A Thermodynamic Description of the Fe-Cr-Si System with Emphasis on the Equilibria of the Sigma (σ) Phase

*M. Lindholm**
Division of Computational Thermodynamics
Department of Materials Science & Engineering
Royal Institute of Technology
Stockholm, Sweden

The Fe-Cr-Si system has been of interest for a long time because of the beneficial effect of silicon on oxidation resistance, and also because of the problems it causes by enhancing brittle σ-phase. The system has been evaluated using recent data, and the description is satisfactory.

(Submitted 12 August 1996; in revised form 12 June 1997)

1. Introduction

The effect of silicon on the Fe-Cr system has been of interest for a long time (phase diagram of Fe-Cr-Si is shown in Fig. 1) because of the oxidation-resistant silica surface film, but there is a problem associated with the enhancing effect of Si on the amount of the brittle σ phase. If control of the σ-phase is obtained, the beneficial properties of Si can be used to a greater extent. The most recent published computer evaluations are from [80Cha], but a more recent evaluation has been done by [87Rag] followed by his revision with [93Har] in 1993. However, recent data from [95Hay] have revealed that a new thermodynamic description of the system is needed. The aim of this work is to improve the descriptions by using the most recent available data and in addition to optimize the number of parameters as well as the parameter values themselves.

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*Now with Sandvik Coromant AB, 126 80 Stockholm, Sweden.

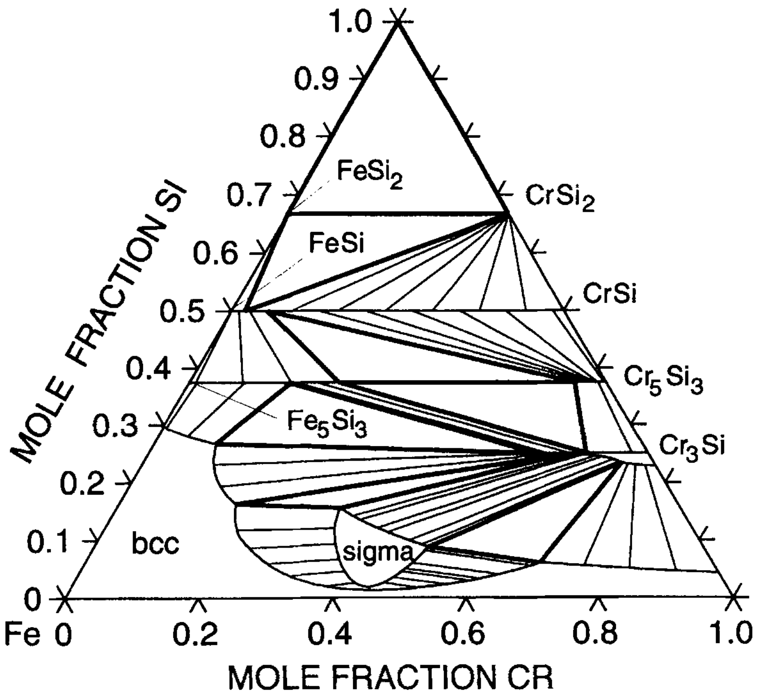

Fig. 1 The calculated phase diagram for the Fe-Cr-Si system at 900 °C.

2. Thermodynamic Modeling

2.1 Method

The model parameters of the thermodynamic description have been fitted to experimental data in the optimization module in Thermo-Calc called Parrot, developed by [84Jan]. The module enables optimization of all kinds of thermodynamic data at the same time by a least squares method. Every single datum is given its own weighted uncertainty, and the difference between the calculated and the experimental value, divided by the uncertainty, produces an error value that the program tries to minimize using the model parameters.

The pure elements are described with a polynomial of the type:

$$G_m^{\mathrm{SER}} = A + BT + CT \ln T + DT^2 + E/T + FT^3 + ...$$

that can be derived from well used C_p descriptions. The abbreviation SER stands for stable element reference (this means the stable state for an element at 298 K and 1 bar). The parameters used for the pure elements are from [91Din] to be compatible with other thermodynamic assessments.

For a substitutional solution phase, ϕ, the following model has been used:

$$G_m^{\phi} = \Sigma\, x_i^0 G_i^{\phi} + RT\, \Sigma x_i \ln x_i + G_m^{E,\phi}$$

where $G_m^{E,\phi}$ is a Redlich-Kister-Muggianu polynomial that can describe regular, subregular, and so forth, parameters and can be extrapolated into multicomponent systems of any order. It is often written:

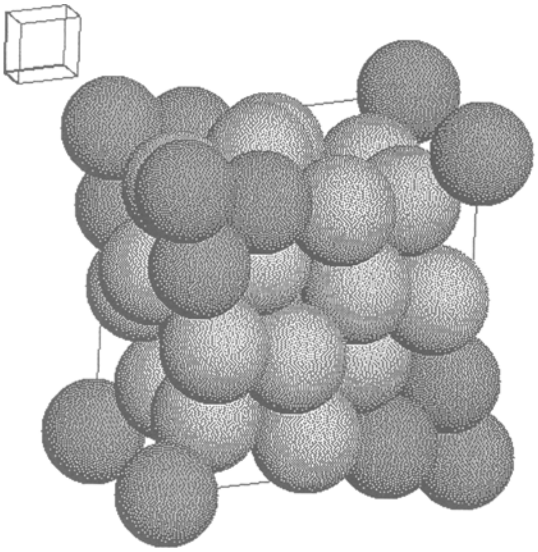

Fig. 2 The σ-phase unit cell with 30 atoms in the Fe-Cr system.

