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Melting Enthalpy and Entropy of Binary Systems of Alloys of 3d Transition VII and VIII Metals and Carbon: Thermodynamic Calculation and Experimental Study[1]

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Thermodynamic calculations have been performed of the melting enthalpy and entropy of the Co–C, Ni–C, and Fe–C binary system alloys having eutectic compositions and of alloys whose compositions correspond to the minimum temperatures of the Mn–C, Fe–Co, Fe–Ni, and Mn–Ni melting diagrams. Heat capacities of one- and two-phase alloys of investigated systems have also been calculated as a function of temperature. In order to express a dependence of the Gibbs energy (G) of the liquid phase on the composition, the model of regular solutions has been used. The relation between the G of interstitial solid solutions and concentration was described by the two-sublattice model. The values have been experimentally verified using a high temperature calorimeter. These results have shown that the discrepancy between experimental and calculated results is within the calorimetric measurement uncertainty and does not exceed 10%.

KEY WORDS: 3d transition metals; binary systems; carbon; heat capacity; high temperatures; melting enthalpy and entropy; scanning calorimetry.

1. INTRODUCTION

Synthetic diamond is known to be produced by crystallization from melts of binary and ternary systems of carbon with 3d transition VII and VIII metals at high pressures under thermodynamic stability conditions. The process is based on phase relations of the above systems. Experimental construction of phase diagrams for multicomponent systems at high

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pressures and temperatures is a highly labor-intensive task. Thermodynamic calculations using phenomenological models of phase relations make the task easier. Some parameters for the models can be found from experimental data on phase equilibria by solving an inverse problem although the solution can be iterative. One of the ways to verify the reliability of the solutions is a comparison between the results of a thermodynamic calculation using the model parameters and those of a direct experiment on measuring calorimetric values.

In the present work, for a number of alloys of binary systems of 3d transition VII and VIII metals and carbon (Mn–C, Fe–Co, Fe–Ni, Mn–Ni, Co–C, Ni–C, Fe–C), thermodynamic calculations were made of melting enthalpies and entropies as well as enthalpy temperature distributions, i.e., heat capacity of a two-phase system over the melting temperature range. These values were also experimentally measured in direct calorimetric studies, and the experimental and calculated results were compared.

2. EXPERIMENTAL PROCEDURE

2.1. Specimens

To prepare alloys of the 3d transition VII and VIII metals with the carbon systems under study, the following materials were used: graphite (99.97%), carbonyl iron, electrolytic manganese, cobalt, and nickel. Samples were prepared by melting components in an argon atmosphere in crucibles of magnesium or hafnium oxide in an electric resistance furnace. Alloys of the following compositions were prepared: 88.5 at% Co, 11.5 at% C; 91 at% Ni, 9 at% C; 83 at% Fe, 17 at% C; 93 at% Mn, 7 at% C; 32 at% Fe, 68 at% Co; and 34 at% Fe, 66 at% Ni. These compositions correspond to the eutectic points in the Co–C, Ni–C, and Fe–C systems and to the temperature minima of the melting diagrams of the Mn–C, Fe–Co, Fe–Ni and Mn–Ni binary systems.

2.2. Procedure

Calorimetric studies were carried out using a device developed earlier in our laboratory [1]. The specimen was placed into an aluminium oxide crucible and heated at a rate of about $0.3\ \mathrm{K \cdot s^{-1}}$. The heating rate was set so that the temperature difference between the heat-leveling container and the cell containing a specimen decreased at a predetermined rate. Thus, the conditions were created, under which a constant heat flow was supplied into the calorimetric cell. The calorimetric device was calibrated against standard samples of thermodynamic properties (Mo, Al_2O_3) and verified by measuring melting enthalpies of reference substances (Cu, Ni, Fe, Pt). The uncertainty of measuring the melting enthalpy of a pure substance did not exceed 5%.

3. RESULTS AND DISCUSSION

For a description of the Gibbs energy concentration dependence of the FCC carbon solid solution in metal alloys, the two-sublattice model [2] was used:

$$\begin{aligned}{}^{o}G^{\gamma}_{m} = {} & y^{1}_{\mathrm{Me}}\, y^{2}_{\mathrm{C}}\, {}^{o}G^{\gamma}_{\mathrm{Me:C}} + y^{1}_{\mathrm{Me}}\, y^{2}_{\mathrm{Va}}\, {}^{o}G^{\gamma}_{\mathrm{Me:Va}} \\ & + RT[y^{2}_{\mathrm{Va}} \ln y^{2}_{\mathrm{Va}} + y^{2}_{\mathrm{C}} \ln y^{2}_{\mathrm{C}}] + \Delta^{E}G^{\gamma}_{m} \end{aligned} \tag{1}$$

where the variable y^{j}_{i} ($i =$ C, Co, Ni, Fe, Mn, Va and $j = 1.2$) is the portion of the i-component in the j-sublattice. The y_i is related to the atomic concentration x_i by the following relations:

$$y^{2}_{\mathrm{C}} = x_{\mathrm{C}}/(1 - x_{\mathrm{C}}), \qquad y^{2}_{\mathrm{Va}} = 1 - y^{2}_{\mathrm{C}} \tag{2}$$

The ${}^{o}G_{i:\,\mathrm{Va}}$ parameter is the Gibbs energy of the i-component and ${}^{o}G_{i:\mathrm{C}}$ is the Gibbs energy of a hypothetical phase having an fcc lattice with all the interstices filled with carbon atoms. The excess Gibbs energy was defined by

$${}^{E}G^{\gamma}_{m} = y^{2}_{\mathrm{C}}\, y^{2}_{\mathrm{Va}}\, y^{1}_{\mathrm{Me}}\, L^{\gamma}_{\mathrm{Me:C,\,Va}} \tag{3}$$

where $L^{\gamma}_{\mathrm{Me:C,\,Va}}$ is the interaction parameter.

