} \to 0$, $x_{A_m B_n} \to 1$.

Will the congruent compounds be dissociated completely or not during the melting or will there be observed two liquids, the questions are still open.

WAYS OF STUDY

Referring to a developed calculation procedure of dissociation rate of the congruent compound [9] through relation of rate of dissociation or association (α) with an equilibrium constant using the osmotic coefficient of Bjerrum-Guggenheim $\left(\Phi'_{A_m B_n}\right)$, the assessment of dissociation rate of congruent compound of $FeCr_2O_4$of FeO-Cr_2O_3 system was performed.

Assessment of dissociation (association) rate of the congruent-melting compound through the osmotic coefficient of Bjerrum-Guggenheim will permit to conclude how strongly do the congruent compounds dissociate during the melting, is presence of two liquids observed, and then a horizontal site will be formed on a phase diagram.

The phase diagram of FeO-Cr_2O_3 [10] is very interesting in terms of behavior of the osmotic coefficient of Bjerrum-Guggenheim near a melting point of the congruent compound of $FeCr_2O_4$ (Figure 2).

The extensive crystallization region of the compound and flat maximum at a melting point made it possible to more accurately find an inflection point or more correctly say a temperature where the melt radically changes its properties.

For crystallization area of $FeCr_2O_4$ of FeO-$FeCr_2O_4$ quasisystem after recal-culating the conversion of gross concentrations to net the run of a curve of dependence diagrams of values of $\Phi''_{FeCr_2O_4}$ and $\Phi'_{FeCr_2O_4}$ on $a^L_{FeCr_2O_4}$ / $a^S_{FeCr_2O_4}$,where a^L/a^S - the ratio of activities in the liquid and solid phases, has obviously convex character, beginning from a melting point of a chemical compound, and, in process of temperature reduction to a horizontal of an eutectic 1 693 K, there is a formation of associates, $FeCr_2O_4$ groups (Figure 3 a).

Table 1 demonstrates the calculated thermodynamic data of the FeO-Cr_2O_3 system. The dissociation rate of $FeCr_2O_4$ compound is very close to 1, i.e. the compound dissociates completely.

V. Tolokonnikova, S. Baisanov, G. Narikbayeva, I. Korsukova, Chemical-Metallurgical Institute, Karaganda, Kazakhstan, e-mail: met.rasplav@mail.ru

Table1 **The calculated thermodynamic data of the FeO-Cr_2O_3 system**

Crystallization region of $FeCr_2O_4$ on diagram of $FeCr_2O_4$-FeO				Crystallization region of $FeCr_2O_4$ on diagram of $FeCr_2O_4$-Cr_2O_3			
T/K	$\Delta G^0/_{kJ/mol}$	Kp	α	T	$\Delta G^0/_{kJ/mol}$	Kp	α
2 433	1 795 980,4	2,7561E-39	0,995632	2 433	1 795 980,4	2,7561E-39	0,5
2 373	1 708 252,9	2,4915E-38	0,994861	2 398	1 744 844,2	9,8041E-39	0,4385
2 273	1 561 331,6	1,3139E-36	0,994213	2 373	1 708 252,9	2,4915E-38	0,4158
2 173	1 413 493,7	1,0499E-34	0,994034	2 323	1 634 904,6	1,7236E-37	0,3840
2 073	1 272 484,9	8,6152E-33	0,993964	2 273	1 561 331,6	1,3139E-36	0,3455
1 973	1 096 499,1	9,3204E-30	0,993862	2 223	1 487 529,6	1,111E-35	0,3093
1 873	968 738,7	9,6078E-28	0,993549	2 173	1 413 493,7	1,0499E-34	0,2868
1 773	923 448,7	6,2108E-28	0,993118		-	-	-
1 693	853 747,4	4,5512E-27	0,992756		-	-	-

Where: ΔG^{0} - energy of Gibbs, Kp - constant of equilibrium of reaction of dissociation, α - degree of dissociation degree of dissociation.

$$x^L_{FeCr_2O_4} = \exp\left[\frac{\dfrac{202\,829}{8,3144}\cdot\left(\dfrac{1}{2433}-\dfrac{1}{T}\right)}{16,6-10,42\cdot a^L_{FeCr_2O_4}\,/\,a^S_{FeCr_2O_4}+6,17\,/\left(a_{kp.}-a^L_{FeCr_2O_4}\,/\,a^S_{FeCr_2O_4}\right)}\right]. \quad (1)$$

The lineal nature of the change in $\Phi''_{FeCr_2O_4}$ and $\Phi'_{FeCr_2O_4}$ from a ratio of activity in the liquid and solid phases (Figure 3 b) shows that by reason of temperature change in the melt, there are mainly Van der Waals interaction forces between particles, but it is also possible to say about the constancy of the dissociation rate of the spinel [11] when the melt composition changes along the liquidus from its melting temperature to the eutectic temperature for a particular system of $FeCr_2O_4$-Cr_2O_3 (Table 1).