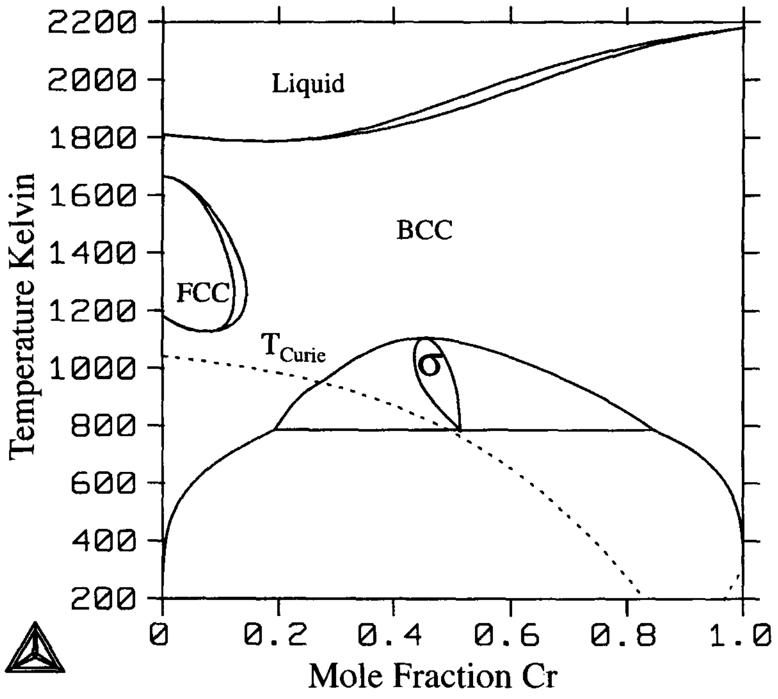

Fig. 3 The calculated Fe-Cr phase diagram.

$$G_m^{E,\Phi} = x_i x_j x_k L_{ijk}^{\Phi} + \Sigma\, x_i x_j\, \Sigma\, (x_i - x_j)^n\, L_{ij}^{n,\Phi}$$

for a ternary system. The latter term stands for the binary parameters, where $L_{ij}^{n,\Phi}$ may depend on temperature and $L_{ij}^{0,\Phi}$ corresponds to the regular solution parameter.

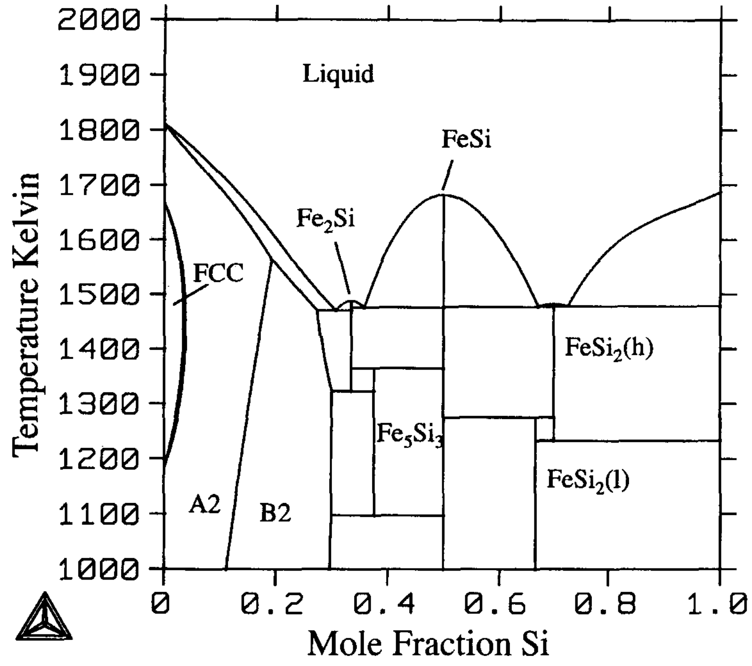

Fig. 4 The calculated Fe-Si phase diagram.

