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Computation of phase equilibria in the Fe–Ni–Cr system based upon mass spectrometric investigations

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Abstract

Phase diagram calculations require only the differences between the chemical potentials of the involved phases. This makes it possible to use even artificial thermodynamic parameter sets which then have to be corrected by means of additional terms. It is demonstrated that mass spectrometric investigations yield a simpler, but more effective algebraic description of the thermodynamic ternary mixing behavior than the results of previous phase diagram assessments: mass spectrometric measurements in the liquid phase, and in the restricted field of fcc-phase in the system Fe–Ni–Cr together with the algebraic descriptions of the three binary boundary systems Fe–Ni, Ni–Cr, and Cr–Fe as reported in previous works make it possible to compute ternary phase equilibria in the system Fe–Ni–Cr, showing better agreement with the experimental phase equilibria data than the assessments as reported by Kundrat and Elliot, Hillert and Qiu, and Lee. Additional advantage of the mass spectrometric determined molar Gibbs energy is that the description of the magnetic contributions $Z_k^{\alpha,\mathrm{mag}}(T,x^\alpha)$ has been merely reduced to the expressions of the pure species. © 1998 Elsevier Science B.V.

Keywords: Mass spectrometry; Metals; Ternary alloys; Thermodynamics; Phase diagrams

1. Introduction

The construction of phase diagrams of alloy systems on the basis of metallographic information alone requires a great deal of labor and materials. Particularly in multi-component systems even the powerful techniques of vacuum deposition of three kinds of metals from three corners, and the multi-component diffusion couple technique do not yield phase equilibria curves within realistic periods of time. However, phase diagrams have not to be established exclusively by experimental techniques. The determination of the phase equilibria can also be based on thermochemical equilibrium conditions, namely at constant temperature T the molar chemical potential (partial molar Gibbs energy) $\mu_j^\alpha(T,x_j^\alpha)$ for each component j (here: j=Fe,Ni,Cr; x_j are the mole fractions) must be equal in each of the coexisting phases $\alpha,\beta\ldots$ $(\alpha,\beta,\ldots= l,f,b,s,\ldots$; l=liquid, f=fcc, b=bcc, s=sigma):

$$\mu_j^\alpha(T,\zeta_{\mathrm{Fe}}^\alpha,\zeta_{\mathrm{Ni}}^\alpha,\zeta_{\mathrm{Cr}}^\alpha) = \mu_j^\beta(T,\zeta_{\mathrm{Fe}}^\beta,\zeta_{\mathrm{Ni}}^\beta,\zeta_{\mathrm{Cr}}^\beta) = \ldots\,(j=\mathrm{Fe},\mathrm{Ni},\mathrm{Cr}), \qquad (1)$$

where $\zeta_j^\alpha,\zeta_j^\beta,\ldots$ are the equilibrium compositions in the phases $\alpha,\beta,\ldots$.

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2. Phase diagram computations

Practical application of computational construction of phase diagrams requires enormous calculations. This procedure was prohibitive, therefore before the industrial development of powerful and cheaper electronic data-processing machines (EDP) took place in the sixties. In the seventies, it was especially the merit of the CALPHAD group to push forward the developments of suitable EDP programs for analysis and synthesis of the phase diagrams by means of computer calculations. It should be noted that this method permits the synthesis of the phase diagrams of real alloys over a wide range of temperature and composition by computation combined with thermodynamic analysis of the experimental data.

In the last years, the technique of computational determination of molar Gibbs energy data suitable for generating phase equilibria boundaries has become so convenient that more and more authors are employing it. However, very often there is a lack of reliable experimental data. In case of multicomponent alloy systems, such as the Fe–Ni–Cr ternary system including the three binary boundary systems the thermodynamic investigations for the determination of reliable molar Gibbs energy data are also very time-consuming, and, usually, beset with considerable experimental difficulties. Therefore, it may be understandable that more and more authors are ignoring the lack of experimental investigations, and produce their own sets of assessed data.

These authors will not always obey the risks of the pure assessment-technique: in the thermochemical equilibrium conditions, Eq. (1) only the differences between the chemical potentials $[\mu_j^\alpha(T,x_j^\alpha)-\mu_j^\beta(T,x_j^\beta)]$, $[\mu_j^\alpha(T,x_j^\alpha)-\ldots]$ of the considered phases $\alpha,\beta,\ldots$ are employed, and not absolute values. This makes it possible to use many different sets of thermodynamic parameters to describe more or less satisfactorily a binary phase diagram. However, discrepancies between calculations and experimental data of phase equilibria in higher order systems more and more can be tracked back to assessments of lower order systems based on those non-realistic thermodynamic data.

Recently, Oates et al. [1] required to put more physics into CALPHAD solution models. And even Hillert, the founder and mentor of the ThermoCalc group, regretted some developments in the phase diagram engineering at the CALPHAD XXVI Conference. He was concerned that CALPHAD had reached a stage where its future scientific status might be in danger [2].

2.1. Algebraic description of the molar functions

Phase diagram computations as well as computer-aided mass spectrometry require algebraic formulas of the molar functions Z (Z=Gibbs energy G, heat of mixing H, entropy S). As long as the general character of the molar properties cannot be derived theoretically, suitable approximation formulas must be used. In the phase α, the molar functions Z are splitted by common modeling into various terms [3]

$$\begin{aligned} Z^\alpha(T,x^\alpha) &= Z^{\alpha,0}(T)+Z^{\alpha,\mathrm{id}}(T,x^\alpha) \\ &\quad + Z^{\alpha,\mathrm{E}}(T,x^\alpha)+Z^{\alpha,\mathrm{mag}}(T,x^\alpha), \end{aligned} \tag{2a}$$

where x^α is the mole fraction. $Z^{\alpha,0}(T)$, and $Z^{\alpha,\mathrm{id}}(T,x^\alpha)$ denote the contributions of the pure species, and 'ideal' alloy, respectively. In Eq. (2a), the terms $Z^{\alpha,\mathrm{E}}(T,x^\alpha)$ and $Z^{\alpha,\mathrm{mag}}(T,x^\alpha)$ are assumed commonly to be due to the intermolecular and magnetic forces, respectively.

The molar functions Z, of an alloy system with K components, are usually called 'integral' molar properties of Z, and are expressed by means of the contributions of their components, $Z_k^\alpha(T,x^\alpha)$,

$$Z^\alpha(T,x^\alpha)=\sum_{k=1}^{K} x^\alpha Z_k^\alpha(T,x^\alpha). \tag{2b}$$

2.2. Advantages of the 'thermodynamically adapted power' (TAP) series concept

The various pseudo-theoretical models as suggested in literature yielded a variety of different formulas for the thermodynamic mixing functions. Often, this makes the employment and/or compilation of literature data difficult. In particular, the expressions of the mixing properties as derived from the various models of short-range ordering in the liquid phase cannot be transformed to expressions commonly used in mixing thermodynamics.