Thus, it was found that for the oxide system of FeO-Cr_2O_3 the dissociation rate of $FeCr_2O_4$ is upon the average 50 % for the quasisystem of $FeCr_2O_4$-Cr_2O_3.

The liquidus line equation for a particular system of FeO-$FeCr_2O_4$ has a dependence of composition on temperature (1):

$x^L_{FeCr_2O_4}$ - the concentration of crystallizing component; $a^L_{FeCr_2O_4}\,/\,a^S_{FeCr_2O_4}$ - the ratio of activities in the liquid and solid phases under the Le-Chatelier-Shreder equation; $a_{cr.}$ - activity at temperature $T > T_{m,A_mB_n}$.

The liquidus line equation of $FeCr_2O_4$ for a particular system of $FeCr_2O_4$-Cr_2O_3 is described by the mathematical formula (2):

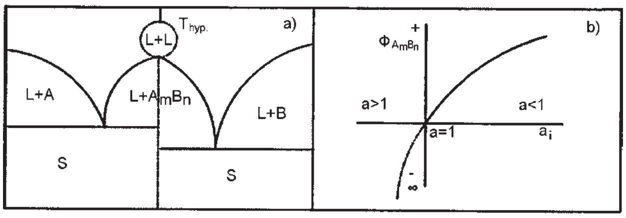

Figure 1 Schematic image of diagrams of the state a) the schematic image of the phase diagram with formation of a complex chemical compound with extending of the liquidus line above a melting point on one side and the other from the A_mB_n compound; b) a dependence diagram of the Bjerrum-Guggenheim coefficient near a melting point of A_mB_n compound.

$$x^L_{FeCr_2O_4} = \exp\left[\frac{\dfrac{202\,829}{8,3144}\cdot\left(\dfrac{1}{2\,433}-\dfrac{1}{T}\right)}{56,4867-56,1023\cdot a^L_{FeCr_2O_4}\,/\,a^S_{FeCr_2O_4}}\right]. \quad (2)$$

For a crystallization line near congruent-melting chemical compounds, the mathematical formula looks like a formula of $\ln x^L_i = \ln a_i\,/\,\Phi_i$. In this case, Φ'_i for them tends to zero with the temperature approaching to T_{m,A_qB_H}, and then at this temperature, avalue of $\Phi'_{A_xB_y}$ tends to infinity, in this case, $\ln x_{A_xB_y} \to \infty$, i.e. $x_{A_qB_H} \to 1$, i.e. the osmotic coefficient makes a loop and returns to 1.

Now it will be observed how equations of (1) and (2) for the crystallization region of $FeCr_2O_4$ will continue the liquidus line above a melting point of $FeCr_2O_4$ at 2 433 K. Table 2 demonstrates such an analysis (Figure 1).

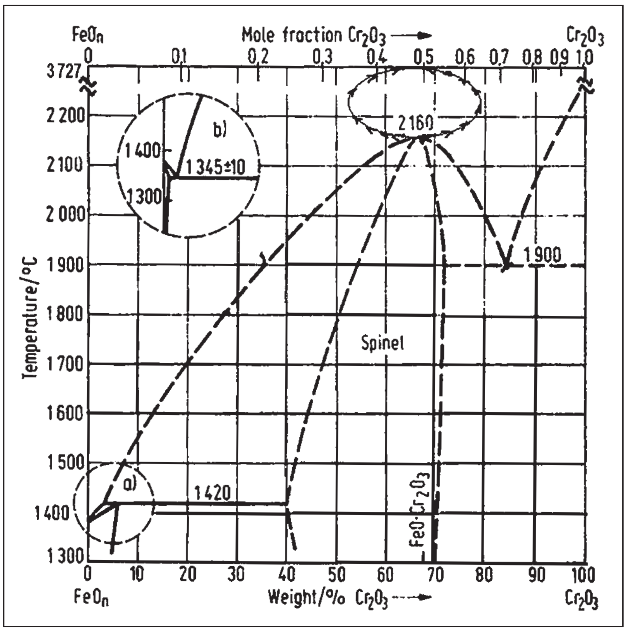

Figure 2 A phase diagram of FeO-Cr_2O_3

Table2 **The calculated data of liquidusline from two sides above melting point of $FeCr_2O_4$**

