Thermodynamic Calculations of Phase Equilibria in the Fe–Cr–S System

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Phase equilibria in the Fe–Cr–S system were analyzed on the basis of the thermodynamic evaluation of the Fe–FeS, Fe–Cr, Cr–CrS and Fe–FeS–CrS–Cr systems. The Gibbs energy of individual phase was approximated by the two sub-lattice model for describing the thermodynamic properties. Most of the experimental information was well described by the present set of thermodynamic parameters. In particular, the calculated liquidus surface in the Fe-rich portion and the solubilities of S in the fcc and the bcc phases were shown to be in excellent agreement with experimental results. Discrepancies observed in some experimental phase diagrams were explained on the basis of the calculated results.

KEY WORDS: chromium sulfide; iron sulfide; thermodynamic properties; CALPHAD; phase diagram.

1. Introduction

Knowledge of phase diagrams and the thermodynamic properties of the iron–oxide and the iron–sulfide systems are essential for understanding the formation mechanism of non-metallic inclusions during the steelmaking process and the mechanism of sulfidation and oxidation. It has also become increasingly obvious that inclusions can be utilized effectively for the control of ferrite microstructure in steel by controlling their composition, morphology and distribution.¹⁾ Hence, the need for prediction of quantitative multi-component phase diagrams that can provide the basic information required for exercising such a control on the non-metallic inclusions. In a previous publication,²⁾ the above authors had thermodynamically assessed the phase equilibria in the Fe–FeS–MnS–Mn system and had shown that there was satisfactory agreement between the calculation and the experimentally observed information. The temperatures of the stable eutectic and the metastable monotectic reactions in the Fe–MnS pseudo-binary system could be calculated, and the difference between the eutectic point and monotectic point was shown to be only 3°C. The changes in the morphology of MnS inclusions in steel were explained on the basis of these calculation results^{3–5)} and similar discussions were extended to other sulfides and metallic systems.^{6–8)}

Another inclusion that has the same importance as MnS is the CrS inclusion, which is one of the popular non-metallic inclusions in stainless steel. This sulfide inclusion modifies the corrosion resistance of free-cutting stainless steel⁹⁾ and also has significant effects on the morphology of MnS

in stainless steel.⁸⁾ The Fe–Cr–S ternary system is one of the basic constituent systems of relevance to stainless steel and the first attempt at examination of the phase diagrams in this system was done by Vogel and Reinbach.¹⁰⁾ Subsequently, some research investigations have been conducted in this system mainly to determine the phase equilibria between the solid solution and the sulfides in the Fe–Cr rich portion.

The aim of the present investigation was to assess thermodynamically the phase equilibria in the Fe–Cr–S system using available experimental information and arrive at thermodynamic parameters to facilitate the calculation of the phase equilibria between the solution phases and the sulfide inclusions over the temperature range 800°C to 2 000°C.

2. Descriptions of Gibbs Energy Models

2.1. Liquid Phase

The Gibbs energy of the liquid phase is described using the two-sublattice model proposed by Hillert and Stafansson¹¹⁾ for dealing with the reciprocal Fe–FeS–MnS–Mn part of the system. For the Fe–Cr–S system two sublattices in the liquid phase are assumed, one containing iron and chromium and the other sulfur and vacancies. Such a division is conventionally represented as (Fe, Cr)(S, Va). The Gibbs energy expression for the liquid phase is given for one mole of Fe and Cr atoms as

$$G^{\text{liq}} = y_{\text{Fe}} y_{\text{Va}} {}^{\circ}G_{\text{Fe}}^{\text{liq}} + y_{\text{Fe}} y_{\text{S}} {}^{\circ}G_{\text{FeS}}^{\text{liq}} + y_{\text{Cr}} y_{\text{Va}} {}^{\circ}G_{\text{Cr}}^{\text{liq}} + y_{\text{Cr}} y_{\text{S}} {}^{\circ}G_{\text{CrS}}^{\text{liq}} + RT(y_{\text{Fe}} \ln y_{\text{Fe}} + y_{\text{Cr}} \ln y_{\text{Cr}} + y_{\text{S}} \ln y_{\text{S}} + y_{\text{Va}} \ln y_{\text{Va}}) + {}^{\text{E}}G^{\text{liq}} \dots (1)$$

where the excess Gibbs energy, $^E G^{\text{liq}}$, describing the deviation from the ideal behavior of solution, is expressed as

$$^E G^{\text{liq}} = y_{\text{Fe}} y_{\text{Cr}} y_{\text{Va}} L_{\text{Cr, Fe: Va}}^{\text{liq}} + y_{\text{Fe}} y_{\text{Cr}} y_{\text{S}} L_{\text{Cr, Fe: S}}^{\text{liq}} + y_{\text{Fe}} y_{\text{S}} y_{\text{Va}} L_{\text{Fe: S, Va}}^{\text{liq}} + y_{\text{Cr}} y_{\text{S}} y_{\text{Va}} L_{\text{Cr: S, Va}}^{\text{liq}} \quad \dots\dots\dots (2)$$

