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. 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, 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 and similar discussions were extended to other sulfides and metallic systems.

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. 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. 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 2000°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 Stafansson for dealing with the reciprocal Fe–FeS–MnS–Mn part of the system. In a previous publication, 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 and similar discussions were extended to other sulfides and metallic systems.

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 steel and also has significant effects on the morphology of MnS in stainless steel. 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. 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.

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\[ G_{\text{liq}} = y_{\text{Fe}}y_{\text{Va}}G_{\text{Fe}}^\text{liq} + y_{\text{Fe}}y_{\text{S}}G_{\text{FeS}}^\text{liq} + y_{\text{Cr}}y_{\text{Va}}G_{\text{Cr}}^\text{liq} + y_{\text{Cr}}y_{\text{S}}G_{\text{CrS}}^\text{liq} + RT(y_{\text{Fe}}\ln y_{\text{Fe}} + y_{\text{Fe}}\ln y_{\text{S}} + y_{\text{Cr}}\ln y_{\text{Cr}} + y_{\text{S}}\ln y_{\text{S}} + y_{\text{Va}}\ln y_{\text{Va}}) + E_{\text{G}}^\text{liq} \]
where the excess Gibbs energy, \( G^e \), describing the deviation from the ideal behavior of solution, is expressed as

\[
G^e = G^e(\text{Fe}, \text{FeS}, \text{S}) + RT \ln \left( \frac{y_{\text{Fe}} y_{\text{FeS}} y_{\text{S}}}{a_{\text{Fe}} a_{\text{FeS}} a_{\text{S}}} \right) + \Delta G_{\text{f}}
\]

In Eqs. (1) and (2), \( G^\text{FeS} \) and \( G^\text{S} \) are the Gibbs energies of pure liquid Fe and Cr, \( G^\text{FeS} \) and \( G^\text{S} \) are the Gibbs energies of pure liquid FeS and pure CrS, \( y_{\text{Fe}} \) and \( y_{\text{Cr}} \) are the site fractions of Fe and Cr atoms occupying the substitutional sublattice, and \( y_{\text{S}} \) and \( y_{\text{Va}} \) are the site fractions of S atom and vacancies occupying the interstitial sublattice. They are related to the ordinary atom fractions \( x \) as

\[
y_{\text{Fe}} = x_{\text{Fe}}/(1-x_{\text{Cr}}), \quad y_{\text{Cr}} = x_{\text{Cr}}/(1-x_{\text{Fe}}), \quad y_{\text{S}} = x_{\text{S}}/(1-x_{\text{Va}}), \quad y_{\text{Va}} = x_{\text{Va}}/(1-x_{\text{S}}).
\]

The L parameters of Eq. (2) are the interaction energies between different atoms. Their concentration dependence is expressed as follows,

\[
L^\text{Fe-Cr} = \sum L_{\text{Fe-Cr}} = \sum (y_{\text{Fe}} - y_{\text{Cr}}) L^\text{Fe-Cr}_{\text{Fe-Cr}}
\]

This model is identical to the ionic two-sublattice model\(^{12} \) using the formulation (Fe\(^{2} \)-2, Cr\(^{2} \)-2)\((S\(-2 \), Va\(-2 \))\(p \)) 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 Staffansson\(^{11} \) 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

\[
G^s = y_{\text{Fe}} G^s_{\text{Fe}} + y_{\text{Cr}} G^s_{\text{Cr}} + y_{\text{S}} G^s_{\text{S}} + y_{\text{Va}} G^s_{\text{Va}} + RT \ln \left( \frac{y_{\text{Fe}} y_{\text{Cr}} y_{\text{S}} y_{\text{Va}}}{a_{\text{Fe}} a_{\text{Cr}} a_{\text{S}} a_{\text{Va}}} \right) + \Delta G_{\text{f}}
\]

where the excess Gibbs energy term, \( G^e \), 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, \( \Delta G_{\text{f}} \), represents the magnetic contribution to the Gibbs energy which is described by the following equation\(^{14} \):

\[
\Delta G_{\text{f}} = RT \ln (\beta^s + 1) f(\tau)
\]

The function \( f(\tau) \) is formulated by the polynomial of the normalized temperature \( \tau \), which is defined as \( \tau = T/T^c \). \( T^c \) is the critical temperature of magnetic ordering and \( \beta^s \) is the Bohr magneton number.

Anderson and Sundman\(^{15} \) used the compound energy model for the sigma phase, \( \sigma \), 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.