Crystallization region for $FeCr_2O_4$ of quasisystem of $FeO-FeCr_2O_4$				Crystallization region for $FeCr_2O_4$ of quasisystem of $Cr_2O_3-FeCr_2O_4$			
T/K	$a^L_{FeCr_2O_4} / a^S_{FeCr_2O_4}$	$\Phi''_{FeCr_2O_4}$, calc.	$x^L_{FeCr_2O_4}$, calc.	T/K	$a^L_{FeCr_2O_4} / a^S_{FeCr_2O_4}$	$\Phi''_{FeCr_2O_4}$, calc.	$x^L_{FeCr_2O_4}$, calc.
2 433	1,0000	0,3844	1,00	2 433	1,0000	0,0154	1,00
2 460	1,1163	-6,1422	0,98	2 600	1,90414	-6,4717	0,91
2 470	1,1621	-8,7078	0,98	2 700	2,69538	-13,7613	0,93
2 480	1,2093	-11,3566	0,98	2 800	3,72187	-23,8208	0,95
2 600	1,9041	-50,3398	0,99	3 000	6,65298	-53,6177	0,97
2 700	2,6954	-94,7303	0,99	3 500	21,25816	-205,092	0,99
3 000	6,6530	-316,7607	0,99	4 000	50,805	-512,652	0,99
4 000	50,8052	-2 793,7998	1,00	5 000	172,045	-1 775,27	1,00

CONCLUSIONS

In order to assess the thermal stability of the congruent compound, the method of the mathematical description of the monovariantphase equilibrium lines based on Bjerrum-Guggenheim conceptwas used [6].

The semi-empirical dependencies of the composition on temperature were obtained as a modified Le Chatelier-Shreder equation. Attention should be paid to the fact that the dependence diagrams of the osmotic coefficientof Bjerrum-Guggenheim on the ratio of the activity of the liquid and solid phases (Le Chatelier-Shreder equation for an ideal system) for the crystallization region of the congruent compound of $FeCr_2O_4$at its melting point of 2 433 K gave a calculationfor the liquid phase which equal to 1 (Table 2). Further, the temperature was increased above a melting point of 2 433 K of $FeCr_2O_4$ compound for each quasisystem separately under equations of (1) and (2).The composition began to decrease and then increase and at a temperature of 4 000 - 5 000 K, respectively, again came to 1.Figure 1 demonstrates the microsite and loop from two sides of the congruent compound of $FeCr_2O_4$. Above the compound, there was observed a hypothetical dome consisting of two immiscible liquids.

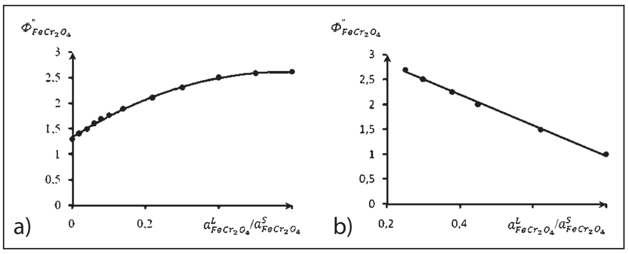

Figure3 The dependence diagrams of an osmotic coefficient of Bjerrum-Guggenheim a) - $FeCr_2O_4$-Cr_2O_3 system, b) - FeO - $FeCr_2O_4$ system

Acknowledgements

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REFERENCES

[1] Glazov V. M., Pavlova L. M. Chemical thermodynamics and phase equilibria. M.: Metallurgy, 1988., 555p.
[2] Zakharov M. A. Calculation of the main types of phase diagrams of binary solutions within the framework of the generalized lattice model //Bulletin of Novgorod State University 98 (2016) 7, 22-26.
[3] Shakhnazarov K. Yu. Features of intermediate phases in the systems of Al-Si, Fe-C and Al-Cu//Bulletin of Moscow State Technical University named after G. I. Nosov 14 (2016)3, 71-77.
[4] Voronin G. F. New possibilities of thermodynamic calculation and construction of phase diagrams of heterogeneous systems //Journal of physical chemistry 77 (2003)10, 1874-1883.
[5] Moshchenskaya E. Yu., Clepushkin V. V. Method of liquids curves constructing of double eutectic systems // Journal of Inorganic Chemistry 60 (2015)1,78-84.
[6] Baisanov S.,Tolokonnikova V., Narikbayeva G., Korsukova I., Mukhambetgaliyev Ye. Mathematical method of phase equilibrium of binary system Cr-Si based on Bjerrum-Guggenheim concept //Metalurgija 59 (2020) 1, 97-100.
[7] Kurnakov N. S. Introduction to physical and chemical analysis. 3rd add. ed. - L.: ONTI, 1936. - 194 p.
[8] Kassenov B. K., Ashlyaeva I. V., Beilina A. Z. Phase equilibrium in CaO- As_2O_5 system //Reports of the Academy of Sciences of the USSR 35 (1990) 5, 452 – 455
[9] Mukhambetgaliev, E. K., Roshchin, V. E., Baisanov, S. O. Analytical expressions for Fe-Si-Al-Mn metal system and phase composition of alumosilicomanganese //Izvestiya Ferrous Metallurgy 7 (2018) 61, 564-571.
[10] Atlas of slags. M.: Metallurgy, 1985. - 400 p.
[11] Akberdin A. A., Kim A. S., Sultangaziev R. B. Planning of numerical and physical experiment in simulation of technological processes //Izvestiya of ferrous metallurgy 9 (2018) 61, 737-742.

Note: The responsible translator for English language is Yelena Issakova, Karaganda, Kazakhstan