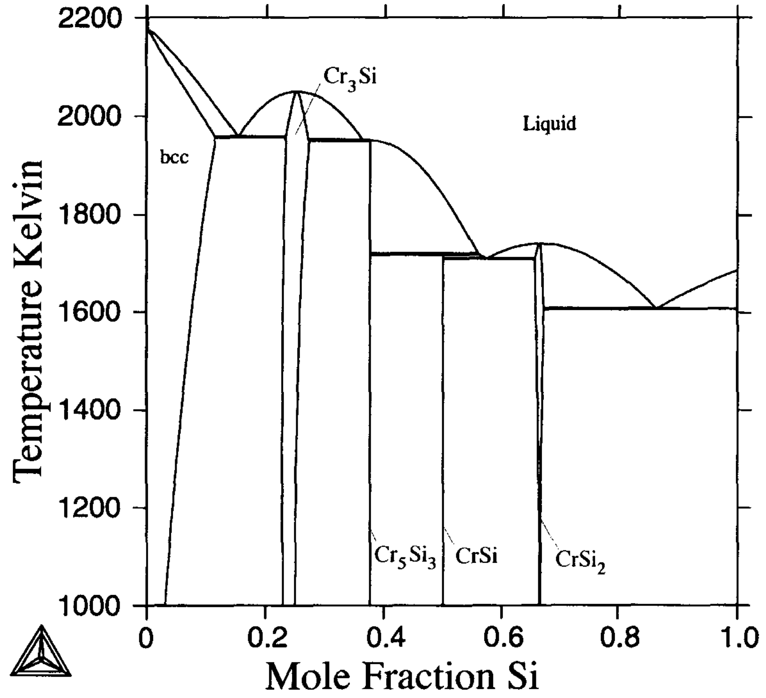

Fig. 5 The calculated Cr-Si phase diagram.

For phases with stoichiometric constraints, the [70Hil] sublattice model later generalized by [81Sun] has been used. The name of this model was later changed to the "compound-energy" model [86And].

For stoichiometric phases with two sublattices the following expression is applied:

$$G_m^\Phi = \Sigma \, \Sigma \, y_i y_j G_{ij}^{0,\Phi} + RT \, \Sigma \, a_s \, \Sigma \, y_i^s \ln y_i^s + G_m^{E,\Phi}$$