In Eqs. (1) and (2), $^{\circ} G_{\text{Fe}}^{\text{liq}}$ and $^{\circ} G_{\text{Cr}}^{\text{liq}}$ are the Gibbs energies of pure liquid Fe and Cr, $^{\circ} G_{\text{FeS}}^{\text{liq}}$ and $^{\circ} G_{\text{CrS}}^{\text{liq}}$ are the Gibbs energies of pure liquid FeS and pure CrS, y_{Fe} and y_{Cr} are the site fractions of Fe and Cr atoms occupying the substitutional sublattice, and y_{S} and y_{Va} are the site fractions of S atom and vacancies occupying the interstitial sublattice. They are related to the ordinary atom fractions x_i as $y_{\text{Fe}} = x_{\text{Fe}}/(1-x_{\text{S}})$, $y_{\text{Cr}} = x_{\text{Cr}}/(1-x_{\text{S}})$ and $y_{\text{S}} = x_{\text{S}}/(1-x_{\text{S}})$. The L parameters of Eq. (2) are the interaction energies between different atoms. Their concentration dependence is expressed as follows,

$$\begin{aligned} L_{\text{Cr, Fe: Va}}^{\text{liq}} &= {}^0 L_{\text{Cr, Fe: Va}}^{\text{liq}} + (y_{\text{Cr}} - y_{\text{Fe}}) {}^1 L_{\text{Cr, Fe: Va}}^{\text{liq}} \\ L_{\text{Cr, Fe: S}}^{\text{liq}} &= {}^0 L_{\text{Cr, Fe: S}}^{\text{liq}} + (y_{\text{Cr}} - y_{\text{Fe}}) {}^1 L_{\text{Cr, Fe: S}}^{\text{liq}} \quad \dots\dots\dots (3) \\ L_{\text{Fe: S, Va}}^{\text{liq}} &= {}^0 L_{\text{Fe: S, Va}}^{\text{liq}} + (y_{\text{S}} - y_{\text{Va}}) {}^1 L_{\text{Fe: S, Va}}^{\text{liq}} \\ L_{\text{Cr: S, Va}}^{\text{liq}} &= {}^0 L_{\text{Cr: S, Va}}^{\text{liq}} + (y_{\text{S}} - y_{\text{Va}}) {}^1 L_{\text{Cr: S, Va}}^{\text{liq}} \end{aligned}$$

This model is identical to the ionic two-sublattice model¹²⁾ using the formulation $(\text{Fe}_{+2}, \text{Cr}_{+2})_p(\text{S}_{-2}, \text{Va})_q$, where $p=q=2$. The ionic two-sublattice model can be extended to S contents higher than $x_{\text{S}}=0.5$ and to metals whose valence is other than +2.

2.2. Solid Solution Phases

Hillert and Staffansson¹¹⁾ applied the classical substitutional regular-solution model for bcc and fcc solid solution phases in Fe–Mn–S system. Ohtani *et al.*¹³⁾ applied the two sublattice model for these phases in the Fe–S binary system and obtained better agreement with experimental data. In view of this, the bcc and fcc solid solution phases in the present study are described using the two-sublattice model assuming one sublattice to be occupied by Fe and Cr, and the other sublattice by S and Va. The Gibbs energy is expressed by the following equation

$$\begin{aligned} G^{\phi} &= y_{\text{Fe}} y_{\text{Va}} {}^{\circ} G_{\text{Fe}}^{\phi} + y_{\text{Fe}} y_{\text{S}} {}^{\circ} G_{\text{FeS}}^{\phi} + y_{\text{Cr}} y_{\text{Va}} {}^{\circ} G_{\text{Cr}}^{\phi} + y_{\text{Cr}} y_{\text{S}} {}^{\circ} G_{\text{CrS}}^{\phi} \\ &+ RT(a\{y_{\text{Fe}} \ln y_{\text{Fe}} + y_{\text{Cr}} \ln y_{\text{Cr}}\} \\ &+ c\{y_{\text{S}} \ln y_{\text{S}} + y_{\text{Va}} \ln y_{\text{Va}}\}) + {}^E G^{\phi} + {}^{\text{mg}} G^{\phi} \quad \dots\dots\dots (4) \end{aligned}$$

where the excess Gibbs energy term, $^E G^{\phi}$, is the same as in Eq. (2). The number of sites in each sublattice, a and c , are taken as $a=1$, $c=3$ for the bcc phase, and $a=1$, $c=1$ for the fcc phase. The last term, ${}^{\text{mg}} G^{\phi}$, represents the magnetic contribution to the Gibbs energy which is described by the following equation¹⁴⁾:

$${}^{\text{mg}} G^{\phi} = RT \ln(\beta^{\phi} + 1) f(\tau) \quad \dots\dots\dots (5)$$

The function $f(\tau)$ is formulated by the polynomial of the normalized temperature τ , which is defined as $\tau = T/T_{\text{C}}^{\phi}$. T_{C}^{ϕ} is the critical temperature of magnetic ordering and β^{ϕ} is the Bohr magneton number.

