Monatshefte für Chemie 127, 135–142 (1996)

Monatshefte für Chemie
Chemical Monthly

Thermodynamic Parameters of Liquid Ternary $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ Alloys

J. Vrestal[1,2], **P. Broz**[1], and **J. Tomiska**[3]

[1] Institute of Theoretical and Physical Chemistry, Masaryk University Brno, CZ-61137 Brno, Czech Republic
[2] Institute of Physical of Materials ASCR Brno, CZ-61662 Brno, Czech Republic
[3] Institute of Physical Chemistry, University of Vienna, A-1090 Vienna, Austria

Summary. Computer-aided *Knudsen* cell mass spectrometry is used for thermodynamic investigations on liquid ternary $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ alloys. The thermodynamic excess properties have been determined by means of the Digital Intensity-Ratio (DIR) method. Liquid ternary $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ alloys are characterized by exothermic molar heats of mixing H^E, negative molar excess *Gibbs* energiesG^E, and negative molar excess entropies S^E. At 1850 K, the minimum H^E value is -3120 J/mol (42.3 at.% Fe), the minimum G^E value is -2540 J/mol (30 at.% Fe), and the minimum S^E value is -0.44 J/(mol K) (60 at. % Fe). At 1850 K, the thermodynamic activities of Fe show slight negative deviations from the ideal behaviour for alloys with a Fe-content of less than 75 at.%, and ideal behaviour for the Fe-rich alloys ($x_{Fe} > 0.75$).

Keywords. Mass spectrometry; Metals; Thermodynamics.

Thermodynamische Parameter flüssiger ternärer $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$-Legierungen

Zusammenfassung. Die Thermodynamik flüssiger ternärer $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$-Legierungen wurde mit Hilfe der computerunterstützten Knudsenzellen-Massenspektrometrie studiert. Die thermodynamische Auswertung der experimentellen Untersuchungen erfolgte nach der digitalen Intensitätsverhältnismethode (DIR). Flüssige ternäre $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$-Legierungen zeigen exotherme molare Mischungswärmen H^E, negative molare *Gibbs*sche Zusatzenergien G^E, und negative molare Zusatzentropien S^E. Bei 1850 K sind die Minimumswerte für H^E -3120 J/mol (42.3 At.% Fe), für G^E -2540 J/mol (30 At.% Fe) und für S^E -0.44 J/(mol K) (60 At.% Fe). Bei 1850 K zeigen die thermodynamischen Aktivitäten von Fe bei Legierungen mit einem Fe-Gehalt von höchstens 75 At.% leichte negative Abweichungen vom idealen Verhalten, die Fe-reichsten Legierungen ($x_{Fe} > 0.75$) verhalten sich hingegen nahezu ideal.

Introduction

Feature of the present study is the first investigation of the thermodynamic excess quantities of ternary $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ alloys in the liquid phase by means of a simple *Knudsen* cell mass spectrometer [1]. The thermodynamic evaluation of the experimental data has been performed by means of the Digital Intensity-Ratio

(DIR) – method, a further development of the well-tried enlarged Algebraic Intensity-Ratio technique [2, 3].

Mass Spectrometric Investigations

The relation between the partial vapor pressure p_j of the alloy components j = Fe, Ni Cr and the molar excess chemical potentials μ_j^E (Partial excess *Gibbs* energies G_j^E) of these components j in the liquid phase,

$$\mu_j^E(T,x_j) = RT(\ln(p_j(T,x_j)/(x_j p_j^o)(T)))) \qquad 1$$

where R is the gas constant, T is the temperature in K, x_j is the mole fraction of component j, and p_j^o is the vapor pressure of pure component j [2, 3], can be used as a convenient tool for the determination of the molar excess functions z^E (z = *Gibbs* energy G, heat of mixing H, entropy S; z = integral function Z, partial function Z_j) of the Fe–Ni–Cr alloy system.

Measuring Principle

The technique of *Knudsen* cell mass spectrometry is to determine the vapor pressures from the effusion of vaporized sample material out of an isothermal vessel which is called *Knudsen* cell [1–3]. Usually *Knudsen* cells are manufactured as (cylindrical) crucibles with a small knife-edge shaped orifice (0.5–1.5 mm diameter) in the lid. The *Knudsen* cell is employed as the gas source, and the effusing molecular beam is directed into the ionization chamber of the connected high-temperature mass spectrometer (compare Ref. [1]). The ion current intensities of the ionized vapor species are then detected by means of an electron multiplier.