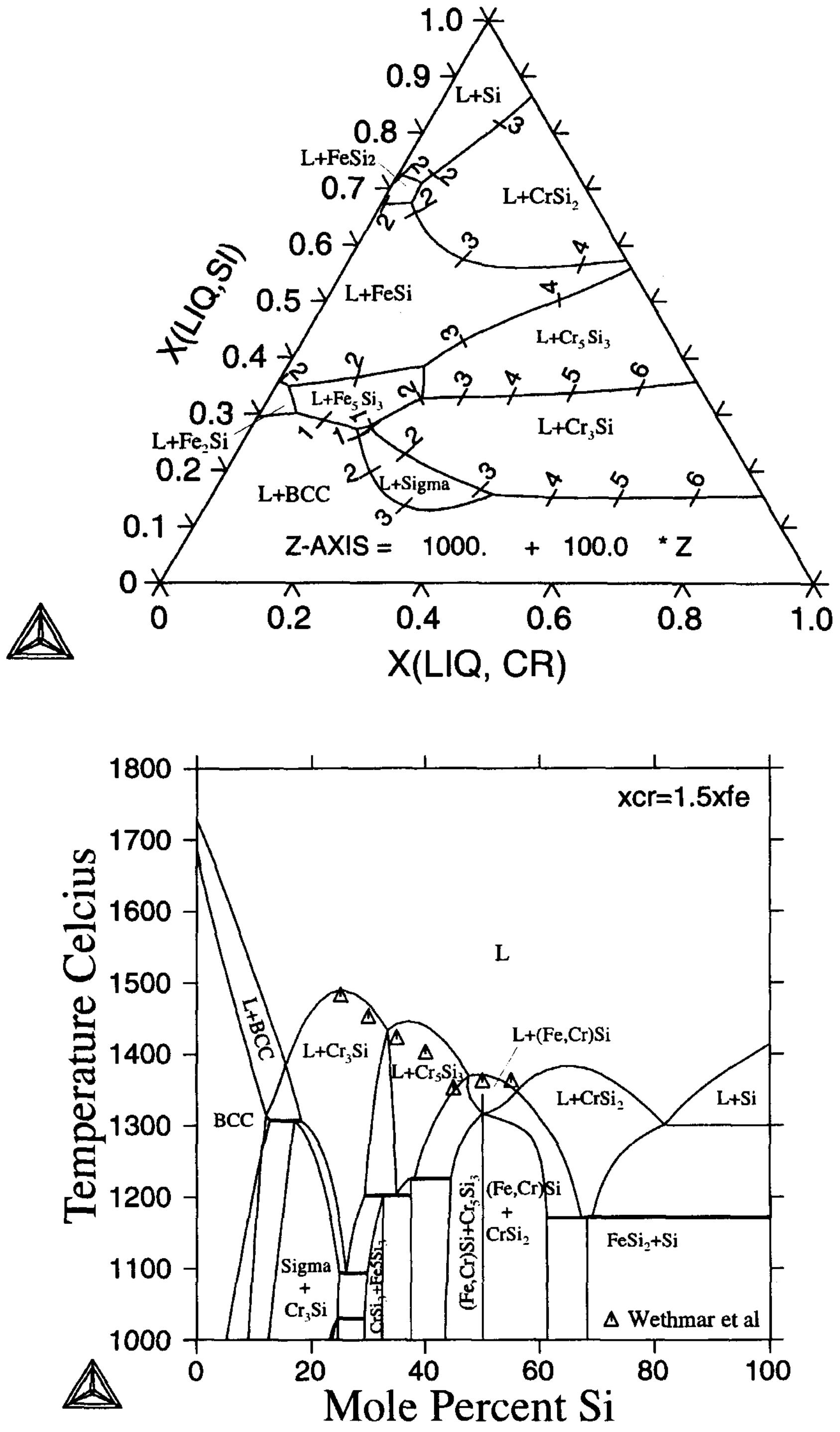

Fig. 6 The upper figure shows the calculated liquidus projection with the temperature in Centigrade on the Z-axis. The lower figure shows a calculated isoplethal phase diagram along the line with 3:2 ratio between mole fraction Fe and Cr.

$G_{ij}^{0,\phi}$ represents the Gibbs energy of formation of a "compound" with element *i* in the first sublattice and *j* in the second. In most cases, this is expressed as the difference between the weighted sum of the pure elements and the phase ϕ as:

$$G_{ij}^{0,\phi} = a_1 G_i^{0,\mathrm{ref}} + a_2 G_j^{0,\mathrm{ref}} + A + BT + CT \ln T$$

This corresponds to a compensation for the difference in enthalpy of formation, entropy, and heat capacity between the compound and the mixture of pure elements.

Furthermore y_i^s is the site fraction of the element *i* on sublattice *s*. The excess term $G_m^{E,\phi}$ can be expressed as:

$$G_m^E = \Sigma\,\Sigma\,\Sigma\, y_i' y_j' y_k'' L_{ij:k} + \Sigma\,\Sigma\,\Sigma\, y_k' y_i'' y_j'' L_{k:ij}$$

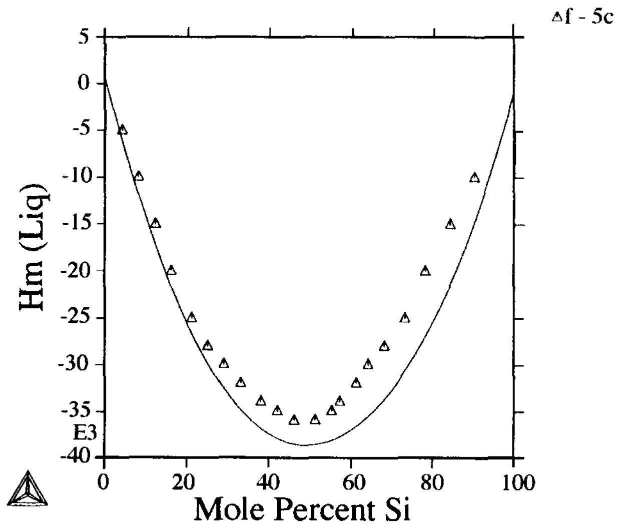

Fig. 7 The enthalpy of mixing for the isopleth $x_{Fe} = 5x_{Cr}$ at 1600 °C [78Pet].

Each interaction parameter, *L*, can be composition dependent with a Redlich-Kister polynomial as for the substitutional solution model.

2.2 The σ-phase: A Short Retrospective

The σ-phase was first characterized by [27Bai] in 1927, and it was briefly described in the 1950s as a "hard, brittle and nonmagnetic phase giving a characteristic x-ray pattern of a 50Cr-50Fe alloy" [51Duw]. After its first characterization this phase was found in a lot of systems (see [66Hal]).

The structure is in most cases referred to with the Pearson symbol *tP*30, which indicates a tetragonal primitive structure containing 30 atoms. The structure has five characteristic sites denoted *M*1 to *M*5. *M*1 contains two atoms, *M*2, *M*3, and *M*4 each contain eight atoms, while *M*5 contains four atoms, where the coordination numbers are 12, 12, 14, 14, and 15 for *M*1 to *M*5, respectively. [51Duw] stated that two conditions have to be fulfilled for the σ-phase to appear:

- The atomic diameter of the elements has to differ by less than 8%.
- One metal has to be bcc, and the other fcc.

These authors only considered binary cases. [76Edm] mention in their review that a larger variation in atomic radius is possible, but already in 1956, [56Kas] suggested that the elements in the σ-phase should be divided into *A* and *B* atoms. The idealized occupancy would then be *B*:*B*:*A* + *B*:*A* + *B*:*A* for a binary alloy. The *A* atoms usually come from groups V and VI (V and Cr) of the Periodic Table, while the *B* atoms preferably come from group VIII (Fe, Co, and Ni). Figure 2 illustrates the σ-phase unit cell with only Fe and Cr present.