Several difficulties, as described above, may be coped with by applying algebraic expansions to describe the dependence of the molar excess functions $Z^{\alpha,\mathrm{E}}(T,x^{\alpha})$ on the mole fraction x^{α}. It has been shown [4] that the Weierstrass approximation theorem [5] guarantees both: (i) that the molar excess functions can be expressed by means of polynomials of sufficient high degree in the mole fraction x without any loss of generality; and (ii) that the derivatives of the excess functions $Z^{\alpha,\mathrm{E}}(T,x^{\alpha})$ are represented by the derivatives of the approximation expansion.

It makes sense, therefore, to use the simplest polynomials for this purpose which fulfills a priori the boundary conditions of the thermodynamic excess properties Z^{E} (vanishing Z^{E}-values for the pure components, and the Gibbs–Duhem equation). Computational effort can then be saved, and mathematical clarity is enhanced. In the late seventies and beginning of the eighties one of the authors demonstrated at several CALPHAD meetings that in case of binary systems $j-k$ (in this work: j,k=1,2,3; 1=Fe, 2=Ni, 3=Cr) the expansion after Redlich–Kister

$$^{j,k}Z^{\mathrm{E}}(x) = x_j x_k \sum_{n=1}^{N} {}^{j,k}B_n (x_k - x_j)^{n-1}, \tag{3}$$

where N is the number of adjustable parameters $^{j,k}B_n$, is the simplest formula published in literature which covers all advantages of any other proposed approximation formulas such as the α-formalism after Kortüm, the Legendre polynomials, etc. This yielded the broad application of the expansion for phase diagram calculations.

However, some years later it has been proved [6] that the simplest applicable polynomial for this purpose is not the Redlich–Kister expansion, but a TAP series:

$$^{j,k}Z^{\mathrm{E}}(x) = x_j \sum_{n=1}^{N} {}^{j,k}C_n x_k^n, \tag{4}$$

where N is the number of adjustable parameters $^{j,k}C_n$. Following the concept of using the simplest possible polynomial, the molar ternary excess functions Z^{E} (all other indices omitted) are represented by

$$Z^{\mathrm{E}} = {}^{\mathrm{BBS}}Z^{\mathrm{E}} + {}^{\mathrm{t}}Z^{\mathrm{E}}, \tag{5a}$$

where the $^{\mathrm{BBS}}Z^{\mathrm{E}}$ is the contribution of the three binary boundary systems (in this work: 1=Fe, 2=Ni, 3=Cr)

$$^{\mathrm{BBS}}Z^{\mathrm{E}} = {}^{1,2}Z^{\mathrm{E}} + {}^{2,3}Z^{\mathrm{E}} + {}^{3,1}Z^{\mathrm{E}}, \tag{5b}$$

and $^{\mathrm{t}}Z^{\mathrm{E}}$ is the 'ternary interaction term', a homogeneous polynomial in all three mole fractions x_j (in this work: j=Fe, Ni, Cr; $^{\mathrm{t}}C_n^{\mathrm{Z}}$ adjustable ternary parameters; n=1,2,...),

$$^{\mathrm{t}}Z^{\mathrm{E}} = x_1 x_2 x_3 [{}^{\mathrm{t}}C_1 + ({}^{\mathrm{t}}C_2 x_1 + {}^{\mathrm{t}}C_3 x_2 + {}^{\mathrm{t}}C_4 x_3) + \ldots], \tag{5c}$$

Use of the TAP series concept makes possible to approximate algebraically all types of molten metal alloys, even those showing short-range ordering. Additional advantage: the customary classification of molten metal alloys with respect to the complexity of their molar excess quantities may be performed with more clarity.

As an illustration of the considerable reduced computational effort in case of using the TAP series concept, in Table 1 are presented the expressions of the contributions: (1) of the three binary boundary systems of a liquid ternary, $^{\mathrm{BBS}}Z^{\mathrm{E}}$; and (2) of its derivative with respect to the mole fraction x_2, in terms of (a) TAP series, Eq. (4), and (b) Redlich–Kister expansion, Eq. (3). Conversion of other polynomial representations of the $^{j,k}Z^{\mathrm{E}}(x)$ into the TAP series, Eq. (4), and vice versa, can be performed easily by means of the algorithm developed in Ref. [7].

2.3. The temperature dependence of the molar excess quantities $Z^{\alpha,E}(T,x^{\alpha})$

Within temperature ranges, in which the logarithms of the partial pressures of all components may be assumed to be proportional to the inverse temperature, both the molar heat of mixing H^{E} as well as the molar excess entropy S^{E} result as temperature independent. The temperature dependence of the molar excess Gibbs energy G^{E} is then given by

$$G^{\mathrm{E}}(T) = H^{\mathrm{E}} - TS^{\mathrm{E}}. \tag{6}$$

Eq. (6) is equivalent to the assumption of vanishing molar excess heat capacity (ΔC_{p}=0), which is expressed by the rule of Neumann and Kopp, according to which the difference between the heat capacity of an alloy and the heat capacities of the corresponding amounts of the pure species at the same tempera-

Table 1
Expressions of the contribution of the three binary boundary systems to Z^{E}

(1) $^{\mathrm{BBS}}Z^{\mathrm{E}} = {}^{1,2}Z^{\mathrm{E}} + {}^{2,3}Z^{\mathrm{E}} + {}^{3,1}Z^{\mathrm{E}}$
(2) $\partial\,{}^{\mathrm{BBS}}Z^{\mathrm{E}}/\partial x_2 = \partial[{}^{1,2}Z^{\mathrm{E}} + {}^{2,3}Z^{\mathrm{E}} + {}^{3,1}Z^{\mathrm{E}}]/\partial x_2$

(a) *TAP* (n=1,. . .,N)
$^{\mathrm{BBS}}Z^{\mathrm{E}} = x_1 \sum^{1,2} C_n x_2^n + x_2 \sum^{2,3} C_n x_3^n + x_3 \sum^{3,1} C_n x_1^n$
$\partial\,{}^{\mathrm{BBS}}Z^{\mathrm{E}}/\partial x_2 = x_1 \sum^{1,2} C_n x_2^{n-1}(nx_1 - x_2) + \sum^{2,3} C_n x_3^n - x_3 \sum^{3,1} C_n x_1^{n-1}$

