Monatsh Chem (1987) 118: 31—41

Monatshefte für Chemie
Chemical Monthly

Enthalpies of Mixing in the Iron—Manganese System by Direct Reaction Calorimetry**

Rainer Kubitz*** and **Frederick Henry Hayes***

Department of Metallurgy and Materials Science, University of Manchester/UMIST, Manchester M1 7HS, England

(Received 8 May 1986. Accepted 23 May 1986)

Integral enthalpies of mixing of solid iron—manganese alloys have been obtained at 1 443 K, 1 073 K and 873 K using a modified Dench-type calorimeter. The modifications in calorimetric technique required to cope with the high volatility of manganese are described. Results are presented and discussed.

(Keywords: Calorimetry; Enthalpies of mixing; Iron-manganese alloys)

Mischungsenthalpien im Eisen—Mangan-System mittels direkter Reaktionskalorimetrie

Mit Hilfe eines adiabatischen Kalorimeters des von *Dench* beschriebenen Typs wurden Mischungsenthalpien fester Eisen—Mangan-Legierungen bei 1 443 K, 1 073 K und 873 K bestimmt. Die Modifikationen, die am Kalorimeter notwendig waren, um mit einem so flüchtigen Metall wie Mangan arbeiten zu können, sind beschrieben und die Ergebnisse diskutiert.

Introduction

Measured thermodynamic quantities for binary alloy systems are required to define quantitatively the stabilities of alloy phases. Such data, together with phase boundary measurements, provide the basis for thermochemical assessments which are used for example in computer calculations of phase relations in multicomponent systems [1]. Over the past twenty years or so the technique of high-temperature adiabatic solid-

---

** Dedicated to Prof. Dr. *Kurt L. Komarek* on the occasion of his 60th birthday on 23rd June 1986.

*** Present Address: International Nickel Company Ltd., Birmingham, England.

state direct-reaction calorimetry has played an important role in the measurement of enthalpies of mixing for a wide range of transition metal alloy systems. Following the pioneering work of *Dench* with *Kubaschewski* [2] on Fe—Ni, Cr—Ni and Cr—Fe alloys in 1963, enthalpies of mixing of several other binary systems including Cr—Mo [3], Co—Ni [4], Cu—Ni [5], Co—Fe [6], Fe—V [7], Co—V [8], Co—Cr [9], Mo with Fe, Co and Ni [10], Fe—Ti and Co—Zr [11] have been obtained via this technique. In addition a number of ternary systems, for example Au—Pd—Pt [12] Co—Fe—Ni [13], Cr—Fe—Ni [14], Co—Cr—Fe [15] and Mo with Fe, Co, Ni [16] have also been studied in this manner. In this paper we describe the extension of this technique to the study of manganese alloys and we report our results for the iron—manganese system. Data for the Fe—Mn system are of interest since manganese is present to some extent in virtually all ferrous materials. Also, in recent years manganese has been used as a significant alloying addition in some commercial steel compositions [17]. Thus, reliable data are required for all binary combinations of manganese with alloying elements commonly used in steels.

The literature contains several reports of *Gibbs* energy studies for the iron—manganese system [18–22]. However, as far as we are aware, there has been only one previous attempt to measure enthalpies of mixing of Fe—Mn directly, namely that by *Kendall* and *Hultgren* [23] who used acid solution calorimetry. They investigated four compositions on the iron-rich side of the system. From results obtained at 294 K enthalpies of mixing at 1 400 K were calculated using heat capacity data. The aim of the present work was to obtain integral enthalpies of mixing for the solid phases in the Fe—Mn system by direct reaction in order to provide a sound basis for a full thermodynamic assessment of this system. The high volatility of manganese compared with that of other transition metals makes such measurements difficult and presents challenging problems to the experimentalist. Thus the calorimetric technique employed in the earlier work listed above had to be modified somewhat to cope with this problem. In addition, for a few experiments the calorimeter was modified further to enable specimens to be heated to temperatures above the liquidus curve to confirm complete reaction.