3. Modeling of the σ-Phase

3.1 General

Solution phases such as this are preferably modeled using sublattice descriptions. In the early 1980s, [84Pra] used a bond-energy model, whereby each nearest neighbor bond in the structure is assigned a certain independent bond energy and the total energy is summed. Their model was proved unphysical by [86And], because for phases with different coordination

Table 1 Phases Appearing in the Ternary Fe-Cr-Si System

Phase	Composition	Pearson symbol	Strukturbericht diagram	Prototype	Ternary solubility
FeCr (σ)	45-50 wt.% Cr	*tP*30	$D8_b$	CrFe	12 wt.% Si (21 at.%)
Cr_3Si	22-30 wt.% Si	*cP*8	*A*15	Cr_3Si	19 wt.% Fe (16 at.%)
Cr_5Si_3	37.5	*tI*32	$D8_m$	W_5Si_3	6 wt.% Fe (4.5 at.%)
CrSi	50	*cP*8	*B*20	FeSi	Complete
$CrSi_2$	66.5-67.2	*hP*9	*C*40	$CrSi_2$	Negligible
$Fe_3Si(\alpha_1)$	...	*cF*16	$D0_3$	BiF_3	≈18 wt.% Cr (17 at.%)
$Fe_3Si(\alpha_2)$	...	*cP*2	*B*2	CsCl	≈18 wt.% Cr (17 at.%)
$Fe_2Si(\beta)$	33-34.5 wt.% Si	*hP*6	...	...	Negligible
$Fe_5Si_3(\eta)$	37.5	*hP*16	$D8_8$	Mn_5Si_3	27 wt.% Cr (23 at.%)
FeSi	49.5-51	*cP*8	*B*20	FeSi	Complete
$FeSi_2(\xi_l)$	66.7	*oC*48	...	...	Negligible
$FeSi_2(\xi_h)$	69.5-73	*tP*3	...	...	Negligible

numbers, such as the σ-phase, it is dependent on the choice of reference states. [86And] instead introduced the compound-energy model, which is identical with the bond-energy model for phases with equal coordination numbers. When applied to the σ-phase in higher-order systems, one has to consider a reduction from the five sublattices directly related to the crystal structure in order to handle a reasonable number of parameters. The most natural way is to merge them into three different sublattices: exclusively A atoms, mixing of A and B atoms, and exclusively B atoms. That corresponds to 10:16:4 sites per sublattice. This model has been shown to describe most systems well, but not all. That is why $M1$ was considered to have more mixing tendencies in some systems and accordingly the model became 8:18:4. An alternative model to describe the extended composition range in some binary systems, for example Ni-V, is to allow some A elements to dissolve in the sublattice for B atoms. This corresponds to $(A,B)_{10}(A,B)_{16}A_4$ for the σ-phase in such systems.

3.2 Modeling of σ with Si

As mentioned above, the σ-phase appears in many systems. In the Fe-Cr-Si system its stability increases with the Si content and σ becomes an exclusively ternary phase at higher temperatures. However, it is uncertain which sublattice Si prefers. There is no clear evidence with respect to the Fe-Cr-Si system, but in the Ni-Cr-Si system the Si atoms occupy the sites $M3$ and $M4$ according to [62Gla], that is, the mixing sites:

$$(Fe)_8(Fe,Cr,Si)_{18}(Cr)_4$$

This is an attractive solution, because the evaluation needs few parameters and still gives a wide possible composition range. It also reflects the fact that there is no stable σ-phase in binary Si systems.

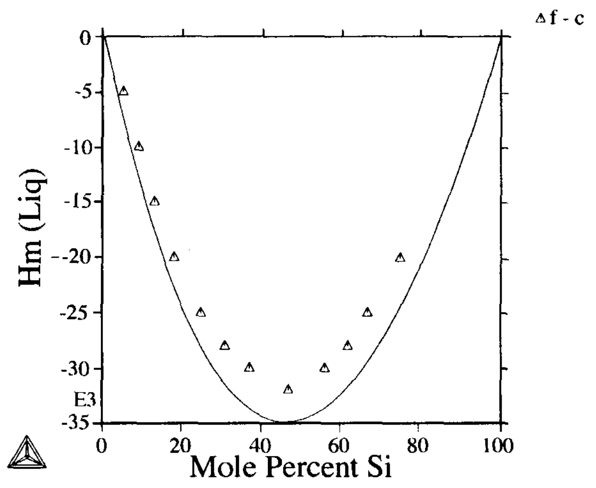

Fig. 8 The enthalpy of mixing for the isopleth $x_{Fe} = x_{Cr}$ at 1600 °C [78Pet].