(b) *Redlich–Kister* ($^{\mathrm{BBS}}Z^{\mathrm{E}}$:$n$=1,. . .,$N$; $\partial\,{}^{\mathrm{BBS}}Z^{\mathrm{E}}/\partial x_2$: n=2,. . .,N)
$^{\mathrm{BBS}}Z^{\mathrm{E}} = x_1x_2 \sum^{1,2} B_n(x_2 - x_1)^{n-1} + x_2x_3 \sum^{2,3} B_n(x_3 - x_2)^{n-1} + x_3x_1 \sum^{3,1} B_n(x_1 - x_3)^{n-1}$
$\partial\,{}^{\mathrm{BBS}}Z^{\mathrm{E}}/\partial x_2 = (x_1 - x_2)\,{}^{1,2}B_1 + \sum^{1,2} B_n(x_2 - x_1)^{n-2}(2nx_1x_2 - x_1^2 - x_2^2) +$
$x_3[{}^{2,3}B_1 + \sum^{2,3} B_n(x_3 - x_2)^{n-2}(x_3 - nx_2)] - x_3[{}^{3,1}B_1 + \sum^{3,1} B_n(x_1 - x_3)^{n-2}(nx_1 - x_3)]$

(1) The three binary boundary systems of a ternary melt, $^{\mathrm{BBS}}Z^{\mathrm{E}}$. (2) Its derivative with respect to the mole fraction (x_3=const.). In terms of (a) TAP series, Eq. (4), and (b) Redlich–Kister expansion, Eq. (3).

ture is zero. Combining Eq. (6) with Eq. (4) and Eq. (5) yields, finally, the required combined temperature and concentration dependence of the molar excess quantities $Z^{\mathrm{E}}(T,x)$.

3. The system Fe–Ni–Cr

The introduction of a magnetic term $Z^{\alpha,\mathrm{mag}}$ in Eq. (2a) is always problematic, because experimental investigations will only yield the total excess sum ($Z^{\alpha,\mathrm{E}}$+$Z^{\alpha,\mathrm{mag}}$). Especially, the databanks offered by the ThermoCalc group are based on the use of magnetic terms $Z^{\alpha,\mathrm{mag}}$ as expressed by Sundman and Agren [8]. From a physico-chemical point of view their description of assumed magnetic influence, $Z^{\alpha,\mathrm{mag}}$, looks strange, e.g. polynomials in temperature up to the power 25 (!) are employed (compare [8]).

Nevertheless, in order to support the efforts of establishing a general database for the reference states of the elements, it is meaningful to employ the elementary magnetic contributions. However, considering binary systems, no reasons may be found to support the problematical splitting of the deviation from the ideal-solution model into two terms.

3.1. The binary boundary system Fe–Ni

Recently, Lee [9] reported that a revision of the thermodynamic assessment data of the Fe–Ni liquid phase as used by Hillert and Qiu [10] is necessary to obtain a better agreement with the experimental data on the bcc/liquid and fcc/liquid tie lines and liquidus temperatures in the Fe-rich region of the Fe–Ni–Cr ternary system than in the previous assessments of Kundrat and Elliott [11], and Hillert and Qiu [10] (compare Fig. 1). This is in full agreement with mass spectrometric investigations of Fe–Ni alloys in the liquid and in the fcc-solid phase, as published earlier [12,13]. Nevertheless, these experimental data have not been considered later on any more, not even in the revision by Lee [9].

The resultant TAP coefficients of Eq. (4) of the mass spectrometric investigations of [12,13] are summarized in Table 2. Fig. 1 shows that by means of these data, the phase boundaries between the liquid and the fcc-solid phase can be computed in full agreement with the experimental data without any binary magnetic correction term. In accordance to Hillert and Qiu [10], and Lee [9], the contributions of the pure species $Z^{\alpha,0}(T)$ in Eq. 2 have been expressed by means of the SGTE system of reference states of pure elements [14],

$$Z_k^{\alpha,0}(T) = c_{1,k} + c_{2,k}T + c_{3,k}T\ln T + c_{4,k}T^2 + c_{5,k}T^3 + c_{6,k}/T + c_{7,k}T^7 + c_{8,k}/T^9, \tag{7}$$

where $c_{n,k}$ (n=1,. . .,8; k=Fe, Ni, Cr) are element dependent parameters.

The results of this work agree entirely with the optimization of Hasebe and Nishizawa [15]. For alloys

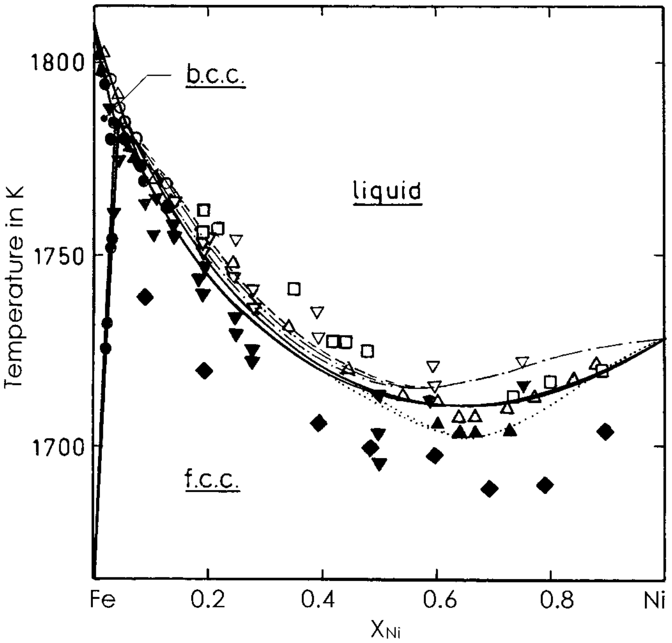

Fig. 1. The liquidus/solidus phase equilibria in the Fe–Ni system. Computations: this work, and Hasebe and Nishizawa [15]: ———; Larrain [16]: . . .; Lee [9]: – · – Experimental data (full symbols: solid, open symbols: liquid): Hansen and Freeman [35], and Kase [36]: Δ; Bennek and Schafmeister [37]: ▽; Jenkins et al. [31]: -; Hellawell and Hume-Rothery [38], and Kundrat [39]: ○; Predel and Mohs [40]: □.

Table 2
TAP parameters C_n^Z of Fe–Ni alloys. This work: liquid and fcc-solid phase from mass spectrometric measurements [12,13]; bcc phase optimized in this work from phase diagram calculations ($C_n^G = C_n^H - TC_n^S$). Lee [9]: liquid phase optimized in Ref. [9]; bcc and fcc phase from Hillert and Qiu [10]. Magnetic data from Ref. [10]. All data converted into TAP series concept

Phase	n	This work		Lee [9]	
		C_n^H (J/mol)	C_n^S (J/mol K)	C_n^H (J/mol)	C_n^S (J/mol K)
liq	1	−10500	−1.85	−6731	−1.016
	2	−12000	−2.35	−20360	−8.293
	3	−6000	−5.05	0	0
bcc	1	−2400	1.90	832.4	3.216
	2	−16000	−7.10	−3578	−3.858
	3	−12000	−4.00	0	0
fcc	1	−6300	−0.80	−1698	1.177
	2	−12200	−1.20	−19260	−8.902
	3	−7500	−6.80	−2903	0
				Beta	Tc
fcc/mag	1	—	—	28.89	1451
	2	—	—	−75.26	1364
	3	—	—	97.88	0
	4	—	—	−49.44	0