### 3. Evaluation of Thermodynamic Parameters

#### 3.1. Fe–FeS System

In the first instance, Hillert and Staffannsson, 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.\(^{19} \) 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 CrS at 1 550°C and a eutectic reaction between Cr metal and CrS at 1 565°C are reported. The melting point of CrS is estimated as 1 565°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\(^{19} \) and Rau\(^{21} \) and Ramanarayanan and Worrell\(^{23} \) 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. \( G^s_{\text{CrS}} = G^s_{\text{Cr}} - \frac{1}{2} G^s_{\text{S}} \) evaluated from these results is shown in Table 1.

Griffing and Healy\(^{25} \) determined the activity coefficient...
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. Taylor and Dinsdale encountered a similar problem in examining similar results reported by the same authors for the Cr–O system. 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. However, Vogel estimated the melting point of CrS as 1600°C from the liquidus line of FeS–CrS system. 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.

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

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

| Parameter value (J/mol) | Reference |
|-------------------------|-----------|
| $G_{\text{FeS}}^\infty - G_{\text{FeS}}^\infty$ = -12040.17-6.55843T+3.6751551 10^{-2}T² | (33) |
| $G_{\text{Cr}}^\text{bcc} - G_{\text{Cr}}^\text{bcc}$ = 24339.955-11.420225T+2.37615 10^{-2}T² | (33) |
| $G_{\text{Cr}}^\text{bcc} - G_{\text{Cr}}^\text{bcc}$ = 18409.36-8.563683T²+2.88526 10^{-2}T² | (2180.00°C<CrS<6000.00°C) |
| $G_{\text{CrS}}^\infty - G_{\text{CrS}}^\infty$ = -148800+50.8T | (2) |
| $G_{\text{CrS}}^\text{bcc} - G_{\text{CrS}}^\text{bcc}$ = 165994+36.57T | (2) |
| $\Delta_{f}G_{\text{CrS}}^\text{bcc}$ = -17737+7.996546T | (15) |
| $\Delta_{f}G_{\text{CrS}}^\text{bcc}$ = -1331 | (15) |
| $\Delta_{f}G_{\text{CrS}}^\text{bcc}$ = -44350-17.95T | (2) |
| $\Delta_{f}G_{\text{CrS}}^\text{bcc}$ = -15850-17.95T | (2) |
| $\Delta_{f}G_{\text{CrS}}^\text{bcc}$ = +11900-57.92T | Present work |
| $\Delta_{f}G_{\text{CrS}}^\text{bcc}$ = +26466-31.71T | Present work |
| $\Delta_{f}G_{\text{CrS}}^\text{bcc}$ = 0 | Present work |
| $\Delta_{f}G_{\text{CrS}}^\text{bcc}$ = -9582 | Present work |

fcc phase with formulation (Fe,Cr)(S,Va),

| Parameter value (J/mol) | Reference |
|-------------------------|-----------|
| $G_{\text{CrS}}^\infty - G_{\text{CrS}}^\infty$ = 146448+48.287T-1.157lnT+6.4 10^{-2}T² | (298.14°C<CrS<1811.00°C) |
| $G_{\text{CrS}}^\text{bcc} - G_{\text{CrS}}^\text{bcc}$ = 47500+42T | (1811.00°C<CrS<6000.00°C) |
| $G_{\text{CrS}}^\text{bcc} - G_{\text{CrS}}^\text{bcc}$ = +58647-19.89T | (2) |
| $T_s$ = -201x_0-109x_0 | (2) |
| $\beta$ = -2.1x_0-2.46x_0 | (2) |
| $\Delta_{f}G_{\text{CrS}}^\infty$ = +10833-7.477T | (15) |
| $\Delta_{f}G_{\text{CrS}}^\text{bcc}$ = +1410 | (15) |
| $\Delta_{f}G_{\text{CrS}}^\text{bcc}$ = -90900 | (15) |

bcc phase with formulation (Fe,Cr)(S,Va),

| Parameter value (J/mol) | Reference |
|-------------------------|-----------|
| $G_{\text{CrS}}^\infty - G_{\text{CrS}}^\infty$ = -168600+145.5T | (33) |
| $G_{\text{CrS}}^\text{bcc} - G_{\text{CrS}}^\text{bcc}$ = +175941-59.67T | (33) |
| $T_s$ = 1043x_0-16500+550(x_0-0.05)x_0-311.5x_0 | (33) |
| $\beta$ = 2.22x_0-0.85x_0-0.01x_0 | (15) |
| $\Delta_{f}G_{\text{CrS}}^\text{bcc}$ = +20500-9.68T | Present work |
| $\Delta_{f}G_{\text{CrS}}^\text{bcc}$ = -214060 | Present work |