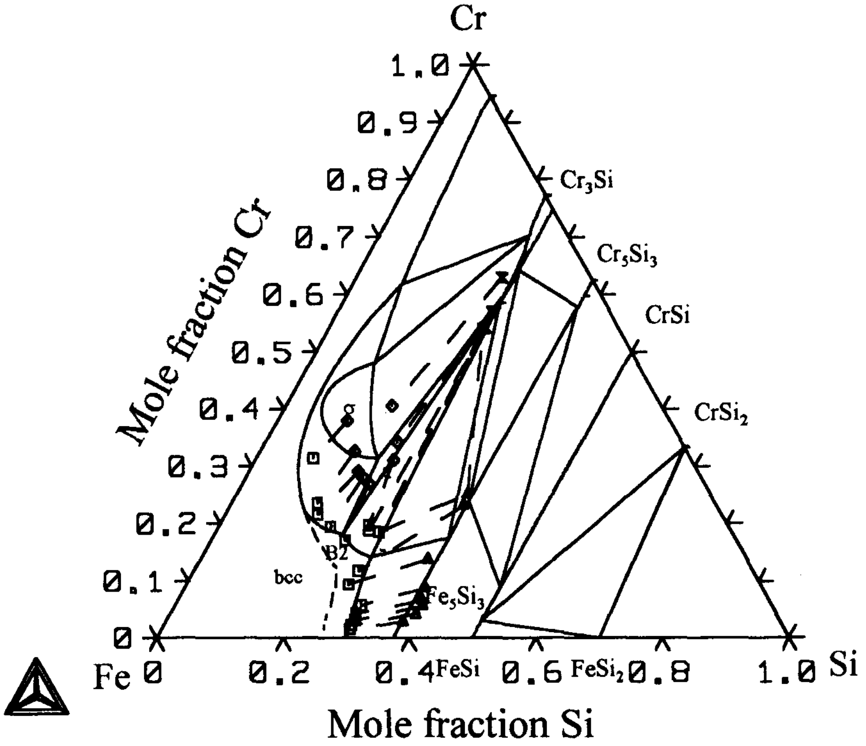

Fig. 9 Calculated isothermal section of the Fe-Cr-Si system at 1047 °C with data from [95Hay]. Note that the dashed line describes the solvus without B2 ordering.

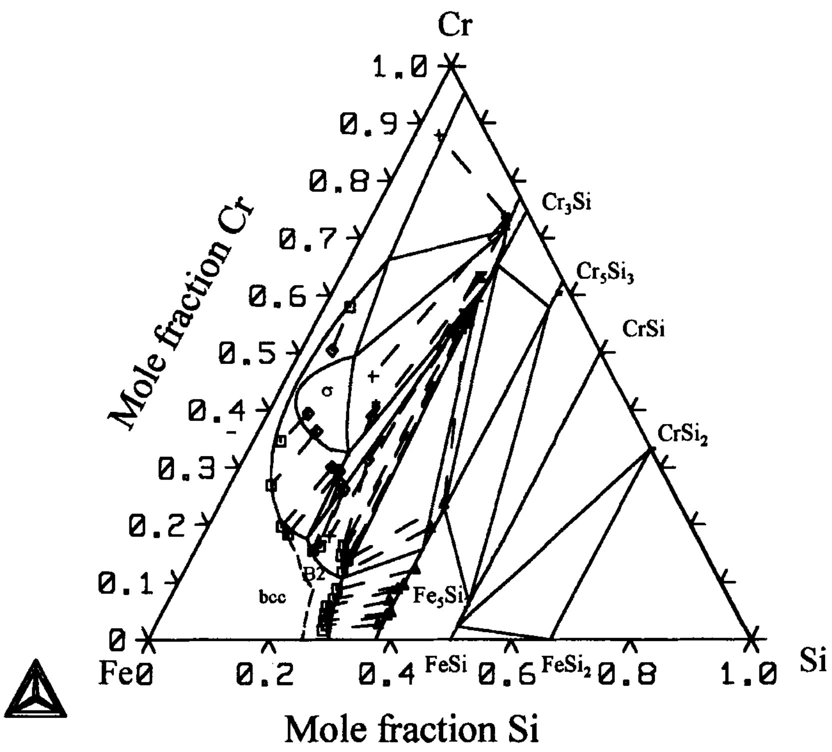

Fig. 10 Calculated isothermal section of the Fe-Cr-Si system at 947 °C with data from [95Hay]. Note that the dashed line describes the solvus without B2 ordering.

4. The Binaries

4.1 Fe-Cr System

The Fe-Cr binary (see Fig. 3) has been evaluated by [87And] using the CALPHAD method. The σ-phase was modeled using a sublattice model with 30 atoms in the unit cell using only three sublattices, as described above. In the first and second sublattices no mixing is assumed, and only two parameters are needed for the description. No interaction parameter has been introduced.

4.2 Fe-Si System

In the Fe-Si system (see Fig. 4) there are two ordered phases at Fe-rich compositions. The sequence $A2/B2/D0_3$ has been reported, with a complex mixture of different kinds of second-order transformations around 700 °C and 10 at.% Si.

The phase diagram also displays a number of phases with near-stoichiometric composition which, with one exception, are stable only in a limited temperature range. The Fe_1Si_1, ε-phase, is the exception and forms congruently from the liquid at *ca* 1410 °C (1683 K). To model all the order/disorder transformations in a simple way is very difficult. The present description, which was reported by [91Lac], describes only the $B2$ ordering and neglects the DO_3. The description will probably be improved soon, because ordering models are now being refined even though not complete.