Andersson and Sundman¹⁵⁾ used the compound energy model for the sigma phase, σ , in the Fe–Cr system. In the present calculation, the same model is applied for the sigma phase assuming that S has no solubility in the sigma phase.

2.3. Sulfide Phases

The sulfides FeS and CrS are treated as stoichiometric sulfide phases. Since both sulfides are of the same crystal structure (NiAs/B8-type), they are denoted as the P phase and described using the two-sublattice model assuming one sublattice to be occupied by Fe and Cr atoms and the other by the S atoms. The Gibbs energy of the P phase is represented by the following equation, Eq. (6).

$$G^{\text{P}} = {}^{\circ} G_{\text{FeS}}^{\text{P}} y_{\text{Fe}} + {}^{\circ} G_{\text{CrS}}^{\text{P}} y_{\text{Cr}} + RT(y_{\text{Fe}} \ln y_{\text{Fe}} + y_{\text{Cr}} \ln y_{\text{Cr}}) + L_{\text{Cr, Fe: S}}^{\text{P}} y_{\text{Fe}} y_{\text{Cr}} \quad \dots\dots (6)$$

where ${}^{\circ} G_{\text{CrS}}^{\text{P}}$ and ${}^{\circ} G_{\text{FeS}}^{\text{P}}$ represent the Gibbs energies of pure FeS and CrS. $L_{\text{Fe, Cr: S}}^{\text{P}}$ is the interaction energy between the Fe and Cr atoms in the sulfide phase. y_{Fe} and y_{Cr} are the atom fractions of Fe and Cr in the metallic sublattice and are related to the ordinary atom fractions as $y_{\text{Fe}} = x_{\text{Fe}}/(x_{\text{Fe}} + x_{\text{Cr}})$ and $y_{\text{Cr}} = x_{\text{Cr}}/(x_{\text{Fe}} + x_{\text{Cr}})$.

3. Evaluation of Thermodynamic Parameters

3.1. Fe–FeS System

In the first instance, Hillert and Staffansson, applied the simple two-sublattice model to the liquid phase of the Fe–FeS system.¹⁶⁾ Later, Ohtani and Nishizawa applied the modified two-sublattice model not only to the liquid phase, but also to the fcc and bcc phases.¹³⁾ Guillermet *et al.* presented an improved version of the two-sublattice model, which could be applied to the entire range of the liquid phase in the Fe–S system.¹⁷⁾ Dinsdale applied a special ionic two-sublattice model, proposed originally by Hillert, to the liquid phase of the Cu–Fe–Ni–S system.¹⁸⁾ Recently, the present authors' group adopted the simple two-sublattice model for describing the liquid, bcc and fcc phases of the Fe–FeS–MnS–Mn system and calculated not only the thermodynamic properties of the liquid, but also the phase equilibrium on the Fe–Mn-rich side.²⁾ The thermodynamic parameters obtained for the Fe–FeS binary system in the above study, as listed in **Table 1**, are used in the present assessment.

3.2. Cr–CrS System

The experimental phase diagram of the Cr–CrS system is shown in **Fig. 1** which is based on the results of thermal analysis and microstructure observation by Vogel and Reinbach.¹⁰⁾ The liquidus line of Cr metal is very steep and a monotectic reaction between Cr metal and liquid at 1550°C and a eutectic reaction between Cr metal and CrS at 1350°C are reported. The melting point of CrS is estimated as 1565°C.

The standard Gibbs energy of formation of CrS at various temperatures reported by some researchers are shown in **Fig. 2**.^{19–23)} The formation energy results of Hager and Elliott,¹⁹⁾ Rau,²¹⁾ and Ramanarayanan and Worrell²³⁾ are in good agreement with one another even though the experimental methods adopted were different. Fujisawa *et al.*²⁴⁾ calculated the formation energy of CrS from the solubility of S in stainless steel and their result is also in good agreement with the results of Hager and Elliott. The formation energy of CrS *i.e.* ${}^{\circ} G_{\text{CrS}}^{\text{P}} - {}^{\circ} G_{\text{Cr}}^{\text{bcc}} - \frac{1}{2} {}^{\circ} G_{\text{S}_2}^{\text{gas}}$ evaluated from these results is shown in Table 1.