Since the ion currents of all characteristic isotopes 1 of the alloy components j (j = Fe, Ni, Cr) are proportional to the corresponding partial pressure in the *Knudsen* cell, Eq. 1 can be transformed to a relation between the measured ion current intensity j_j and the molar excess chemical potential μ_j^E of this component j in the liquid phase inside the *Knudsen* cell:

$$\mu_j^E(T,x_j) = RT(\ln(J_j(T,x_j)T/D_I) - \ln x_j - \ln(D_j(T)p_j^o(T))) \qquad 2$$

where D_I and $D_j(T)$ are an instrumental geometric constant sensitivity factor and an isotope specific constant, respectively [2, 3]. The measured ion current intensities J_j can be fitted by means of Eq. 3

$$\ln(J_j(T,x_j)T/D_I) = d_j^o(x_j) + d_j^1(x_j)/T \qquad 3$$

where $d_j^o(x_j)$, $d_j^1(x_j)$ are best fit parameters within the temperature ranges in which the temperature dependence of the logarithms of the partial pressures of the components j may be assumed as inverse proportional to temperature.

The numerical value of the instrumental sensitivity factor D_I in Eq. 3 depends strongly on the actual position of the *Knudsen* cell with respect to the ion source [2, 4]. With liquid ternary $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ alloys, these difficulties can be overcome without any additional effort by determining the thermodynamic mixing effects from the differences of the molar excess chemical potentials of the two alloy components Fe and Cr, because these differences are independent from the D_I constant [2, 4].

For the presented mass spectrometric investigations it has been convenient to determine the ion current intensities of $^{56}Fe^+$ and $^{52}Cr^+$. Substituting Eq. 3 in Eq. 2 and forming the difference $\mu^E_{Fe} - \mu^E_{Cr}$ yields (x denotes dependence on both x_{Fe} and x_{Cr})

$$\mu^E_{Fe} - \mu^E_{Cr} = RT(d^o(x) + d^1(x)/T - \ln(x_{Fe}/x_{Cr})) - {}^tC^G_o(T) \qquad 4a$$

with

$$ {}^tC^G_o(T) = RT\ln((D_{Fe}\,p^o_{Fe}) - (D_{Cr}\,p^o_{Cr})], \qquad 4b$$

and

$$d^i(x) = d^i_{Fe}(x_{Fe}) - d^i_{Cr}(x_{Cr})\ (i = 0, 1). \qquad 4c$$

${}^tC^G_o(T)$ denotes the calibration constant for the two components Fe and Cr in the liquid ternary Fe–Ni–Cr system. The value of ${}^tC^G_o(T)$ is determined by the actual ratings of the experimental set-up [4].

Data Evaluation

Employing a suitable algebraic representation of the left hand side of Eq. 4a yields the desired best fit formula for the regression of the mass spectrometric data. Most useful is the representation of the ternary thermodynamic excess functions Z^E by

$$Z^E = {}^tZ^E + {}^{Fe,Cr}Z^E + {}^{Cr,Ni}Z^E + {}^{Ni,Fe}Z^E, \qquad 5a$$

where ${}^tZ^E$ is called "ternary interaction term", a homogeneous polynomial in all three mole fractions x_j (${}^tC^Z_n$ adjustable ternary parameters; n = 1, 2, $\cdots$) [2, 4]:

$$ {}^tZ^E = x_{Cr}x_{Ni}x_{Fe}\,({}^tC^Z_1 + ({}^tC^Z_2\,x_{Fe} + {}^tC^Z_3\,x_{Ni} + {}^tC^Z_4\,x_{Cr}) + \cdots). \qquad 5b$$

In Eq. 5a the terms ${}^{j,k}Z^E$ denote the contributions of the three binary systems j–k (j, k = 1, 2, 3; 1 = Fe, 2 = Ni, 3 = Cr) which are represented by means of the Thermodynamic Adapted Power series (TAP-series) [5]

$$ {}^{j,k}Z^E(x) = x_j \sum_{n=1}^{N} {}^{j,k}C_n\,x^n_k, \qquad 5c$$

where N is the number of adjustable parameters ${}^{j,k}C_n$. The *Weierstrass* approximation theorem guarantees that the approximation of molar excess functions can be carried out over the entire range of composition by means of Eq. 5, sufficient high numbers of parameters supposed [5]. In case of a necessary exchange of the components (for $x_k \to x_j$ and $x_j \to x_k$: ${}^{j,k}C_1 \to {}^{k,j}C_n$), the values of the new TAP-parameters ${}^{k,j}C_n$ can be computed from the given ${}^{j,k}C_1$-values after [5] by

$$ {}^{k,j}C_n = \sum_{l=1}^{N} {}^{j,k}C_l\,(-1)^{l-n}\binom{l-1}{n-1}\ (n = 1, 2, \cdots, N). \qquad 6$$