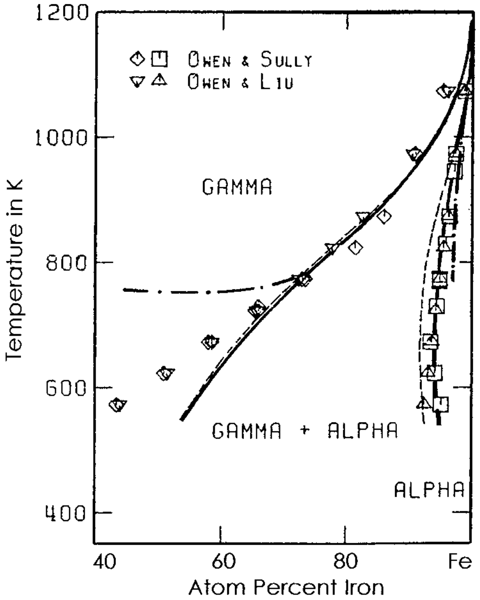

Fig. 2. Comparison of the computations of the fcc (γ)–bcc (α) phase equilibrium in the Fe–Ni system with experimental informations [17,18]. This work: ———; Larrain [16]: - - -; Lee [9]: -.-.

containing <40 at% Ni Larrain [16] compiled liquid–fcc equilibria which agree well with the corresponding results of Hasebe and Nishizawa [15], and of this work. However, Larrain [16] compiled a melting minimum which is ca. 5 K lower. The parameter values as used by Lee [9] are also given in Table 2. The results of Lee's [9] phase diagram optimization for the liquid–solid equilibria are also plotted in Fig. 1. Comparing with the results of this work in Fig. 1 and Table 2 shows that the use of a magnetic correction neither will simplify the thermodynamic description nor improve the quality of the Fe–Ni phase diagram.

Based on the mass spectrometric data of the liquid and the fcc-solid phases the thermodynamic excess behavior of the bcc-solid phase has been assessed as presented in Table 2. Fig. 2 shows that the assessment of this work yields fcc (γ)–bcc (α) equilibrium lines in full agreement with the compilation of Larrain [16]. The results of this work show a distinctly better agreement with the experimental data of Owen and Sully [17], and Owen and Liu [18] than the optimization of Lee [9], which is also plotted in Fig. 2. Concerning the fcc (γ)–bcc (α) equilibrium lines Lee's assessment using a magnetic fcc solid contribution instead of the mass spectrometrically determined excess Gibbs energies of Ref. [13] yielded distinctly less agreement with experimental investigations.

3.2. The binary boundary systems Cr–Fe and Ni–Cr

In the Cr–Fe system mass spectrometric studies on the bcc-solid phase [3] yielded again molar excess Gibbs energies G^E distinctly different to data assessed previously by Anderson and Sundman [19], and Lee [9]. As pointed out in Refs. [3,20], phase diagram calculations based on these mass spectrometric data, and on the SGTE reference states of pure elements [14] yielded a better agreement with experimental phase equilibrium data than the assessments by Anderson and Sundman [19], and Lee [9].

The advantage of constructing phase diagrams by means of experimentally determined molar Gibbs energies, is demonstrated also by considering the third binary boundary system, Ni–Cr: the bcc solid Ni–Cr alloys have been investigated, recently, by means of the Knudsen cell mass spectrometry [21]. Despite, the very restricted field of the bcc phase these experimental studies yielded molar excess Gibbs energies G^E which can be employed successfully for calculations of the binary phase diagram based on the SGTE reference states of pure elements [14]: the results in Ref. [21] agree well with the assessment by Nash [22].

3.3. Ternary phase equilibria

Construction of phase equilibria based on the experimental thermodynamic data of the three binary boundary systems as described above, and on the ternary molar excess Gibbs energy G^E assessed in Refs. [11,10], respectively, could not be performed successfully. This assured the authors to investigate mass spectrometrically the ternary Fe–Ni–Cr system. Experimental studies could be performed successfully on both liquid and on the fcc solid alloys. Whereas the phase field of stable bcc solid Fe–Ni–Cr alloys is too small for experimental investigations.

4. Mass spectrometric investigations

The Knudsen effusion technique in combination with a mass spectrometer makes possible to determine the thermodynamic excess properties z^{E} (z=G,H,S; z=integral function Z, partial function Z_j) of alloy systems even at high temperatures. Following this technique the sample is heated in an isothermal vessel which is called 'Knudsen cell'. Usually, Knudsen cells are manufactured as (cylindrical) crucibles with a small knife-edge shaped orifice (0.5–1.5 mm diameter) in the lid. Inside the Knudsen cell the condensed sample is in thermodynamic equilibrium with its gas phase. This Knudsen cell is now employed as a 'gas source', and the effusing molecular beam is directed into the ionization chamber of the connected high-temperature mass spectrometer (compare [12,23,24]). The ion current intensities J_j of the ionized vapor species are then detected by means of an electron multiplier.

4.1. Thermodynamic evaluation

The ion current intensities of the characteristic isotopes of the alloy components j (j=Fe, Ni, Cr) are proportional to the corresponding partial pressures in the Knudsen cell. This makes it possible to relate them to the molar excess chemical potentials μ_j^{E} ('Partial molar excess Gibbs energies G_j^{E}') of these components j in the condensed phase. However, Knudsen cell mass spectrometry will only yield the vapor pressures of the investigated species in arbitrary units. With metal alloy systems as the ternary Fe–Ni–Cr the problems connected with the calibration of the experimental values to absolute vapor pressure data can be avoided by measuring the ion-current intensities J_k of two alloy components. Choosing the two characteristic isotopes $^{56}\mathrm{Fe}^{+}$ and $^{52}\mathrm{Cr}^{+}$ makes possible to determine directly the difference of the molar excess chemical potentials of Fe and Cr, $(\mu_{\mathrm{Fe}}^{\mathrm{E}} - \mu_{\mathrm{Cr}}^{\mathrm{E}})$ by

$$\mu_{\mathrm{Fe}}^{\mathrm{E}} - \mu_{\mathrm{Cr}}^{\mathrm{E}} = RT[\ln(J_{\mathrm{Fe}}/J_{\mathrm{Cr}}) - \ln(x_{\mathrm{Fe}}/x_{\mathrm{Cr}}) - {}^{\mathrm{t}}C_0^{\mathrm{G}}(T)] \tag{8}$$