Griffing and Healy²⁵⁾ determined the activity coefficient

Table 1. Thermodynamic parameters for the Fe–FeS–CrS–Cr system.

Parameter value (J/mol)	Reference
Liquid phase with formulation (Fe,Cr)(S,Va)	
$^{\circ}G_{\text{Fe}}^{\text{liq}} - ^{\circ}G_{\text{Fe}}^{\text{bcc}} = +12040.17 - 6.55843T - 3.6751551 \cdot 10^{-21}T^7$ (298.14 < T < 1811.00)	(33)
$+14544.751 - 8.01055T - 2.2960305 \cdot 10^{-21}T^9$ (1811.00 < T < 6000.00)	
$^{\circ}G_{\text{Cr}}^{\text{liq}} - ^{\circ}G_{\text{Cr}}^{\text{bcc}} = +24339.955 - 11.420225T + 2.37615 \cdot 10^{-21}T^7$ (298.14 < T < 2180.00)	(33)
$+18409.36 - 8.563683T + 2.88526 \cdot 10^{-21}T^9$ (2180.00 < T < 6000.00)	
$^{\circ}G_{\text{FeS}}^{\text{liq}} - ^{\circ}G_{\text{Fe}}^{\text{liq}} - \frac{1}{2}^{\circ}G_{\text{S}_2}^{\text{gas}} = -148800 + 50.8T$	(2)
$^{\circ}G_{\text{CrS}}^{\text{liq}} - ^{\circ}G_{\text{Cr}}^{\text{liq}} - \frac{1}{2}^{\circ}G_{\text{S}_2}^{\text{gas}} = -165994 + 36.57T$	Present work
$^0L_{\text{Cr,Fe,Va}}^{\text{liq}} = -17737 + 7.996546T$	(15)
$^1L_{\text{Cr,Fe,Va}}^{\text{liq}} = -1331$	(15)
$^0L_{\text{FeS,Va}}^{\text{liq}} = +43950 - 17.95T$	(2)
$^1L_{\text{FeS,Va}}^{\text{liq}} = +15850 - 17.95T$	(2)
$^0L_{\text{CrS,Va}}^{\text{liq}} = +119000 - 57.92T$	Present work
$^1L_{\text{CrS,Va}}^{\text{liq}} = +26466 - 31.71T$	Present work
$^0L_{\text{Cr,FeS}}^{\text{liq}} = 0$	Present work
$^0L_{\text{Cr,FeS,Va}}^{\text{liq}} = -9582$	Present work
fcc phase with formulation (Fe,Cr)(S,Va)	
$^{\circ}G_{\text{Fe}}^{\text{fcc}} - ^{\circ}G_{\text{Fe}}^{\text{bcc}} = -1462.4 + 8.282T - 1.15T \ln T + 6.4 \cdot 10^{-4}T^2$ (298.14 < T < 1811.00)	(33)
$-1713.815 + 0.94001T + 0.4925095 \cdot 10^{-31}T^9$ (1811.00 < T < 6000.00)	
$^{\circ}G_{\text{Cr}}^{\text{fcc}} - ^{\circ}G_{\text{Cr}}^{\text{bcc}} = +7284 + 0.163T$	(33)
$^{\circ}G_{\text{FeS}}^{\text{fcc}} - ^{\circ}G_{\text{Fe}}^{\text{fcc}} - \frac{1}{2}^{\circ}G_{\text{S}_2}^{\text{gas}} = -47500 + 42T$	(2)
$^{\circ}G_{\text{CrS}}^{\text{fcc}} - ^{\circ}G_{\text{Cr}}^{\text{fcc}} - \frac{1}{2}^{\circ}G_{\text{S}_2}^{\text{gas}} = +58647 - 19.89T$	Present work
$T_{\text{C}}^{\text{fcc}} = -201x_{\text{Fe}} - 1109x_{\text{Cr}}$	(33)
$\beta^{\text{fcc}} = -2.1x_{\text{Fe}} - 2.46x_{\text{Cr}}$	(33)
$^0L_{\text{Cr,Fe,Va}}^{\text{fcc}} = +10833 - 7.477T$	(15)
$^1L_{\text{Cr,Fe,Va}}^{\text{fcc}} = +1410$	(15)
$^0L_{\text{Cr,FeS}}^{\text{fcc}} = -98000$	Present work
bcc phase with formulation (Fe,Cr)(S,Va) ₃	
$^{\circ}G_{\text{FeS}}^{\text{bcc}} - ^{\circ}G_{\text{Fe}}^{\text{bcc}} - \frac{3}{2}^{\circ}G_{\text{S}_2}^{\text{gas}} = -168600 + 145.5T$	(2)
$^{\circ}G_{\text{CrS}}^{\text{bcc}} - ^{\circ}G_{\text{Cr}}^{\text{bcc}} - \frac{3}{2}^{\circ}G_{\text{S}_2}^{\text{gas}} = +175941 - 59.67T$	Present work
$T_{\text{C}}^{\text{bcc}} = 1043x_{\text{Fe}} + \{1650 + 550(x_{\text{Cr}} - x_{\text{Fe}})\}x_{\text{Fe}}x_{\text{Cr}} - 311.5x_{\text{Cr}}$	(33)
$\beta^{\text{bcc}} = 2.22x_{\text{Fe}} - 0.85x_{\text{Fe}}x_{\text{Cr}} - 0.01x_{\text{Cr}}$	(33)
$^0L_{\text{Cr,Fe,Va}}^{\text{bcc}} = +20500 - 9.68T$	(15)
$^0L_{\text{Cr,FeS}}^{\text{bcc}} = -241060$	Present work
P phase with formulation (Fe,Cr)S	
$^{\circ}G_{\text{FeS}}^{\text{P}} - ^{\circ}G_{\text{Fe}}^{\text{fcc}} - \frac{1}{2}^{\circ}G_{\text{S}_2}^{\text{gas}} = -174730 + 225T - 22T \ln T + 0.004T^2$	(2)
$^{\circ}G_{\text{CrS}}^{\text{P}} - ^{\circ}G_{\text{Cr}}^{\text{bcc}} - \frac{1}{2}^{\circ}G_{\text{S}_2}^{\text{gas}} = -202312 + 56.012T$	Present work
$^0L_{\text{Cr,FeS}}^{\text{P}} = 0$	Present work
Sigma phase with formulation Fe ₈ Cr ₄ (Fe,Cr) ₁₈	
$^{\circ}G_{\text{FeCrCr}}^{\text{Sigma}} - 22^{\circ}G_{\text{Cr}}^{\text{bcc}} - 8^{\circ}G_{\text{Fe}}^{\text{fcc}} = 92300 - 95.96T$	(15)
$^{\circ}G_{\text{FeCrFe}}^{\text{Sigma}} - 4G_{\text{Cr}}^{\text{bcc}} - 8^{\circ}G_{\text{Fe}}^{\text{fcc}} - 18^{\circ}G_{\text{Fe}}^{\text{bcc}} = 117300 - 95.96T$	(15)

