

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 ($\Phi'_{A_m B_n}$) 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-Cr₂O₃ oxide system, the assessment of dissociation rate of congruent compound of FeCr₂O₄ was performed. The demonstration material of behavior of the osmotic coefficient of Bjerrum-Guggenheim under boundary conditions as assessment criterion of melt structure was presented.

Keywords: FeO-Cr₂O₃ 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 now there is no general thermodynamic justification for the existence of a singular maximum [1-5].

Some phase diagrams of the metal and oxide systems were analyzed using the concept of the osmotic coefficient of Bjerrum-Guggenheim ($\Phi'_{A_m B_n}$), 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-SiO₂, MgO-SiO₂, CaO-P₂O₅ [8,9], etc. demonstrated that if the liquidus line continues above a melting point, it makes a loop and returns to unity (Figure 1a).

Figure 1b demonstrates a dependence diagram of ($\Phi'_{A_m B_n}$) 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 $\Phi'_{A_m B_n} \rightarrow \infty$, $\ln x_{A_m B_n} \rightarrow 0$, $x_{A_m B_n} \rightarrow 1$.

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 ($\Phi'_{A_m B_n}$), the assessment of dissociation rate of congruent compound of FeCr₂O₄ of FeO-Cr₂O₃ 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-Cr₂O₃ [10] is very interesting in terms of behavior of the osmotic coefficient of Bjerrum-Guggenheim near a melting point of the congruent compound of FeCr₂O₄ (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 FeCr₂O₄ of FeO-FeCr₂O₄ quasisystem after recalculating the conversion of gross concentrations to net the run of a curve of dependence diagrams of values of $\Phi''_{\text{FeCr}_2\text{O}_4}$ and $\Phi'_{\text{FeCr}_2\text{O}_4}$ on $a^L_{\text{FeCr}_2\text{O}_4} / a^S_{\text{FeCr}_2\text{O}_4}$, 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, FeCr₂O₄ groups (Figure 3 a).

Table 1 demonstrates the calculated thermodynamic data of the FeO-Cr₂O₃ system. The dissociation rate of FeCr₂O₄ 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-Cr₂O₃ system

| Crystallization region of FeCr ₂ O ₄ on diagram of FeCr ₂ O ₄ -FeO | | | | Crystallization region of FeCr ₂ O ₄ on diagram of FeCr ₂ O ₄ -Cr ₂ O ₃ | | | |
|--|-------------------------|------------|----------|---|-------------------------|------------|--------|
| T/K | ΔG ⁰ /kJ/mol | Kp | α | T | ΔG 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: ΔG⁰ - energy of Gibbs, Kp - constant of equilibrium of reaction of dissociation, α - degree of dissociation degree of dissociation.

$$x_{FeCr_2O_4}^L = \exp \left[\frac{202\,829 \cdot \left(\frac{1}{2433} - \frac{1}{T} \right)}{16,6 - 10,42 \cdot a_{FeCr_2O_4}^L / a_{FeCr_2O_4}^S + 6,17 / \left(a_{kp} - a_{FeCr_2O_4}^L / a_{FeCr_2O_4}^S \right)} \right] \quad (1)$$

The lineal nature of the change in Φ["]_{FeCr₂O₄} and Φ[']_{FeCr₂O₄} 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 FeCr₂O₄-Cr₂O₃ (Table 1).

Thus, it was found that for the oxide system of FeO-Cr₂O₃ the dissociation rate of FeCr₂O₄ is upon the average 50 % for the quasisystem of FeCr₂O₄-Cr₂O₃.

The liquidus line equation for a particular system of FeO-FeCr₂O₄ has a dependence of composition on temperature (1):

$x_{FeCr_2O_4}^L$ - the concentration of crystallizing component; $a_{FeCr_2O_4}^L / a_{FeCr_2O_4}^S$ - the ratio of activities in the liquid and solid phases under the Le-Chatelier-Shreder equation; a_{cr} - activity at temperature $T > T_{m,A_m B_n}$.

The liquidus line equation of FeCr₂O₄ for a particular system of FeCr₂O₄-Cr₂O₃ is described by the mathematical formula (2):

$$x_{FeCr_2O_4}^L = \exp \left[\frac{202\,829 \cdot \left(\frac{1}{2433} - \frac{1}{T} \right)}{56,4867 - 56,1023 \cdot a_{FeCr_2O_4}^L / a_{FeCr_2O_4}^S} \right] \quad (2)$$

For a crystallization line near congruent-melting chemical compounds, the mathematical formula looks like a formula of $\ln x_i^L = \ln a_i / \Phi_i$. In this case, Φ_i for them tends to zero with the temperature approaching to $T_{m,A_m B_n}$, and then at this temperature, a value of Φ_{A_xB_y}' tends to infinity, in this case, $\ln x_{A_x B_y} \rightarrow \infty$, i.e. $x_{A_x B_y} \rightarrow 1$, 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 FeCr₂O₄ will continue the liquidus line above a melting point of FeCr₂O₄ at 2 433 K. Table 2 demonstrates such an analysis (Figure 1).