where R is the gas constant. In Eq. (8)${}^{\mathrm{t}}C_0^{\mathrm{G}}(T)$ denotes the calibration constant for the two components Fe and Cr in the corresponding phase of the ternary Fe–Ni–Cr system. The ${}^{\mathrm{t}}C_0^{\mathrm{G}}(T)$ factor depends on isotope specific data as well as on the actual ratings of the experimental set-up [3,12]. Forming the corresponding TAP expression for $(\mu_{\mathrm{Fe}}^{\mathrm{E}} - \mu_{\mathrm{Cr}}^{\mathrm{E}})$ by means of Eq. 5, substituting in the left-hand side from Eq. (8), and rearranging yields the required best-fit formula for the determination of the TAP parameters ${}^{\mathrm{a}}C_n$:

$$RT[\ln(J_{\mathrm{Fe}}/J_{\mathrm{Cr}}) - \ln(x_{\mathrm{Fe}}/x_{\mathrm{Cr}})] = {}^{\mathrm{t}}C_0^{\mathrm{G}}(T) + ({}^{\mathrm{BBS}}\mu_{\mathrm{Fe}}^{\mathrm{E}} - {}^{\mathrm{BBS}}\mu_{\mathrm{Cr}}^{\mathrm{E}}) + x_1x_2x_3[{}^{\mathrm{t}}C_1^{\mathrm{G}}(T) + \ldots]. \tag{9a}$$

with

$${}^{\mathrm{BBS}}\mu_j^{\mathrm{E}} = {}^{\mathrm{Fe,Ni}}\mu_j^{\mathrm{E}} + {}^{\mathrm{Ni,Cr}}\mu_j^{\mathrm{E}} + {}^{\mathrm{Cr,Fe}}\mu_j^{\mathrm{E}}. \tag{9b}$$

With the Fe–Ni–Cr system the mass spectrometric measurements were performed in both the liquid as well as the fcc-solid phases in 16 runs for eight different alloy concentrations [20,25]. Employing the best-fit technique as suggested in Ref. [26] enabled one algebraic overall best-fit of all experimental data along all investigated constant ratio sections. As described above, the thermodynamic data of the three binary systems are well-established in literature. The best-fit problem, Eq. 9, is reduced, therefore, only for adjusting the ternary parameters [20,25]:

$$RT[\ln(J_{\mathrm{Fe}}/J_{\mathrm{Cr}}) - \ln(x_{\mathrm{Fe}}/x_{\mathrm{Cr}})] - ({}^{\mathrm{BBS}}\mu_{\mathrm{Fe}}^{\mathrm{E}} - {}^{\mathrm{BBS}}\mu_{\mathrm{Cr}}^{\mathrm{E}}) = {}^{\mathrm{t}}C_0^{\mathrm{G}}(T) + x_1x_2x_3[{}^{\mathrm{t}}C_1^{\mathrm{G}}(T) + \ldots]. \tag{10}$$

4.2. Experimental

The Knudsen cell–mass spectrometric system employed for investigations on ternary Fe–Ni–Cr alloys was described recently in detail [23,24]. The simple monopole instrument model MX 7304 (Electron, Ukraine) having the mass range 2–200 amu. was modified in the Institute of Physics of Materials ASCR. The Knudsen cell part of the combination with mass spectrometer consists of the alumina effusion cell containing the sample, which was closed by an alumina lid having an orifice of 1.1 mm diameter. The alumina effusion cell is enclosed in an outer molybdenum cell with a tantalum lid, which is heated by a resistance furnace. The temperature of the sample in the effusion cell is measured with a Pt/PtRh10 thermocouple, calibrated by means of the melting points of several pure metal samples [24]. Ions were formed by means of a 15 eV electron beam having a current of 50 μA.

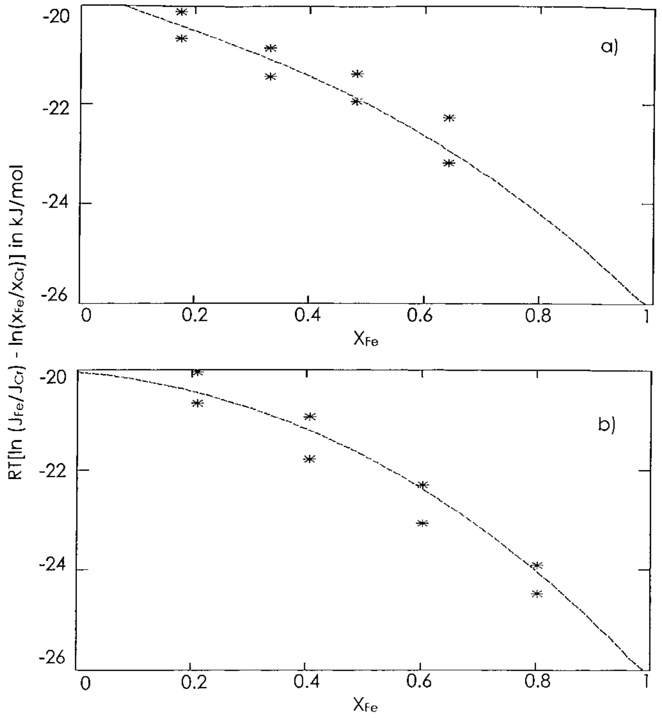

Fig. 3. RT[ln $(J_{Fe}/J_{Cr})-\ln(x_{Fe}/x_{Cr})$] as a function of the mole fraction x_{Fe} of liquid ternary Fe–Ni–Cr alloys at 1850 K (Overall best-fit curve based upon Eq. (8) ———; Experimental points *). (a) $x_{Cr}/x_{Ni}=0.19$ [28]; (b) $x_{Cr}/x_{Ni}=0.46$ [25].

4.3. Results and discussion

As reported elsewhere in detail, satisfactory best-fits are obtained for the measurements on both the fcc solid [20,27] as well as the liquid [25,28] ternary Fe–Ni–Cr alloys by using simple homogeneous polynomials of third order as ternary interaction term (one adjustable parameter). Fig. 3 shows the results for the liquid Fe–Ni–Cr alloys for the mean temperature of investigations, T=1850 K. In Fig. 4, the results of the mass spectrometric investigations on fcc solid Fe–Ni–Cr alloys at the mean temperature T=1650 K are presented. The resultant molar excess Gibbs energies G^E are plotted in Fig. 5 for the liquid phase, and in Fig. 6 for the fcc phase. As can be seen from Fig. 5, the mass spectrometric investigations on liquid ternary Fe–Ni–Cr alloys yielded at the mean temperature 1850 K negative molar excess Gibbs energies G^E nearly over the entire range of composition. Only alloys with approximately binary Cr–Fe compositions show slight positive G^E-values. Details are presented and discussed in Ref. [25]. Fig. 6 shows that at 1650 K the molar excess Gibbs energy G^E determined mass spectrometrically in Refs. [20,27] are negative over the whole field of stable fcc phase. Concerning details of the thermodynamic mixing behavior of fcc solid ternary Fe–Ni–Cr alloys as well as for the discussion of the results see [20].