Fig. 1. Experimental Cr–CrS phase diagram.¹⁰⁾ **Fig. 2.** Gibbs energy of formation of CrS.

of sulfur in the Fe–Cr–S melts. They also investigated the two-liquid separation region in the Cr–S binary system, and estimated the monotectic reaction temperature to be higher than 1760°C. This estimated monotectic temperature is quite different from the monotectic temperature determined by Vogel and Reinbach.¹⁰⁾ Taylor and Dinsdale encountered a similar problem in examining similar results reported by the same authors for the Cr–O system.²⁶⁾ The results of Vogel and Reinbach are thought to be unreliable as far as the monotectic temperatures are concerned. Vogel and Reinbach also estimated the melting point of CrS as 1565°C by extrapolation of the slope of liquidus line from Cr–CrS binary system to CrS.¹⁰⁾ However, Vogel estimated the melting point of CrS as 1600°C from the liquidus line of FeS–CrS system.²⁷⁾ In the present work, the melting point of CrS was reevaluated as 1595°C by extrapolation of the liquidus lines of their data. The thermodynamic parameters for the liquid phase were evaluated from the eutectic point, liquidus near eutectic point and melting point of CrS while that of the bcc phase was evaluated from the data on solubility limit of sulfur in the bcc phase.²⁸⁾

In addition, the thermodynamic parameters for the metastable fcc phase were assumed to be the same as that for the bcc phase. All the thermodynamic parameters utilized in the calculations are listed in Table 1. The calculated Cr–CrS binary phase diagrams are shown in Fig. 3 with the

Fig. 3. Calculated phase diagrams of (a) the Cr-CrS system and of (b) the Cr-rich end of the Cr-CrS system.

Fig. 4. Comparison of the calculated and the experimental FeS-CrS pseudo-binary phase diagrams.

experimental data superimposed on the diagram. The eutectic point and liquidus of CrS are well reproduced. However, the calculated monotectic temperature is higher than 1800°C, which differs by more than 200°C from that of Vogel's result. Further investigations are needed in this system.

3.3. Fe-Cr System

The thermodynamic assessment of the Fe-Cr system was carried out by Andersson and Sundman¹⁵⁾ who used the subregular solution model for describing the Gibbs energy of the liquid, fcc and bcc phases and the compound energy model for describing the sigma phase. Since the calculated diagram using their parameters is in good agreement with the experimentally determined diagram, the same parameters have been adopted in the present work.