Experimental

Materials

The materials used were (a) sponge iron powder grade MH 300.25 kindly supplied by Hoganas Ltd. (typical analysis H_2-loss 0.2%, C 0.01%, SiO_2 0.33%, Mn 0.05%, S 0.015%, P 0.015%) and (b) electrolytic manganese chips supplied by Alfa Products Ltd. (Mn 99.8%, S 0.02%, Fe 0.001%, Si 0.001%). The manganese chips were ground in a commercial hammer mill installed in a glove box swept by high purity argon gas. All specimen powders were sieved and the fraction passing a 45 μm sieve aperture was retained for calorimetric sample preparation. Surface oxide was reduced by heating the iron powder in a stream of purified hydrogen at 773 K for one hour. Powders were weighed and mixed for 16 hours in a rotary mixer and compacted in a hardened steel die using a hydraulic pressure.

The Calorimeter

(a) General

The design and operating principles of the calorimeter are similar to those described by *Dench* [2, 24]. The calorimeter consists of the following parts: specimen capsule, specimen heater, adiabatic enclosure, furnace, water-cooled vacuum chamber and electronic control and measurement circuitry. A solid sample, consisting of about 0.8 of a mole, made by cold compaction of an intimate mixture of the component metal powders, is heated in the calorimeter under adiabatic conditions from a temperature T_1, at which the rate of alloying is negligibly low, to a temperature T_2, at which alloying goes to completion within about ten minutes. The electrical energy q_1 dissipated by the heater in this adiabatic heating operation during which the alloy is formed directly from the components is measured. In a separate experiment the energy q_2 required to heat the component metals from T_1 to T_2 without reaction is also obtained either (a) by experiment with a composite specimen in which the pure components are isolated from each other or (b) by calculation from the results of experiments with the pure components. The integral enthalpy of mixing of the alloy at T_2 is then obtained from the difference between the two energy inputs q_1 and q_2 adjusted for one mole of alloy. In addition by measuring in a separate experiment the energy q_3 required to heat the fully alloyed sample over exactly the same temperature range, one also obtains the enthalpy of mixing of the alloy at the safe temperature T_1 from the difference between q_1 and q_3. Heat inputs to the calorimeter were measured directly using a calibrated Joulemeter (Ferranti type FN 12 ± 0.5%) and a constant voltage transformer (Advance Voltstat 12 V). Prior to experiments with Fe—Mn alloys, the satisfactory operation of the calorimeter was demonstrated by a series of measurements on Fe—Co alloys. Results were in good agreement with those given by *Müller* and *Hayes* [6].

(b) Achieving Adiabatic Conditions

Dench's original design [2] employed three differential thermocouples positioned with their junctions in the equatorial plane of the specimen, symmetrically spaced at 120 degree intervals with one junction each immediately inside and immediately outside the adiabatic enclosure. These differential couples were connected in series and the net signal used to control the furnace current [24]. In the present work in which an electronic three term controller [Gulton, West Instruments, digital set point Viscount (DPID-T-U) in conjunction with a thyristor stack (Gulton, KR 12)] were used, it was found after a series of experiments that better control was achieved when just one differential thermocouple was used rather than three. This enabled the other thermocouples to be used to assess the temperature distribution within the specimen. The results of these experiments showed (i) that all points situated at an equal distance from the central axis of the calorimeter in the equatorial plane have the same temperature within experimental error (± 0.5 K) and (ii) that the thermocouple located between the specimen and the adiabatic enclosure indicates a temperature only marginally higher (0.5 ± 0.5 K) than that of the specimen itself. This relation has been verified even for temperatures as low as 763 K.

(c) Changes Required for Manganese Alloys

In general the calorimeter used in the present work followed the design of *Dench* [2] very closely. However due to the high volatility of manganese, the specimen had to be completely isolated to prevent rapid contamination of the calorimeter particularly of the ceramic electrical insulation. Thus an extra specimen container was introduced in addition to the folded tantalum capsule used by *Dench* and subsequent NPL researchers.