4.3 Cr-Si System

The thermodynamic assessment of the Cr-Si system (see Fig. 5 for phase diagram) was made by [94Cou]. They present a careful evaluation that includes a comparison between different two-sublattice models for the Cr_3Si and the $CrSi_2$ phases. The preferred model, which describes the system in the most reasonable way, can be written:

$$(Cr,Si)_p(Si,Cr)_q$$

The model extends to the pure elements, which means that pure element data for this structure have to be estimated and must be the same in all systems where the phase appears, otherwise compatibility is not maintained.

5. Thermodynamic Data

5.1 Liquid Phase

A number of authors have reported thermodynamic data for the liquid phase in the ternary diagram. [64Bow] and [64Wad] have carried out activity measurements using two different methods (the former providing Si activities and the latter providing Cr activities) at low Si content. In addition, there are liquidus measurements by [73Wet] at different Cr/Fe ratios. There are also two Russian papers concerning the enthalpy of mixing in liquid Fe-Cr-Si alloys: [75Igu] and [78Pet].

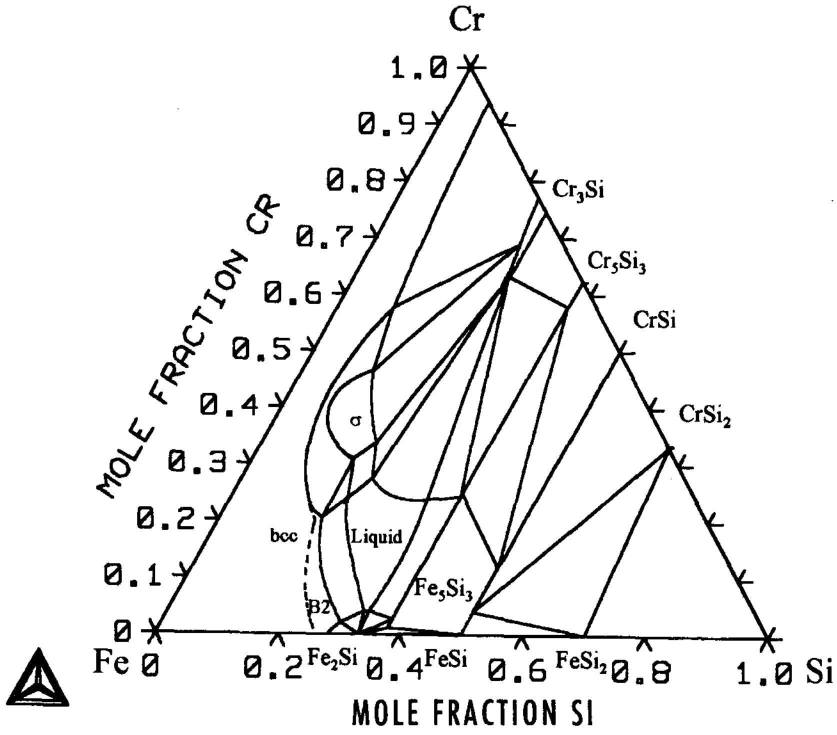

Fig. 11 Calculated isothermal section of the Fe-Cr-Si system at 1150 °C. Note that the dashed line describes the solvus without B2.

5.2 Solid Phases

For solid alloys, an isoactivity Si-content trend measurement has been carried out by [81Fuj] for the bcc phase at 1400 °C and low Cr-contents. [87Rag], who made the latest evaluation, quotes a Russian paper [66Gla] with respect to an isothermal section at 900 °C, and [80Cha] made an evaluation with respect to an isothermal section at 427 °C. The latter was produced by thermodynamic modeling based on the same isothermal section by [66Gla]. However, recent measurements at 947 and 1047 °C by [95Hay] provide new information.

6. Crystallographic Information for Solid Phases

The solid phases present in the ternary system have been summarized in Table 1. Notable is the complete solubility possible between FeSi and CrSi. Furthermore, the Cr$_3$Si phase dissolves over 10% Fe according to [95Hay]. That is the highest solubility in Cr-Si alloys with the exception of the aforementioned FeSi. On the Fe-Si side the Fe$_5$Si$_3$ phase can dissolve about 20% Cr and the *D*0$_3$-ordered Fe$_3$Si phase also has a solubility of about 20% Cr. No new ternary phase exists in the system, although the σ-phase is stable at higher temperatures in the ternary than in the binary Fe-Cr system.

7. Results and Discussion of the Evaluation

The evaluated parameters in Appendix 1 are based mainly on the data from [95Hay], while the liquid phase has been evaluated subsequently essentially using the liquidus data from [73Wet] (Fig. 6) and the enthalpy measurements by [78Pet] (Fig 7, 8). The liquid data gave a reasonable fit and provide a good representation of the temperature stability of the solid phases.