5. Phase equilibria

The computational construction of ternary Fe–Ni–Cr phase equilibria has been performed by means of the so-called ‘PD-Package’ (PD-pp) recently developed for isobaric phase equilibrium calculations [29]. The program is written in FORTRAN 77, and it is based on the solution model for phases with several components and sublattices, according to Sundman and Agren [8]. Following this model, at constant temperatures and pressures the computation of chemical compositions, and of relative weight amounts of phases in thermodynamic equilibrium at given total compositions are equivalent to the determination of

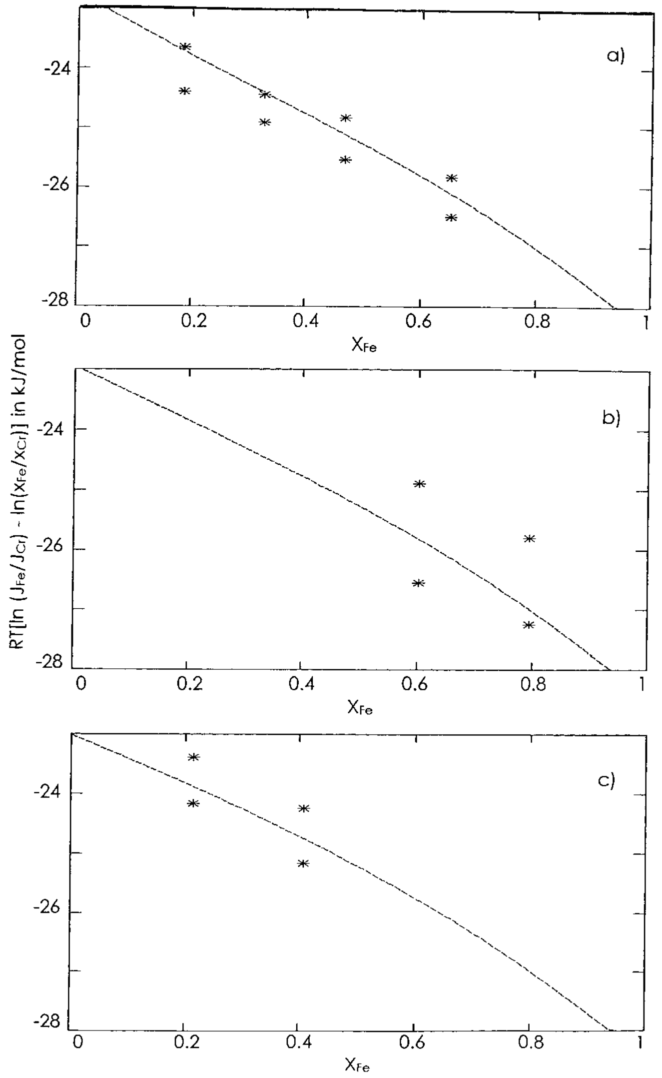

Fig. 4. RT[ln (J_{Fe}/J_{Cr})−ln(x_{Fe}/x_{Cr})] as a function of the mole fraction x_{Fe} of fcc solid ternary Fe–Ni–Cr alloys at 1650 K (Overall best-fit curve based upon Eq. (8) ——; Experimental points *). (a) x_{Cr}/x_{Ni} =0.17 [27]; (b) x_{Cr}/x_{Ni}=0.3 [20]; (c) x_{Cr}/x_{Ni}=0.4 [20].

the sets of weight amount of the individual components in equilibrium phases at minimum of the total molar Gibbs energy of the system. Of course, the stoichiometry as well as the mass conservation law have to be respected.

This so-called 'integral formulation' of the thermochemical equilibrium conditions, Eq. (1), represents from the mathematical point of view a constrained minimization problem. Such a problem can only be solved by employing suitable numeric methods of minimization. The PD-pp involves for this purpose the corresponding subroutines generated by the 'Universal Functional Optimization' system (UFO) [30] in which special algorithms of the variable metric method are programmed. The PD-pp makes possible to deal with systems showing eight components contained in four phases. The description allows employing of four sublattices in each phase at the most. The computations are restricted by the limited precision of the minimization program UFO which employs vari-

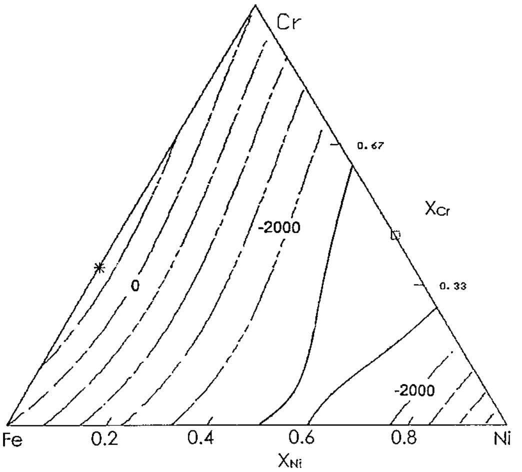

Fig. 5. Molar excess Gibbs energy G^E of liquid ternary Fe–Ni–Cr alloys at 1850 K in J/mol.

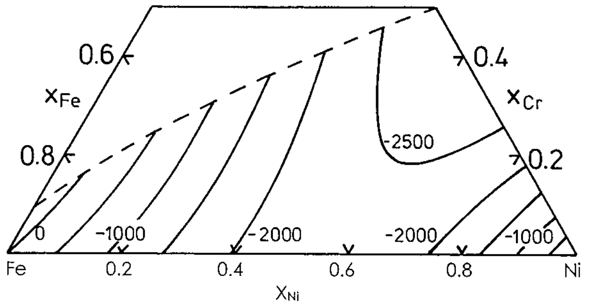

Fig. 6. Molar excess Gibbs energy G^E of fcc solid ternary Fe–Ni–Cr alloys at 1650 K in J/mol. Fcc phase field boundary: – – –.

ables and functions in the usual FORTRAN double precision declaration (REAL*8). However, neither in binary nor in ternary systems these restrictions will influence the construction of phase equilibria in any way [29]. Test calculations on several published phase diagram data proved the reliability of the algorithm developed in PD-pp [29]. Furthermore, computation of the phase equilibria of the binary alloy systems Fe–Ni, Cr–Fe, Ni–Cr, and Co–Cr by means of PD-pp yielded identical results as employing an algorithm [21], which makes possible to solve Eq. (1) directly by means of the generalized Newton method.

The contributions of the pure species $Z^{\alpha,0}(T)$ in Eq. (2) have been expressed by means of the SGTE system of reference states of pure elements, Eq. (7), and the description of the magnetic contributions $Z_k^{\alpha,\mathrm{mag}}(T,x^\alpha)$ has been merely reduced to the expressions of the pure species. For this purpose the algorithm from Sundman and Agren [8] has been chosen, consequently.