This extra specimen container consisted of a stainless steel tube (i.d. = 20 mm, o.d. = 21 mm, length 30 mm) to which a stainless steel lid was welded. Two stainless steel tubes (i.d. = 2.5 mm, o.d. = 3.5 mm, length 31 and 25 mm) were welded into the lid to accommodate the heater and the absolute thermocouple respectively. The absolute thermocouple tube had a closed lower end whilst the heater tube was open at both ends, the heater tube projected 1 mm beyond the lower end of the enclosure.

Before the specimen was slid into position from the lower end, the walls and the top of the steel container were lined with 0.05 mm thick tantalum sheet, which was also wrapped around the heater and thermocouple tubes. Then the specimen was inserted and its base was covered with a 0.05 mm thick tantalum disc in which there was a hole for the heater tube. The tantalum sheet covering the container walls was folded in upon this disc so that the specimen was completely wrapped up in tantalum inside the container thus making no direct contact with the steel. A stronger close-fitting disc of 0.13 mm thick tantalum was then pressed into the container tube from below thus forming the base of the container and preventing the specimen from falling out. (Originally, both threaded and press-fit stainless steel bases were used but it was found to be virtually impossible to remove these after heating to the safe temperature. Thus they could not be used on a routine basis.) The stainless steel container was now itself slid into a capsule folded from 0.05 mm thick tantalum sheet. This capsule served as a screen against evaporation from the container material itself.

The mass of the stainless steel container was about 18 g and that of the tantalum envelopes about 6 g. The calorimeter blanks, i.e. the enthalpy increments of the calorimeter itself over the relevant temperature ranges, were determined by heating the calorimeter with an empty specimen container. Even with this extra specimen container frequent changes of the Pt/Pt — 13% Rh thermocouples and the alumina insulation were necessary to maintain satisfactory operation of the calorimeter.

The tantalum used for the specimen capsules and other calorimeter parts was supplied by Metallwerk Plansee, Austria, as was the molbdenum sheet used for the furnace.

(d) Completion of Reaction

Clearly for valid enthalpy of mixing data to be obtained using the present experimental technique, alloying must go to completion during the course of the measurement. To check this experimentally two methods were used. Firstly the equiatomic 50 mol% composition specimen after an alloying run in the calorimeter was examined using X-ray diffraction. No evidence of the presence of unalloyed iron or manganese was found in the diffraction patterns thus indicating complete alloying within the sample. Secondly two alloying runs were taken beyond the liquidus temperature for the 80 atomic percent manganese samples. For these experiments a sealed alumina crucible was used as the specimen container in the calorimeter. As can be seen from Fig. 3 the results of these experiments are in agreement with those where alloying occurred at 1 473 K showing that alloying is in fact complete at 1 473 K.

(e) Accuracy of Results

The overall accuracy in the present work is expected to be similar to that given in previous error estimates e.g. by *Kubaschewski* and *Grundmann* [15] namely $\pm 400\,\mathrm{J\,mol^{-1}}$. For specimens rich in manganese the overall error is however likely to be substantially higher. Despite the higher affinity of manganese for oxygen, heat effects arising from transfer of oxygen from iron to manganese is not thought to be a problem. Any transfer that does occur is expected to be largely complete at the safe temperature, since no evidence was found for a negative intercept at pure iron in the enthalpy of mixing versus composition curves.

Results

Enthalpy Increment Determinations

In the course of the present experiments the enthalpy increments given below for iron and manganese were determined. Each value is the average of three or four measurements. With a nickel sample a standard deviation of $\pm 59\,\mathrm{J\,mol^{-1}}$ was obtained with ten measurements over the same temperature range.