The temperature dependence of the G^E-values makes possible to determine the molar heat of mixing H^E and the molar excess entropy S^E in accordance with Eq. 3 by

$$G(T) = H - TS. \qquad 7$$

Experimental

The *Knudsen* cell mass spectrometric system employed in this work was described recently [1, 6]. The simple monopole instrument model MX 7304 (Electron, Ukraine) having a mass range of 2–200 a.m.u. was modified in the Institute of Physics of Materials ASCR. The *Knudsen* cell part of the combination with the mass spectrometer consists of an alumina effusion cell containing the sample which was closed by an alumina lid having an orifice of 1.2 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/PtRh 10 thermocouple, calibrated by means of the melting points of several pure metal samples [6]. Ions were formed by means of a a 15 eV electron beam having a current of 50 mA.

A section with constant ratio of the mole fractions $x_{Cr}/x_{Ni} = 1/5$ has been investigated. The alloys were prepared by induction melting in an argon atmosphere in a centrifugal casting equipment. Zone melted iron (99.95%; 0.01% C), electrolytic chromium (99.99 wt.% Cr; Ni, Fe the rest), and nickel (Johnson & Matthey Chem. Ltd. 99.99%; Si, Fe as impurities) were used as base materials. Finally, the samples were homogenized by casting in the cold cylindrical mold. Electron microanalysis confirmed the homogeneity and the composition of prepared samples.

The temperature range covered in these investigations was about 70 to 120 K. To prevent crystallization of the sample, the lower temperature limit was varied in relation to the composition of the sample. Data were collected by scanning the principal isotope peak for one component 10 times and 4 times for background and the same for the other components. The temperature was then lowered about 10–15 K, until the lower end of the temperature interval was reached. The vacuum system consist of ion-discharge and ion-sublimation pumps and ensure an oil-free vacuum in the order of 10^{-6} Pa. No oxidation of the sample surface was observed after the experiments. Check measurements of the sample composition after experiments by means of an electron microanalyser proved good agreement of all ingots with the original sample compositions.

Results and Discussion

In 8 runs, 4 different alloy compositions have been investigated mass spectrometrically (Table 1). The deviations of the experimental data from the computed regression lines (Eq. 3) were in no case higher than 5%. The constants d^o and d^1 summarized in Table 1 were computed according to Eq. 4c from the corresponding $d^i_{Cr}(x_{Cr})$ and $d^i_{Fe}(x_{Fe})$ values of Eq. 3 (i = 0, 1). The thermodynamic data of the liquid phase of the three binary systems are well established in the literature: the TAP parameters of liquid Fe–Ni–alloys [7] have been determined mass-spectrometrically, and those of the liquid binary alloy systems Fe–Cr [3] and Ni–Cr [8] have been assessed by means of phase boundary calculations based upon experimental data of the *bcc* and *fcc* phases. The G^E-values of all three binary boundary systems can be used successfully for the calculations of the binary phase diagrams [3, 7, 8]. The regression problem is, therefore, reduced to the adjusting of the ternary parameters ${}^tC_n$ [5, 7]. For the mean temperature $T = 1850$ K it is shown in Fig. 1 that a satisfying best fit is achieved using the simple homogeneous polynomial of third order as ternary interaction term (1 adjustable parameter).

The best data yield the molar excess *Gibbs* energy G^E listed in Table 2 and displayed in Fig. 2 for the investigated section ($x_{Cr}/x_{Ni} = 1/5$) at 1850 K. Figure 3 shows the molar heats of mixing H^E for 1850 K along the investigated section ($X_{Cr}/x_{Ni} = 1/5$). Numerical H^E-data as well as the molar excess entropies S^E of the liquid ternary $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ alloys are listed in Table 2. The resulting ther-

Table 1. Constants d^0 and d^1 of Eq. 4c, the relation between the ion current ratios $\ln(J_{Fe}/J_{Cr})$ and the inverse sample temperature of the investigated liquid ternary $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ alloys (x_{Ni},x_{Cr} mole fractions of nickel and chromium, respectively)