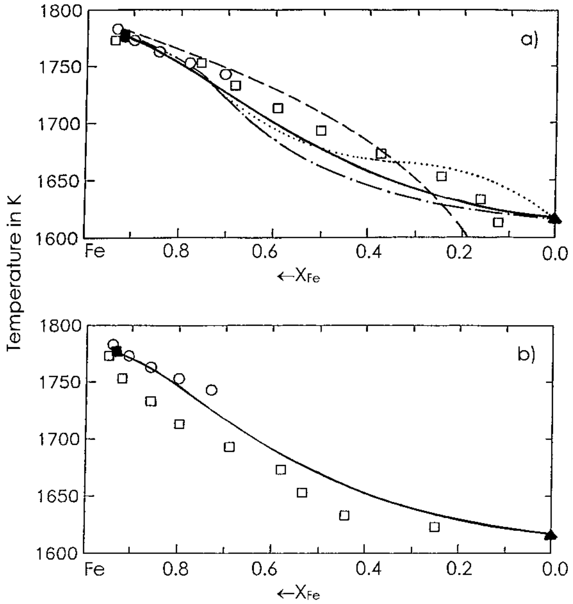

Fig. 7. The Fe content of the (a) liquid and, (b) fcc-solid phase of the three phase equilibrium liquid–fcc–bcc vs. temperature in the Fe–Ni–Cr system. Experimental data: Binary Fe–Ni [12]: ■; Binary Ni–Cr [21]: ▲; Jenkins et al. [31]: □; and by Schürmann and Voss [32]: ○; Calculations: This work: ———; Kundrat and Elliot [11]: - - -; Hillert and Qiu [10]: – · –; Lee [9]: . . . .

The computational construction of phase equilibria, as described above, yields the liquidus and fcc solidus in the three phase liquid–fcc–bcc equilibrium from 1618 K (binary Ni–Cr) up to 1775 K (binary Fe–Ni), according to the new description of the thermodynamic mixing behavior, as presented in Fig. 7. The corresponding results of experimental investigations performed by Jenkins et al. [31], and Schürmann and Voss [32] as well as the results of the previous assessments [9,10] are also plotted in Fig. 7. Comparison shows good agreement between the computations based on mass spectrometric investigations and the experimentally determined points.

As can be seen from Fig. 7 the assessment of Kundrat and Elliot [11] deviates distinctly from the common accepted liquidus equilibrium concentration of the binary boundary system Ni–Cr. The boundary of liquid phase in three phase liquid–fcc–bcc equilibrium as reported by Hillert and Qiu [10] shows especially in the medium temperature interval (1720–1640 K) more deviations from the experimental data than the corresponding determined in this work (Fig. 7). As described in the beginning, Lee [9] performed a revision of the thermodynamic assessment of the Fe–Ni liquid phase to obtain a better agreement with the experimental data on the bcc/liquid or fcc/liquid tie lines and liquidus temperatures in the Fe-rich region of the Fe–Ni–Cr ternary system than in the previous assessments. Fig. 7 shows that Lee [9] obtained a dependence of the liquidus temperatures on the Fe content in the three phase liquid–fcc–bcc equilibrium which is closer to the experimental data than in the two previous assessments, but not as close as the results of this work.

Fig. 8 shows the calculated isothermal section of the fcc–bcc equilibrium of the Fe–Ni–Cr system at 1473 K. The required mixing behavior of the bcc solid Fe–Ni–Cr alloys has been assessed by means of the results of the mass spectrometric investigations on liquid and on fcc solid Fe–Ni–Cr alloys. As can be seen from Fig. 8, the resultant phase boundaries agree well with the experimental data by Schultz and Merrick [33], Hasebe and Nishizawa [15] and Mundt and Hoffmeister [34].

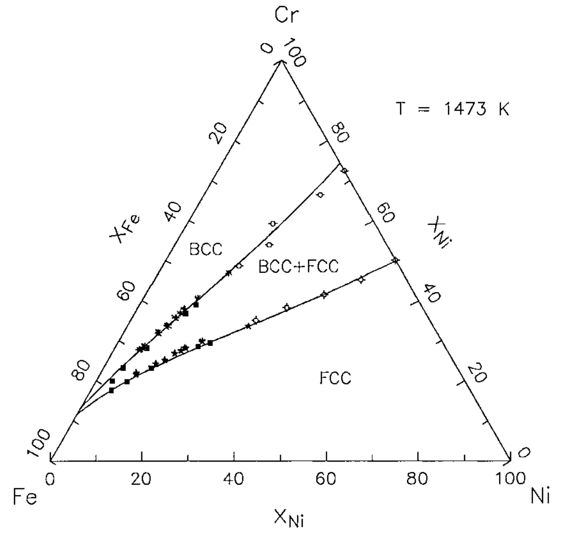

Fig. 8. The isothermal section of the Fe–Ni–Cr system at 1473 K for fcc–bcc equilibrium. This work: ———; Experimental data: Schultz and Merrick [33]: ○; Hasebe and Nishizawa [15]: □; and Mundt and Hoffmeister [34]: *.

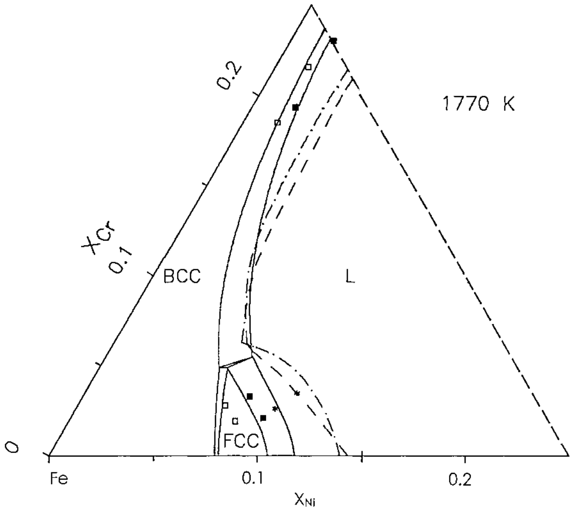

Fig. 9. The liquidus, fcc solidus, and bcc solidus equilibrium lines at 1770 K in the Fe–Ni–Cr system. Experimental data: Schürman and Voss [32], liquidus: □, solidus: □, Kundrat and Elliot [11] *; Calculations: This work: ———; liquidus line from Kundrat and Elliot [11]: - - -; liquidus line from Hillert and Qiu [10]: – · –.