(i) Iron

$$H_{\mathrm{Fe}}(1\,443\,\mathrm{K}) - H_{\mathrm{Fe}}(873\,\mathrm{K}) = 26\,132\,\mathrm{J\,mol^{-1}}$$

$$H_{\mathrm{Fe}}(1\,073\,\mathrm{K}) - H_{\mathrm{Fe}}(873\,\mathrm{K}) = 10\,528\,\mathrm{J\,mol^{-1}}$$

(ii) Manganese

$$H_{\mathrm{fcc\text{-}Mn}}(1\,393\,\mathrm{K}) - H_{\alpha\text{-}\mathrm{Mn}}(873\,\mathrm{K}) = 24\,401\,\mathrm{J\,mol^{-1}}$$

$$H_{\beta\text{-}\mathrm{Mn}}(1\,073\,\mathrm{K}) - H_{\alpha\text{-}\mathrm{Mn}}(873\,\mathrm{K}) = 9\,483\,\mathrm{J\,mol^{-1}}$$

Enthalpies of Mixing

The present series of measurements have enabled the following enthalpies of mixing to be obtained.

$$(1-x)\,\mathrm{Fe\,(fcc)} + x\mathrm{Mn\,(fcc)} \rightarrow \mathrm{Fe}_{(1-x)}\mathrm{Mn}_x\,\mathrm{(fcc)} \qquad \text{(a)}$$
$$T = 1\,443\,\mathrm{K}$$

for $0.05 \leqslant x \leqslant 0.90$.

Results are given in Table 1 and Fig. 1.

Table 1. *Enthalpies of mixing of* Fe—Mn *alloys at 1443 K.* Standard states: Fe (fcc), Mn (fcc), alloy (fcc); $T = 1\,443$ K except where indicated

x_{Mn}	ΔH_m/J mol^{-1}
0.05[a]	—286
0.15	—1 886
0.20	—2 183
0.20	—2 243
0.30	—3 052
0.30[a]	—2 500
0.40[b]	—2 624
0.40[a]	—2 850
0.50	—2 970
0.50[a]	—2 812
0.50	—2 813
0.60	—1 792
0.70	—2 054
0.80	—1 464
0.80	—862
0.90	—48
0.90	—1 097

[a] $T = 1\,423$ K; [b] $T = 1\,381$ K (0.75 hour).

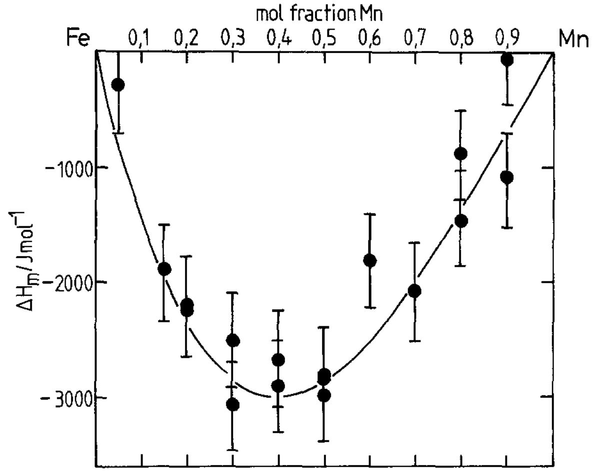

Fig. 1. Enthalpies of mixing of Fe—Mn alloys at 1 443 K. Standard states are fcc Fe, fcc Mn and fcc alloys

$$(1-x)\,\mathrm{Fe\,(bcc)} + x\mathrm{Mn}\,(\alpha) \rightarrow \mathrm{Fe}_{(1-x)}\,\mathrm{Mn}_x\,\mathrm{(fcc)} \qquad \text{(b)}$$
$$T = 873\,\mathrm{K}$$

and $(1-x)\,\mathrm{Fe\,(fcc)} + x\mathrm{Mn\,(fcc)} \rightarrow \mathrm{Fe}_{(1-x)}\,\mathrm{Mn}_x\,\mathrm{(fcc)}$

$$0.15 \leqslant x \leqslant 0.50$$

Results are given in Table 2 and Fig. 2.

$$(1-x)\,\mathrm{Fe\,(bcc)} + x\mathrm{Mn}\,(\beta) \rightarrow \mathrm{Fe}_{(1-x)}\,\mathrm{Mn}_x\,(\beta) \qquad \text{(c)}$$
$$T = 1\,073\,\mathrm{K}$$

for $0.7 \leqslant x \leqslant 0.9$.

Results are given in Table 3 and Fig. 3.