3.4. FeS-CrS Pseudo-binary System

According to the early work of Vogel,²⁷⁾ the FeS-CrS pseudo-binary system is completely miscible in both the solid and liquid states which suggests that the interaction parameters, $L_{Cr,Fe:S}^P$ and $L_{Cr,Fe:S}^{Liq}$ would be close to zero. Although El Goresy and Kullerud²⁹⁾ reported that a Cr_2FeS_4 spinel phase is formed at temperatures lower than 700°C and a two-phase separation of NiAs-type of FeS and CrS phase occurs at 700°C, there is no other reliable thermodynamic data for assessment. For this reason the phase equilibria

at temperatures lower than 700°C was not considered in this work. The calculated FeS-CrS pseudo-binary system above 700°C is shown in Fig. 4. The calculated result is in good agreement with the experimental data.

3.5. Fe-FeS-CrS-Cr System

Even though, the thermodynamic parameters evaluated in the previous sub-systems could be deemed as sufficient for the description of phase equilibria in the whole of the Fe-FeS-CrS-Cr system, it was thought that use could be made of further information such as the Wagner's interaction parameter, ϵ_S^{Cr} in obtaining a better description of the interaction parameters. ϵ_S^{Cr} is a measure of the effect of small additions of Cr on the activity of S in the homogeneous solution phase ϕ . In the present model, ϵ_S^{Cr} at very low alloy contents can be related to the interaction parameters through the following expression

$$RT\epsilon_S^{Cr} = \left({}^\circ G_{MnS}^\phi - {}^\circ G_{Mn}^\phi - \frac{1}{2} {}^\circ G_{S_2}^{gas} \right) - \left({}^\circ G_{FeS}^\phi - {}^\circ G_{Fe}^\phi - \frac{1}{2} {}^\circ G_{S_2}^{gas} \right) + ({}^0L_{Mn:S,Va}^\phi - {}^1L_{Mn:S,Va}^\phi) - ({}^0L_{Fe:S,Va}^\phi - {}^1L_{Fe:S,Va}^\phi) + \frac{1}{c} ({}^0L_{Cr,Fe:S}^\phi - {}^0L_{Cr,Fe:Va}^\phi - {}^1L_{Cr,Fe:Va}^\phi) \quad \text{.....(7)}$$

Fujiwara *et al.*²⁴⁾ studied the sulfur activity in the fcc and the bcc phases of Fe-Cr alloys at 1300°C. They obtained the value of $\epsilon_S^{Cr} = -1.81$ and $\epsilon_S^{Cr} = -6.61$ for bcc and fcc phases, respectively. Using this information, the interaction parameters of $L_{Cr,Fe:S}^\phi$ were estimated by the present authors as listed in Table 1. The value of ϵ_S^{Cr} in the liquid phase has been reported as -4.3 ³⁰⁾ at 1650°C, -4.05 ²⁵⁾ at 1600°C and -2.28 ³¹⁾ at 1550°C. Dondelinger *et al.*³²⁾ also obtained the value of $\epsilon_S^{Cr} = -20083.44/T + 8.528$ at 1525–1755°C in excellent agreement with that of Ban-ya and Chipman.³¹⁾ Since the thermodynamic parameter, ${}^0L_{Cr,Fe:S}^{liq}$, in the liquid phase was already taken as zero, the another liquid parameter, $L_{Cr,Fe:S,Va}^{liq}$, in Eq. (7) was evaluated from the result of Ban-ya and Chipman³¹⁾ as shown in Table 1.

The set of parameters of the Fe-FeS-CrS-Cr system assessed in the present study is summarized in Table 1. The lattice stability of pure elements corresponds to the data from SGTE (Scientific Group Thermodata Europe).³³⁾ The

Fig. 5. Calculated isothermal section diagrams of the Fe-FeS-CrS-Cr system at (a) 1600°C, (b) 1500°C, (c) 1370°C, (d) 1300°C, (e) 1090°C and (f) 950°C.

phase diagram calculation has been conducted by using Thermo-Calc.³⁴⁾

4. Calculated Results and Discussion

4.1. Liq.+fcc, Liq.+bcc, P+fcc and P+bcc Phase Equilibria

Various isothermal section diagrams in the temperature range from 1600°C down to 950°C are presented in Fig. 5. Figs. 5(c), 5(d) and 5(e) are compared with the experimental tie lines of Dahl and Van Vlack³⁵⁾ and Kaneko *et al.*³⁶⁾ The calculated slope of the tie lines agrees with the experimental results. As shown in Fig. 5(e), the slope of the (P+fcc) equilibrium tie lines in the low Cr region is parallel to the Fe-FeS direction. As the Cr content increases, Cr atoms distribute into the P phase rather than into the fcc phase,