Finally, the liquidus, fcc solidus and bcc solidus in equilibrium at 1770 K, according to the new description of the thermodynamic mixing behavior, are presented in Fig. 9 together with the results of experimental investigations performed by Schürmann and Voss [32], and Kundrat and Elliot [11]. Also plotted in Fig. 9 are the liquid phase boundaries as constructed by Kundrat and Elliot [11], and Hillert and Qiu [10]. As can be seen from Fig. 9, after Schürmann and Voss [32] the liquid–fcc solid two-phase region is shifted to alloys containing about 2 at% more Fe than reported by Kundrat and Elliot [11]. However, the melting and solidification temperatures of the binary Fe–Ni alloys cover only a small temperature interval of ca. 100 K over the whole range of compositions. And, the two binary boundary systems Fe–Ni and Cr–Fe show very narrow liquid–solid two-phase regions. Therefore, a more precise experimental determination of temperature dependence of the corresponding binary and ternary equilibrium compositions cannot be expected.

Following the improved binary Fe–Ni phase diagram, the liquid–fcc solid equilibrium concentration determined experimentally by Kundrat and Elliot [11], as well as the computed liquidus lines of these authors, and of Hillert and Qiu [10] are shifted a bit to much to the Ni corner of the Fe–Ni–Cr ternary phase diagram (Fig. 9). As can be seen from Fig. 9, by means of computations based on the mass spectrometric investigations a liquid–fcc solid two phase region is obtained which is in reasonable agreement with the results of both experimental investigations. Fig. 9 shows that the computations of this work yield a liquid–bcc solid two phase region which is in full agreement with the experimental results of Schürmann and Voss [32], whereas the corresponding liquidus of the assessments by Kundrat and Elliot [11], and Hillert and Qiu [10] show deviations.

6. Conclusions

The mass spectrometric measurements in the liquid phase, and in the restricted field of fcc-phase in the system Fe–Ni–Cr, together with the algebraic descriptions of the three binary boundary systems Fe–Ni of this work (based on [3]), Ni–Cr from [12], and Cr–Fe from [21] yield a simpler, but more effective algebraic description of the thermodynamic ternary mixing behavior, than the results of previous phase diagram assessments. These data make it possible to compute ternary phase equilibria in the system Fe–Ni–Cr, showing better agreement with the experimental phase-equilibria data than the assessments as reported by Kundrat and Elliot [11], Hillert and Qiu [10], and Lee [9]. Additional advantage of the mass spectrometric determined molar Gibbs energy is that the description of the magnetic contributions $Z_k^{\alpha,\mathrm{mag}}(T,x^\alpha)$ has been merely reduced to the expressions of the pure species.

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References

[1] W.A. Oates, H. Wenzl, T. Mohri, CALPHAD 20 (1996) 37–45.

[2] M. Hillert, Proc. of CALPHAD XXVI Conference, Palm Coast, Florida, May 11–16, 1997, 6e.

[3] J. Vrestal, P. Broz, J. Tomiska, Ber. Bunseng. 98 (1994) 1601–1607.

[4] J. Tomiska, CALPHAD 9 (1985) 15–28.

[5] H. Meschkowsky, Mathematisches Begriffswörterbuch. Mannheim, Bibliographisches Institut, 1966.

[6] J. Tomiska, CALPHAD 10 (1986) 91–100.

[7] J. Tomiska, Thermochim. Acta, 151 (1989) 145–158; 159–170.

[8] B. Sundman, J. Agren, J. Phys. Chem. Solids 42 (1981) 297–301.

[9] B.J. Lee, CALPHAD 17 (1993) 251–268.

[10] M. Hillert, C. Qiu, Metall. Trans. 21A (1990) 1673–1680.

[11] D.M. Kundrat, J.F. Elliot, Metall. Trans. 19A (1988) 899–908.

[12] J. Tomiska, Z. Metallkd. 76 (1985) 532–537.

[13] J. Tomiska, A. Neckel, Ber. Bunseng. 89 (1985) 1104–1109.

[14] A.T. Dinsdale, CALPHAD 15 (1991) 317–425.

[15] M. Hasebe, T. Nishizawa, National Bureau of Standards, SP 496, Proc. of Workshop, NBS, Gaithersburg, MD, Jan. 10–12, 1977, 911–954.

[16] J.M. Larrain, CALPHAD 4 (1980) 155–171.

[17] E.A. Owen, A.H. Sully, Phil. Mag. 27 (1939) 614–636.

[18] E.A. Owen, Y.H. Liu, J. Iron Steel Inst. 163 (1949) 132–137.

[19] J.-O. Anderson, B. Sundman, CALPHAD 11 (1987) 83–92.

[20] J. Tomiska, P. Broz, J. Vrestal, in: R.Y. Lin, Y.A. Chang, R.G. Reddy, C.T. Liu (Eds.), Design Fundamentals of High Temperature Composites, Intermetallics, and Metal-Ceramics Systems, TMS, Warrendale, PA, 309–321, 1996.

[21] J. Tomiska, K. Kopecky, M.S. Belegratis, C. Myers, Metall. Trans. 26A (1995) 259–265.

[22] P. Nash, Bull. Alloy Phase Diagrams 7 (1986) 466–476.

[23] J. Vrestal, J. Tomiska, J. Non-Cryst. Solids 156–158 (1993) 429–432.

[24] J. Vrestal, J. Tomiska, Mh. Chemie 124 (1993) 1099–1106.

[25] J. Vrestal, M.S. Belegratis, P. Broz, J. Tomiska, to be published.

[26] J. Tomiska, High Temp.-High Pressures 14 (1982) 417–422.

[27] P. Broz, J. Vrestal, J. Tomiska, Ber. Bunseng. 99 (1995) 802–806.

[28] J. Vrestal, P. Broz, J. Tomiska, Mh. Chemie 127 (1996) 135–142.

[29] J. Sopousek, A. Kroupa, R. Dojiva, J. Vrestal, CALPHAD 17 (1993) 229–235.

[30] L. Luksan, M. Siska, M. Tuma, UFO System. Prague, SVT CSAV, Res.Rep. No. V, 1990, 485.

[31] C.H.M. Jenkins, E.H. Bucknall, C. R Austin, G.A. Mellor, J. Iron Steel Inst. 136 (1937) 187–222.

[32] E. Schürmann, H-J. Voss, Arch. Eisenhüttenw. 48 (1977) 3–7.
[33] J.W. Schultz, H.F. Merrick, Metall. Trans. 3 (1972) 2479–2483.
[34] R. Mundt, H. Hoffmeister, Arch. Eisenhüttenw. 54 (1983) 253–256.
[35] D. Hansen, J.R. Freeman, J. Iron Steel Inst. 107 (1923) 301–314.
[36] T. Kase, Sci. Rep. Tohoku Imp. Univ. 14 (1925) 173–180.
[37] H. Bennek, P. Schafmeister, Arch. Eisenhüttenw., 5 (1931-2) 123–125.
[38] A. Hellawell, W. Hume-Rothery, Phil. Trans. Royal Society London A249 (1957) 417–459.
[39] D.M. Kundrat, Private Communication to [9].
[40] B. Predel, R. Mohs, Arch. Eisenhüttenw. 41 (1970) 143–149.