P phase with formulation (Fe,Cr,S)

| Parameter value (J/mol) | Reference |
|-------------------------|-----------|
| $G_{\text{CrS}}^\infty - G_{\text{CrS}}^\infty$ = -174730+225T+22.3lnT+0.004T² | (33) |
| $G_{\text{CrS}}^\text{bcc} - G_{\text{CrS}}^\text{bcc}$ = -202312+56.012²+T | (33) |
| $T_s$ = 0 | (15) |

Sigma phase with formulation Fe₂Cr₂(Fe,Cr)₄₈

| Parameter value (J/mol) | Reference |
|-------------------------|-----------|
| $G_{\text{Sigma}}^\text{bcc}$ = -22G_{\text{CrS}}^\text{bcc}-8G_{\text{CrS}}^\text{bcc}+92300-95.96T | (15) |
| $G_{\text{Sigma}}^\text{bcc}$ = -4G_{\text{CrS}}^\text{bcc}-8G_{\text{CrS}}^\text{bcc}+117300-95.96T | (15) |
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 Sundman 15) 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, \( L_{\text{Cr,Fe:S}}^{P} \) and \( L_{\text{Cr,Fe:S}}^{\text{liq}} \) would be close to zero. Although El Goresy and Kullerud 29) reported that a CrFeS\(_2\) 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, \( \varepsilon_{\text{S,Cr}}^{\text{f}} \) in obtaining a better description of the interaction parameters. \( \varepsilon_{\text{S,Cr}}^{\text{f}} \) is a measure of the effect of small additions of Cr on the activity of S in the homogeneous solution phase \( \phi \). In the present model, \( \varepsilon_{\text{S,Cr}}^{\text{f}} \) at very low alloy contents can be related to the interaction parameters through the following expression

\[
RT \varepsilon_{\text{Cr,Fe:S}}^{\text{f}} = \frac{\varphi \varepsilon_{\text{Fe,S}}^{\text{f}} - \varphi \varepsilon_{\text{Cr,S}}^{\text{f}}}{2} \quad \text{(7)}
\]

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 \( \varepsilon_{\text{S,Cr}}^{\text{f}} = -1.81 \) and \( \varepsilon_{\text{S,Cr}}^{\text{f}} = -6.61 \) for bcc and fcc phases, respectively. Using this information, the interaction parameters of \( L_{\text{Cr,Fe:S}}^{\text{f}} \) were estimated by the present authors as listed in Table 1. The value of \( \varepsilon_{\text{S,Cr}}^{\text{f}} \) 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 \( \varepsilon_{\text{S,Cr}}^{\text{f}} = -20083.44/T + 8.528 \) at 1525–1755°C in excellent agreement with that of Ban-ya and Chipman. 31) Since the thermodynamic parameter, \( \varphi \varepsilon_{\text{Cr,Fe:S}}^{\text{f}} \), in the liquid phase was already taken as zero, the another liquid parameter, \( L_{\text{Cr,Fe:S}}^{\text{liq}} \), in Eq. (7) was evaluated from the result of Ban-ya and Chipmann 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
phase diagram calculation has been conducted by using Thermo-Calc.\textsuperscript{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 Vlack\textsuperscript{35} and Kaneko et al.\textsuperscript{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.\textsuperscript{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 bcc phase increases markedly with increasing Cr below \( y_{\text{Cr}}^{\text{fcc}} = 0.1 \), while it becomes asymptotic towards \( y_{\text{Cr}}^{\text{P}} = 1 \).

Vogel and Reinbach\textsuperscript{10} conducted thermal analyses and

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.
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, although 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 + L2) 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 + L2 + 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.
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.\textsuperscript{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\textsubscript{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[mass% Cr] · [mass% S], in the fcc and bcc phase at 1 mass% Cr and 18 mass% Cr compared with that of MnS in the Fe–Mn–S system.\textsuperscript{21} These solubility products, log[mass% Cr] · [mass% 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.
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. 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 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–CrS pseudo-binary calculated phase diagram. If the (Fe,Cr)-rich alloy is cooled from L₁ 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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