and tie lines become parallel to the Fe-CrS diagonal when Cr content is <10 mass% in fcc phase. Furthermore, the Cr content in the P phase is almost identical to the pure CrS when Cr > 10 mass% in bcc phase. The slope of tie lines in the (P+bcc), (Liq.+fcc) and (Liq.+bcc) fields has the same tendency as that in the (P+fcc) equilibrium. Tie lines in the two-liquid separation field also have the same tendency. Figure 6 shows the distribution of Cr between the fcc or bcc and liquid or P phases compared with the experimental results by Fujisawa *et al.* at 1300°C.²⁴⁾ The calculated result is in good agreement with the experimental results. The distribution of Cr in the liquid and the P phase equilibrated with the fcc or the bcc phase increases markedly with increasing Cr below $y_{Cr}^{fcc}=0.1$, while it becomes asymptotic towards $y_{Cr}^P=1$.

Vogel and Reinbach¹⁰⁾ conducted thermal analyses and

optical microscopic observations of many samples and estimated a set of vertical section phase diagrams in the Fe–Cr–S system. **Figures 7 and 8** show a comparison between Vogel's phase diagrams and the calculated vertical section diagrams together with the corresponding thermal analysis data at $S=19.5$ mass% and $Fe:Cr=4:1$, respectively. It is interesting to note that the calculated phase boundaries agree with the thermal analysis data points, al-

Fig. 6. Comparison of the calculated line and the experimental points on partition behavior of Cr between the fcc or the bcc and the liquid or the P phases.

though the configuration of the phase fields is quite different from that of Vogel's phase diagrams. For example, in Vogel's phase diagrams as shown in Fig. 7(a) the (fcc+P) two-phase region is narrow and exists at $Cr < 5$ mass% and the (bcc+P) two-phase region is rather wide and extends to $Cr > 30$ mass%. The calculated (fcc+P) two-phase region, on the other hand, is rather wide and exists at temperatures higher than 900°C while the calculated (bcc+P) two-phase region exists only at temperatures lower than 900°C as shown in Fig. 7(b). Vogel and Reinbach did not indicate the presence of the (fcc+ L_2) and (fcc+P) two-phase regions in the high S portion of the Fe–20Cr–(Cr, Fe)S diagram as shown in Fig. 8(a). The presence of a (fcc+P) two-phase region, however, has been confirmed by Dahl and Van Vlack³⁵⁾ and Fujisawa *et al.*²⁴⁾ as shown in Fig. 5. Since the slope of tie lines in the (fcc+P) equilibrium field changes from 90° to 45° on increasing Cr content in the fcc phase, the (fcc+P) two-phase region should be expected to widen with increasing S content in the vertical section diagram. A comparison of Fig. 7(a) with Fig. 8(a) exposes discrepancies in Vogel's phase diagrams. For example, there is a (bcc+ L_2 +P) three phases region at 1200°C and 19.5 mass% S in Fig. 8(a) whereas there is (bcc+P) two-phase region at the corresponding condition in Fig. 7(a). These observations point out that there exist some contradictions in the early experimental data by Vogel and Reinbach and the present calculations are more reliable than their predictions of vertical section diagrams in this system.

Fig. 7. Vertical section diagrams for the Fe–FeS–CrS–Cr system at 19.5 mass% S, (a) experimental¹⁰⁾ and (b) calculated.

Fig. 8. Vertical section diagrams for the Fe–FeS–CrS–Cr system at $Fe:Cr=4:1$, (a) experimental¹⁰⁾ and (b) calculated.

Fig. 9. Comparison of calculated and experimental solubilities of S in the bcc and the fcc phases at various temperatures.

Fig. 10. Calculated solubility of S in the bcc and fcc phases equilibrated with the liquid or the P phase at various S contents.

4.2. Solubility of S in fcc and bcc

There have been some investigations on the solubility of S in the fcc and bcc phases at equilibrium with the P phase.^{24,28,37} These results are compared with the calculated results in Fig. 9. The solubility data (from Refs. 24), 28) and 37)) were not used directly in evaluating the thermodynamic parameters in this assessment. The good agreement between the above experimental data and the calculated results shows that the parameters used in the calculation are valid for further predictions where results do not exist. The solubility of S in the fcc phase is smaller than that in the bcc phase. Figure 10 summarizes the vertical section phase diagrams from 0.001 to 0.1 mass% S and shows the change of the solubility of S in the bcc and the fcc phases in equilibrium with either the P or the L_2 phase. The S solubility limit increases with increasing temperature. For the same S content, the solubility limit is at a higher temperature in the fcc phase than in the bcc phase.