N. B. To obtain Mn in fcc reference state at 1 443 K (or 1 423 K) the enthalpy increment for pure Mn was measured to 1 393 K and extrapolated to 1 443 K (or 1 423 K) using:

$$C_p(\mathrm{fccMn}) = [6.03 + (3.56\cdot10^{-3})T - (443\cdot10^5)T^{-2}]4.184\,\mathrm{JK^{-1}mol^{-1}}$$

(taken from *Barin* and *Knacke* [25]).

Thus

$$(H_{1443\,(1423)} - H_{873})_{\text{fcc-Mn}} = \underbrace{(H_{1393} - H_{873})_{\text{fcc-Mn}}}_{\textit{measured}} + \int_{1393}^{1443\,(1423)} C_p(\mathrm{fcc\,Mn})\,\mathrm{d}T$$

Table 2. *Enthalpies of mixing of* Fe—Mn *alloys at 873 K*. Standard states: Fe (bcc), Mn (α), alloy fcc; $T = 873\,\mathrm{K}$

x_{Mn}	$\Delta H_m/\mathrm{J\,mol^{-1}}$	$\Delta H_m{}^*/\mathrm{J\,mol^{-1}}$ [a]
0.1	(4 833)[b]	(—975)[b]
0.15	3 008	—2 724
0.20	2 865	—2 791
0.20	2 817	—2 839
0.20	2 906	—2 750
0.30	2 751	—2 752
0.30	2 434	—3 069
0.30	2 729	—2 774
0.40	2 537	—2 814
0.40	2 146	—3 205
0.50	1 971	—3 227
0.50	1 852	—3 346

[a] $\Delta H_m{}^*$ = fcc Fe + fcc Mn → fcc alloy (last column calculated from second column) with the aid of transformation enthalpies given by *Hultgren* et al. [27] and the magnetic enthalpy contribution of iron given by *Kubaschewski* et al. [28].

[b] Two phase (bcc + fcc) alloy.

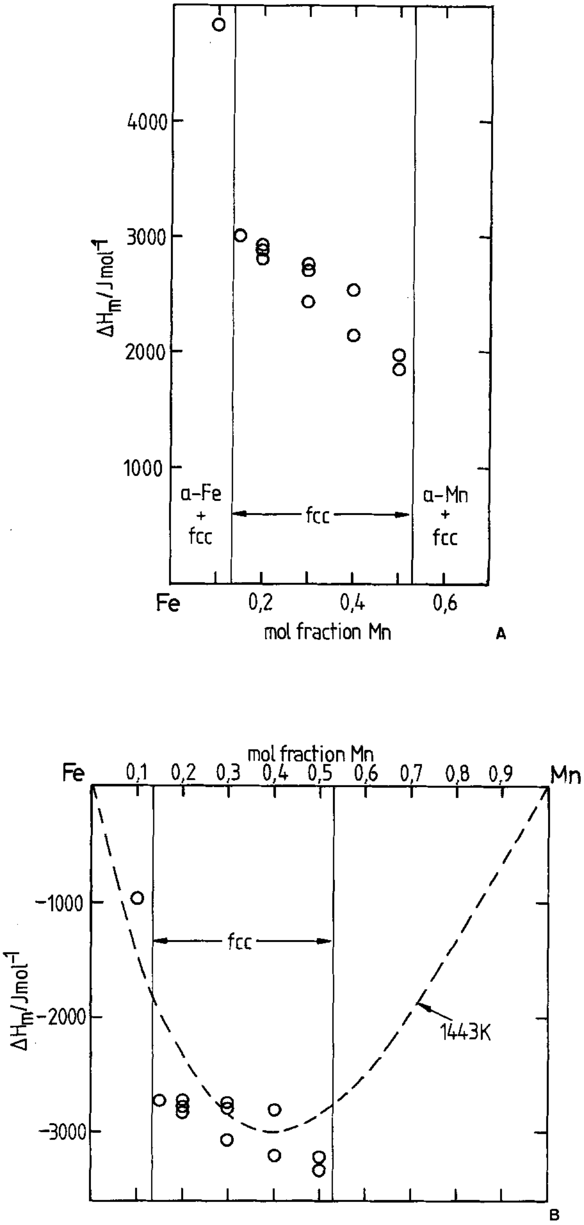

Fig. 2*A*. Enthalpies of mixing of Fe—Mn alloys at 873 K. Standard states are bcc Fe, α-Mn and fcc alloys. *B* Enthalpies of mixing of Fe—Mn alloys at 873 K. Standard states are fcc Fe, fcc Mn and fcc alloys