Nr.	x_{Ni}	x_{Cr}	d^0	d^1
1	0.302	0.057	0.400	950
2	0.302	0.057	0.546	789
3	0.440	0.080	0.145	474
4	0.440	0.080	0.129	435
5	0.558	0.111	−0.386	226
6	0.558	0.111	−0.361	109
7	0.685	0.138	−1.179	155
8	0.685	0.138	−1.068	16.5

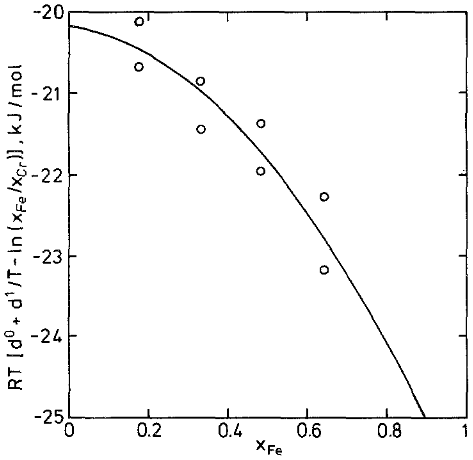

Fig. 1. $RT(d^0 + d^1/T - \ln(x_{Fe}/x_{Cr})$ as a function of the mole fraction x_{Fe} of liquid ternary $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ alloys at 1850 K (experimental points o; regression curve Eq. 4——)

modynamic activities of iron, a_{Fe}, along the investigated section ($x_{Cr}/x_{Ni} = 1/5$) are shown in Fig. 4 and listed in Table 2.

The DIR method also allows to check the quality of the experimental results by determining the heats of mixing H^E by means of Eq. 8

$$(H^E_{Fe} - H^E_{Cr}) + {}^tC^H_o(T) = (Rd^1(x)) \qquad 8$$

where ${}^tC^H_o$ (T) is the corresponding ternary calibration constant for the two components Fe and Cr [3]. The results of these calculations are presented in Fig. 5. The small scattering of the experimental data indicates satisfactory accuracy of the best fit data achieved in this work. The H^E values resultant from the best fit based upon Eq. 8 are necessarily identical with the H^E data computed from the temperature dependence of the molar excess Gibbs energy G^E by means of Eq. 7 [5, 7].

The mass spectrometric investigations of this work yielded exothermic molar heats of mixing H^E, negative molar excess *Gibbs* energies G^E, and negative molar excess entropies S^E for all liquid ternary $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ alloys at 1850 K. At

Table 2. Molar heats of mixing H^E, molar excess entropies S^E, and molar excess *Gibbs* energies G^E as well as the thermodynamic activities of Fe, a_{Fe}, of the investigated liquid ternary $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ alloys at 1850 K obtained by best fit of the mass spectrometric data (x_{Cr},x_{Fe} mole fractions of chromium and iron, respectively)

x_{Cr}	x_{Fe}	G^E (J/mol)	H^E (J/mol)	S^E (J/(mol K))	a_{Fe}
0.15	0.1	−2240	−1620	0.34	0.07
0.13	0.2	−2480	−2420	0.031	0.16
0.12	0.3	−2540	−2880	−0.19	0.26
0.10	0.4	−2450	−3060	−0.33	0.36
0.08	0.5	−2240	−3000	−0.41	0.47
0.07	0.6	−1920	−2730	−0.44	0.58
0.05	0.7	−1510	−2280	−0.42	0.69
0.03	0.8	−1040	−1670	−0.34	0.80
0.02	0.9	− 530	− 910	−0.21	0.90
0.00	1.0	0	0	0	1.00

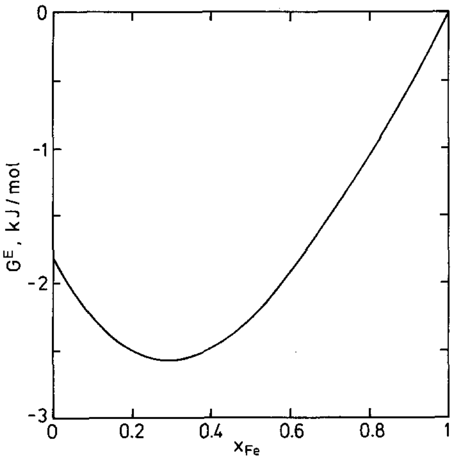

Fig. 2. Molar excess *Gibbs* energy G^E as a function of the mole fraction x_{Fe} of liquid ternary $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ alloys at 1850 K