There are two crucial three-phase equilibria in the solid ternary system for the thermodynamic evaluation:

- The equilibrium among Fe$_5$Si$_3$, *D*0$_3$, and Cr$_3$Si (*A*)
- The equilibrium among σ, *D*0$_3$, and Cr$_3$Si (*B*)

These are linked by the narrow two-phase field of Cr$_3$Si and *D*0$_3$, shown also in the isothermal section by [66Gla].

[95Hay] gives a number of tie lines between the *D*0$_3$ and the Fe$_5$Si$_3$ phase, which provides a good guide for parameter optimization. A fit resulted in a minor error of about 1% at the solvus line near the three-phase triangle. This was accepted because it can be explained as an effect of the missing *D*0$_3$ ordering model and cannot be avoided because *D*0$_3$ is not included in the description of the binary Fe-Si system. The three-phase field *A* then gives the new extension of the Cr$_3$Si phase. Having decided on this, the three-phase field *B* gives a hint on the stability of the σ-phase if combined with all the available tie lines, and by using a method suggested by [95Luk], which makes use of binary estimations as described by [93Tan]. The result is shown in the three isotherms (Fig. 9 to 11). Notable are the somewhat overestimated solvus between the disordered bcc and the σ-phase and the shape of the σ-phase field. The latter is worth a comment. The σ-phase is stable with less than 20% Si and therefore very dependant on the Fe-Cr description. A significant change of the σ-phase field in the ternary cannot be obtained without changing the binary Fe-Cr description. The other solid phases are described accurately using available data and have not caused any difficulties.

Appendix 1 List of Parameters

$L^{\mathrm{bcc}A2}_{\mathrm{Fe,Cr,Si}} = -54\ 000$

$G^{\mathrm{bcc}B2}_{\mathrm{Cr:Fe}} = G^{\mathrm{bcc}B2}_{\mathrm{Fe:Cr}} = 3\ 000 + 0.5G^{\mathrm{SER}}_{\mathrm{Cr}} + 0.5G^{\mathrm{SER}}_{\mathrm{Fe}}$

$G^{\mathrm{bcc}B2}_{\mathrm{Cr:Si}} = G^{\mathrm{bcc}B2}_{\mathrm{Si:Cr}} = -20\ 000 + 0.5G^{\mathrm{SER}}_{\mathrm{Cr}} + 0.5G^{\mathrm{SER}}_{\mathrm{Si}}$

$G^{\mathrm{Cr_3Si}}_{\mathrm{Fe:Cr}} - 3G^{\mathrm{SER}}_{\mathrm{Fe}} - G^{\mathrm{SER}}_{\mathrm{Cr}} = 8\ 000$

$G^{\mathrm{Cr_3Si}}_{\mathrm{Fe:Si}} - 3G^{\mathrm{SER}}_{\mathrm{Fe}} - G^{\mathrm{SER}}_{\mathrm{Si}} = -75\ 000 + 8T$

$L^{\mathrm{Cr_3Si}}_{\mathrm{Fe,Cr:Si}} = 10\ 000$

$G^{\mathrm{Cr_5Si_3}}_{\mathrm{Fe:Si}} - 5G^{\mathrm{SER}}_{\mathrm{Fe}} - 3G^{\mathrm{SER}}_{\mathrm{Si}} = -180\ 000$

$L^{\mathrm{Cr_5Si_3}}_{\mathrm{Fe,Cr:Si}} = 12\ 000$

$G^{\mathrm{Fe_5Si_3}}_{\mathrm{Cr:Si}} - 5G^{\mathrm{SER}}_{\mathrm{Cr}} - 3G^{\mathrm{SER}}_{\mathrm{Si}} = -216\ 000 + 2.16T$

$L^{\mathrm{L}}_{\mathrm{Fe,Cr,Si}} = -53\ 600 - 13.3T$

$L^{B20}_{\mathrm{Fe,Cr:Si}} = 15\ 000$

$G^{\sigma}_{\mathrm{Fe:Cr:Si}} - 8G^{\mathrm{fcc}}_{\mathrm{Fe}} - 4G^{\mathrm{SER}}_{\mathrm{Cr}} - 18G^{\mathrm{bcc}}_{\mathrm{Si}} = -1\ 100\ 000 + 275T$

$L^{\sigma}_{\mathrm{Fe:Cr:Cr,Si}} = -2\ 115\ 000 + 155T$

$L^{\sigma}_{\mathrm{Fe:Cr:Fe,Si}} = -2\ 015\ 000 + 155T$

where $G^{\mathrm{fcc}}_{\mathrm{Fe}}$ is the Gibbs energy of pure Fe in the fcc state and $G^{\mathrm{bcc}}_{\mathrm{Si}}$ is the Gibbs energy of pure Si with bcc structure taken from [91Din].

Acknowledgments

The author wishes to express his gratitude to Prof. Bo Sundman for support and encouragement, Dr. Nigel Saunders for some vital hints for the modeling, Dr. Fred Hayes for permission to use his data prior to publication in modeling this system, Dr. Byeong-Joo Lee for sending some additional papers used in the evaluation, and finally the Swedish Research Council for Engineering Sciences (TFR) for sponsoring this work.

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