Table 3. *Enthalpies of mixing of* Fe—Mn *alloys at 1073 K.* Standard states: Fe (bcc), Mn (β), alloy (β); T = 1 073 K

x_{Mn}	ΔH_m/J mol^{-1}
0.7	—1 693
0.7	—1 047
0.8	—1 298
0.8	—686
0.9	—389

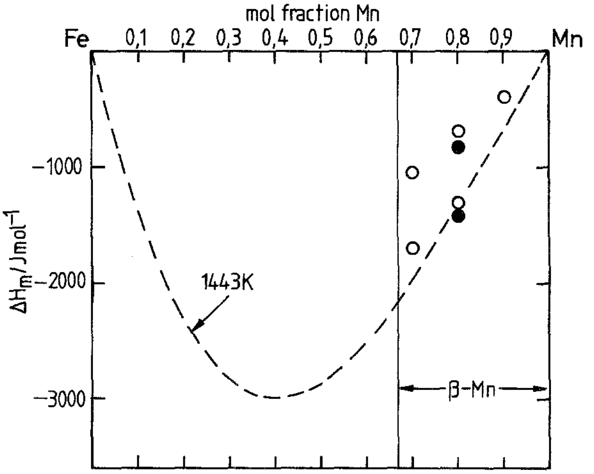

Fig. 3. Enthalpies of mixing of Fe—Mn alloys at 1 073 K. Standard states are bcc Fe, β-Mn and β-alloys. ○ alloying at 1443 K; ● alloying above liquidus temperature

Discussion

Comparison of Present Results with Previous Work

There has been only one previous attempt to measure enthalpies of mixing of Fe—Mn alloys directly: the work of *Kendall* and *Hultgren* [23] using acid solution calorimetry. They investigated four compositions on the iron-rich side and from their results they calculated enthalpies of mixing at 1 400 K. These are compared with the present results in Fig. 4 where it is seen that the enthalpies of mixing obtained in the present work are appreciably less negative than those of the previous work. *Kendall* and *Hultgren* give an uncertainty of $\pm$ 1 255 J mol^{-1} whilst the error in the present work for the temperature and composition range under con-

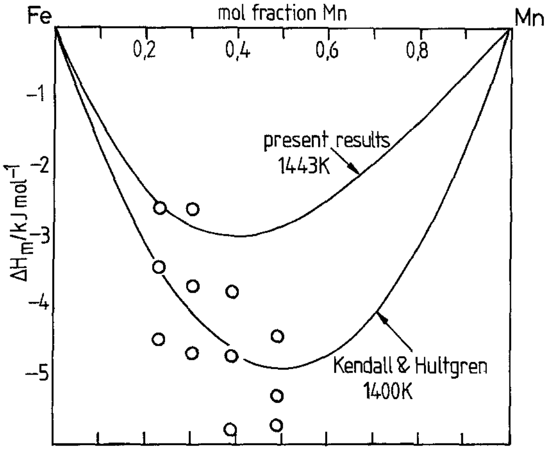

Fig. 4. Comparison of present results at 1 443 K with previous work. ○ are *Kendall* and *Hultgren*'s results at 1 400 K [23]

sideration could be ± 700 J mol^{-1} under the worst circumstances envisaged.

The present results for the enthalpy of mixing of fcc Fe—Mn from fcc metals at 1 443 K may be described by the equation

$$\Delta H_m^{\text{fcc}} = x_{\text{Fe}} x_{\text{Mn}} [-11\,458 - 5\,208 (x_{\text{Fe}} - x_{\text{Mn}})] \text{ J mol}^{-1}$$

with a mean deviation of 172 J mol^{-1}.