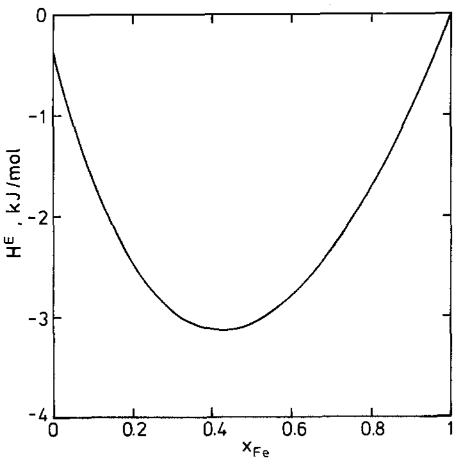

Fig. 3. Thermodynamic activity a_{Fe} as a function of the mole fraction x_{Fe} of liquid ternary $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ alloys at 1850 K

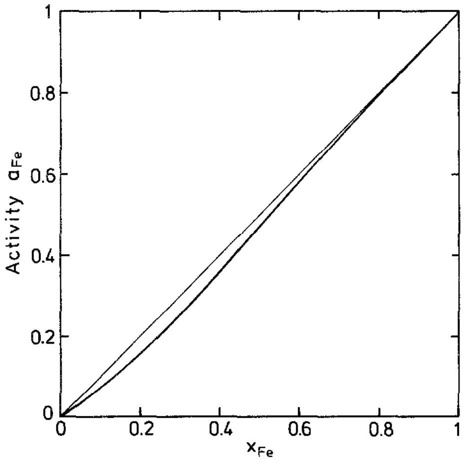

Fig. 4. Molar heat of mixing H^E as a function of the mole fraction x_{Fe} of liquid ternary $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ alloys at 1850 K

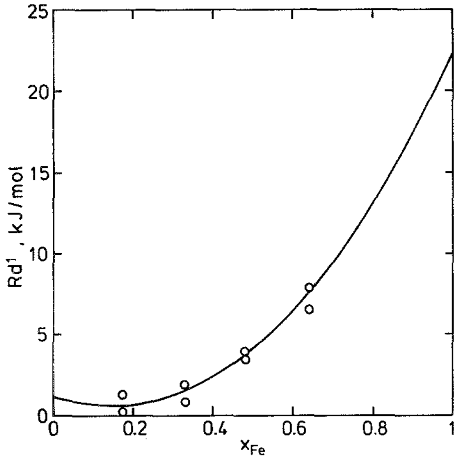

Fig. 5. (Rd^1) as a function of the mole fraction x_{Fe} of liquid ternary $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ alloys at 1850 K (experimental points o; regression curve Eq. 8——)

1850 K, the minimum H^E value is −3120 J/mol (42.3 at.% Fe), the minimum G^E value is −2540 J/mol (30 at.% Fe), and the minimum S^E value is −0.44 J/(mol K) (60 at.% Fe). The present work yielded Fe-activities for liquid ternary $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ alloys which show slight negative deviations from the ideal behavior for alloys with $x_{Fe} < 0.75$, and ideal behaviour for alloys with $x_{Fe} > 0.75$ (Fig. 4). The mass spectrometric investigations of this work yielded the first experimental data for the thermodynamic mixing behaviour of liquid $Fe_{1-x}(Ni_{5/6}Cr_{1/6})_x$ alloys.

Acknowledgements

Grateful acknowledgement is made for the financial support by the *Action Program Austria–Czech Republic, Wissenschafts- und Erziehungskooperation.*

References

[1] Vrestal J, Tomiska J (1993) Monatsh Chem **124**: 1099

[2] Tomiska J, Belegratis MS, Kopecky K, Neckel A (1993) J Non-Crystallines **156–158**: 425

[3] Vrestal J, Broz P, Tomiska J (1994) Ber Bunsenges Phys Chem **98**: 1601
[4] Tomiska J (1982) High Temp High Pressures **14**: 417
[5] Tomiska J (1989) Thermochim Acta **151**: 145; **151**: 159
[6] Vrestal J, Tomiska J (1993) J Non-Crystallines **156–158**: 429
[7] Tomiska J (1985) Z Metallkd **76**: 532
[8] Tomiska J, Kopecky K, Belegratis MS, Myers C (1995) Met Trans A **26A**: 269

Received August 18, 1995. Accepted September 12, 1995