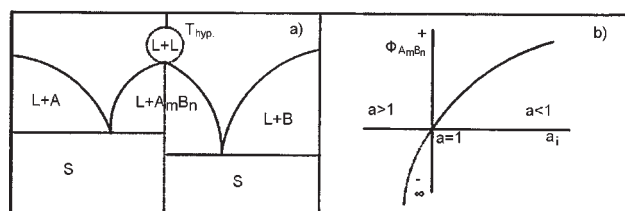


Figure 1 Schematic image of diagrams of the state a) the schematic image of the phase diagram with formation of a complex chemical compound with extending of the liquidus line above a melting point on one side and the other from the A_mB_n compound; b) a dependence diagram of the Bjerrum-Guggenheim coefficient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

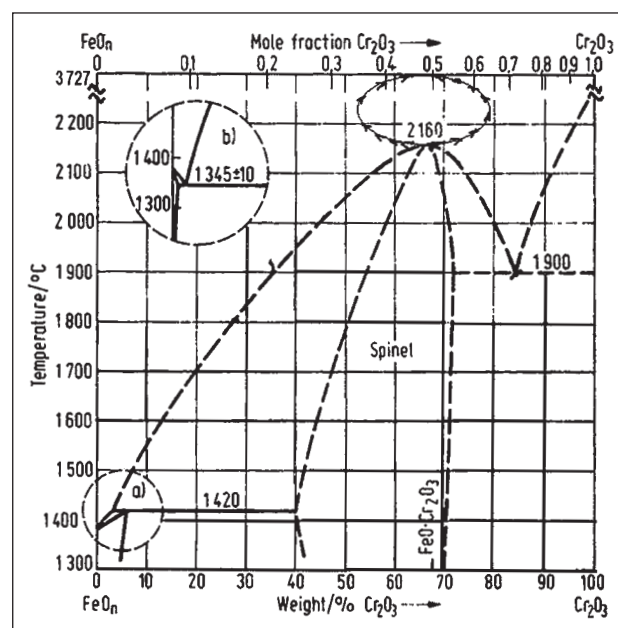


Figure 2 A phase diagram of FeO-Cr₂O₃

Table 2 The calculated data of liquidusline from two sides above melting point of FeCr_2O_4

| Crystallization region for FeCr_2O_4 of quasisystem of $\text{FeO}-\text{FeCr}_2\text{O}_4$ | | | | Crystallization region for FeCr_2O_4 of quasisystem of $\text{Cr}_2\text{O}_3-\text{FeCr}_2\text{O}_4$ | | | |
|---|---|--|---|--|---|--|---|
| T/K | $a_{\text{FeCr}_2\text{O}_4}^L / a_{\text{FeCr}_2\text{O}_4}^S$ | $\Phi_{\text{FeCr}_2\text{O}_4}^r$, calc. | $X_{\text{FeCr}_2\text{O}_4}^L$, calc. | T/K | $a_{\text{FeCr}_2\text{O}_4}^L / a_{\text{FeCr}_2\text{O}_4}^S$ | $\Phi_{\text{FeCr}_2\text{O}_4}^r$, calc. | $X_{\text{FeCr}_2\text{O}_4}^L$, 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 monovariant phase equilibrium lines based on Bjerrum-Guggenheim concept was 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 coefficient of 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 calculation for 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.

Acknowledgements

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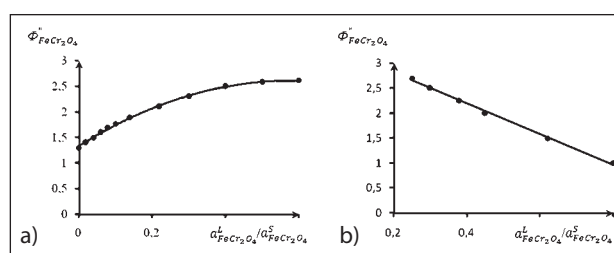


Figure 3 The dependence diagrams of an osmotic coefficient of Bjerrum-Guggenheim a) - $\text{FeCr}_2\text{O}_4-\text{Cr}_2\text{O}_3$ system, b) - $\text{FeO}-\text{FeCr}_2\text{O}_4$ system

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