Figure 11 shows the solubility products, $\log[\text{mass}\% \text{Cr}] \cdot [\text{mass}\% \text{S}]$, in the fcc and bcc phase at 1 mass% Cr and 18 mass% Cr compared with that of MnS in Fe–Mn–S ternary system.²⁾ These solubility products, $\log[\text{mass}\% \text{Cr}] \cdot$

Fig. 11. Solubility products for the P phase in the fcc and bcc phases at 1 mass% Cr and 18 mass% Cr.

Fig. 12. Relationship between temperature and Cr content in the P phase equilibrated with the bcc phase at various Cr contents.

$[\text{mass}\% \text{S}]$, are larger than that observed in the case of MnS in the Fe–Mn–S system. The solubility product at 1 mass% Cr is smaller than that at 18 mass% Cr and also the slope of the solubility product with temperature at 1 mass% Cr is slightly smaller than that at 18 mass% Cr. Assuming that the P phase is in equilibrium with the bcc phase, the relationship between temperature and Cr content in the P phase is calculated at various Cr contents in bcc phase as shown in Fig. 12. Cr and Fe contents in the P phase decrease and increase respectively with decreasing Cr content in bcc phase. Cr content in the P phase increases with decreasing temperature. Such a tendency is very pronounced in the case of 1 mass% Cr bcc phase and tends to become progressively smaller with increasing Cr content. Since the P phase is stabilized by increasing the Fe content in the P phase and that is drastically influenced by temperature at 1 mass% Cr as shown in Fig. 12, the solubility product in 1 mass% Cr becomes smaller than that in the 18 mass% Cr and the temperature dependence of the solubility product in the 1 mass% Cr is smaller than that of 18 mass% Cr.

Fig. 13. Calculated phase boundaries for the (fcc+bcc+P), (fcc+bcc+P+Liq.), and (fcc+bcc+Liq.) equilibria at various S contents.

Fig. 14. Liquidus surfaces in the Fe-FeS-CrS-Cr system.

4.3. fcc+bcc+Liq. and fcc+bcc+P Phase Equilibria

Thin lines in Fig. 13 show the (fcc+bcc+Liq) and the (fcc+bcc+P) three-phase region in the Fe-Cr-S system and the thick lines the (fcc+bcc) two-phase region in the Fe-Cr binary system. Although S is considered to be a bcc stabilizer in steel, the γ -loop shifts to higher Cr contents on increasing the S content in the Fe-Cr-S system. This is because of the fact that the solubility of S is very small and the formation of the P phase is instantaneous. Cr distributes into the P and liquid phases rather than into the bcc and the fcc phases, rendering the three-phase region parallel to the Fe-CrS diagonal as shown in Fig. 5.

4.4. Liq.+P; fcc and Liq.+P+bcc Phase Equilibria

Figure 14 shows the liquidus surface in the Fe-rich portion of the Fe-FeS-CrS-Cr system, together with the corresponding data from Vogel and Reinbach.¹⁰⁾ It should be noted that the calculated monotectic line of (Fe,Cr)-rich liquid, S-rich liquid and bcc phases agree well with the experimental results. The monotectic line does not intersect the eutectic line of the S-rich liquid, P and fcc or the bcc phase. This result agrees with the estimation of Vogel and Reinbach. However, the calculated invariant four phase

Fig. 15. Calculated Fe-Cr pseudo-binary phase diagrams.

equilibrium between S-rich liquid, P, fcc and bcc phases is located at a higher Cr content than that estimated by Vogel and Reinbach. Figure 15 shows the Fe-Cr pseudo-binary calculated phase diagram. If the (Fe,Cr)-rich alloy is cooled from L_1 phase region, the alloy solidifies via the monotectic reaction and sulfide is formed as a liquid.

5. Conclusions

Thermodynamic analysis has been carried out to arrive at parameters that enable the calculation of the phase diagram in the Fe-Cr-S system. The Gibbs energy of each of the phases has been described using the two-sublattice model and the thermodynamic parameters have been evaluated from phase boundary and thermodynamic data.

(1) The calculated phase diagrams show satisfactory agreement with most of the experimental information excepting the ones from the Cr-CrS binary system. In particular, the liquidus surface in Fe-rich portion and the solubility of S in the fcc and bcc phase were well described by the present set of thermodynamic parameters.

(2) The calculated vertical section phase diagrams allow one to rationalise the observed discrepancies found in the previous experimental phase diagrams. In particular, the extension of the fcc/P two-phase region to the high S region can be explained as due to the drastic change in the direction of tie line from the Fe-FeS side to the Fe-CrS diagonal.

(3) The solubility products, [mass% Cr] · [mass% S], in the bcc and fcc phases and their temperature dependence are a function of the Cr content, because the Cr content in the P phase is drastically influenced by temperature and the Cr content in the fcc and bcc phases.

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