The Fe—Mn *System*

Published *Gibbs* energy values for the Fe—Mn system [18–22] exhibit considerable scatter. Nevertheless the results of *McHugh* [18], *Benz* [19], *Paxton* [20], *Hawkins* [21] and *Eremenko* [22] do show at least a qualitative agreement. These values taken together with the present enthalpies of mixing at the assessed Fe—Mn phase diagram data [26] now allow a complete assessment to be made of the thermodynamic properties of the iron—manganese system. A previous assessment by *Kaufman* [29] had only the limited calorimetric data of *Kendall* and *Hultgren* [23] and Second Law evaluations available.

Acknowledgements

The authors wish to thank Prof. *K. M. Entwistle* and Prof. *Edwin Smith* for the provision of laboratory space and facilities and to Hoganas Ltd. for donating the iron powder.

References

[1] *Kaufman L, Nesor H* (1973) Z Metallk 64: 249
[2] *Dench WA* (1963) Trans Faraday Soc 59: 1279
[3] *Kubaschewski O, Chart TG* (1964) J Inst Metals 93: 329
[4] *Hayes FH, Müller F, Kubaschewski O* (1970) J Inst Metals 98: 20
[5] *Müller F, Elford L* (1969) Ber Bunsengesellschaft 73: 601
[6] *Müller F, Hayes FH* (1971) J Chem Therm 3: 599
[7] *Spencer PJ, Putland FH* (1973) J.I.S.I. 1973: 293
[8] *Spencer PJ, Putland FH* (1976) J Chem Therm 8: 551
[9] *Bell HB, Hajra JP, Putland F, Spencer PJ* (1973) Metal Sci J 7: 185
[10] *Spencer PJ, Putland FH* (1975) J Chem Therm 7: 531
[11] *Dinsdale A* (1978) 8th U.K. Experimental Thermodynamics Conference, University of Surrey, April 1978
[12] *Hayes FH, Kubaschewski O* (1971) Metal Sci J 5: 37
[13] *Spencer PJ, Hayes FH, Elford L* (1971) Chemical metallurgy of iron and steel. University of Sheffield, Iron and Steel Institute
[14] *Kubaschewski O, Stuart LEH* (1967) J Chem Eng Data 12: 418
[15] *Kubaschewski O, Grundmann J* (1977) Ber Bunsengesellschaft 81: 1239
[16] *Kubaschewski O, Hoster T* (1983) Z Metallk 74: 607
[17] *Roscoe CV, Gradwell KJ, Lorimer GW* 'Stainless Steels' (1984) Structure/property relationships in a series of duplex stainless steels, p 563
[18] *McHugh G* (1975) PhD Thesis, University of Manchester
[19] *Benz R* (1974) Met Trans 5: 2217
[20] *Smith JH, Paxton HW, McCabe CL* (1961) Trans AIME 221: 479; 221: 895
[21] *Hawkins RJ* (1971) Chemical metallurgy of iron and steel. University of Sheffield, Iron and Steel Institute, p 310
[22] *Eremenko VN, Lukashenko GM, Sidorko VR* (1969) Isv Akad Nauk SSSR Metal 2: 170
[23] *Kendall WB, Hultgren R* (1961) Trans Amer Soc Met 53: 199
[24] *Dench WA* (1966) NPL Report, Met Rep 32, M3378, ML5/36/01, January 1966
[25] *Barin I, Knacke O* (1973) Thermochemical properties of inorganic substances. Springer, Berlin Heidelberg New York
[26] *Kubaschewski O* (1981) Binary phase diagrams of iron. Springer, Berlin Heidelberg New York
[27] *Hultgren R, Desai PD, Hawkins DT, Gleiser M, Kelley KK, Wagman DD* (1973) Selected values of the thermodynamic properties of the elements. ASM, Ohio
[28] *Kubaschewski O, Alcock CB* (1979) Metallurgical thermochemistry, 5th edn. Pergamon Press
[29] *Kaufman L* (1978) Calphad J 2: 122