To express the Gibbs energy of a liquid, the regular solution model was used [3]:

$${}^{o}G^{L}_{m} = x_1\, {}^{o}G^{L}_{1} + x_2\, {}^{o}G^{L}_{2} + RT[x_1 \ln x_1 + x_2 \ln x_2] + x_1 x_2 L^{L}_{1,2} \tag{4}$$

where x is the regular atomic concentration. A similar model was used to describe fcc-substitutional solid solutions.

Table I gives parameters of phase models of the systems being studied. Some of the parameters were taken from the literature [4–9], and some were found from phase equilibria by solving the inverse problem [10–12].

The following equations were used to calculate melting enthalpies and entropies of binary system alloys:

$$\Delta H_m = \left(G^L - T\frac{dG^L}{dT}\right)_{T=T_L} - \left(G^S - T\frac{dG^S}{dT}\right)_{T=T_S} \tag{5}$$

$$\Delta S_m = \left(-\frac{dG^L}{dT}\right)_{T=T_L} - \left(-\frac{dG^S}{dT}\right)_{T=T_S} \tag{6}$$

Table I. Parameters of Thermodynamic Models

	Liquid phase ($\mathrm{J \cdot mol^{-1}}$)
${}^{o}G^{L}_{\mathrm{Ni}}$	$11{,}235.527 + 108.457T - 22.096T \ln T - 4.8407 \times 10^{-3}T^{2} - 3.82318 \times 10^{-21}T^{7}$
${}^{o}G^{L}_{\mathrm{Mn}}$	$-13{,}048 + 284.3T - 46T \ln T$
${}^{o}G^{L}_{\mathrm{Fe}}$	$13{,}265 + 117.576T - 23.5143T \ln T - 4.39752 \times 10^{-3}T^{2} - 5.89269 \times 10^{-8}T^{3}$ $-3.6751551 \times 10^{-21}T^{7} + 77{,}358.5T^{-1}$
${}^{o}G^{L}_{\mathrm{Co}}$	$15{,}394.612 + 124.434078T - 25.0861T \ln T - 2.6547387 \times 10^{-3}T^{2}$ $-1.7348 \times 10^{-7}T^{3} + 72{,}526.92T^{-1} - 2.19804786 \times 10^{-21}T^{7}$
${}^{o}G^{L}_{\mathrm{C}}$	$100{,}000 + 146.1T - 24.3T \ln T - 4.723 \times 10^{-4}T^{2} + 2{,}562{,}600T^{-1}$ $-2.643 \times 10^{8}T^{-2} + 1.2 \times 10^{10}T^{-3}$
$L^{L}_{\mathrm{Mn,\,C}}$	$-111{,}684$
$L^{L}_{\mathrm{Ni,\,Mn}}$	$(-64{,}434 + 10.878T)\, x_{\mathrm{Mn}} + (-76{,}986 + 10.878T)\, x_{\mathrm{Ni}}$
$L^{L}_{\mathrm{Ni,\,C}}$	$-110{,}160 + 34.6T$
$L^{L}_{\mathrm{Fe,\,C}}$	$-124{,}320 + 28.5T + 19{,}300(x_{\mathrm{C}} - x_{\mathrm{Fe}}) + (49{,}260 - 19T)(x_{\mathrm{C}} - x_{\mathrm{Fe}})^{2}$
$L^{L}_{\mathrm{Co,\,C}}$	$-107{,}940.6 + 24.956T - 9{,}805.5(x_{\mathrm{C}} - x_{\mathrm{Fe}})$
$L^{L}_{\mathrm{Fe,\,Ni}}$	$-18{,}378.86 + 6.03912T + (x_{\mathrm{Ni}} - x_{\mathrm{Fe}})(9228.1 - 3.54642T)$
$L^{L}_{\mathrm{Fe,\,Co}}$	$-9312 - 1752(x_{\mathrm{Co}} - x_{\mathrm{Fe}})$
$L^{L}_{\mathrm{Fe,\,Mn}}$	$-23{,}506 + 168T + x_{\mathrm{Mn}}(-8150 + 6.87T)$
	fcc-solid solution ($\mathrm{J \cdot mol^{-1}}$)
${}^{o}G^{\gamma}_{\mathrm{Ni}}$	$-5179.159 + 117.854T - 22.096T \ln T - 4.8407 \times 10^{-3}T^{2}$
${}^{o}G^{\gamma}_{\mathrm{Mn}}$	$-29{,}498 + 295.2T - 46T \ln T$
${}^{0}G^{\gamma}_{\mathrm{Fe}}$	$-237.57 + 132.416T - 24.6643T \ln T - 0.00375752T^{2}$ $-5.89269 \times 10^{-8}T^{3} + 77{,}358.5T^{-1}$
${}^{o}G^{\gamma}_{\mathrm{Co}}$	$737.166 + 132.750762T - 25.0861T \ln T - 2.6547387 \times 10^{-3}T^{2}$ $-1.7348 \times 10^{-7}T^{3} + 72{,}526.92T^{-1}$
${}^{o}G^{\gamma}_{\mathrm{Ni:C}}$	${}^{o}G^{\gamma}_{\mathrm{Ni}} + {}^{o}G_{\mathrm{Gr}} + 45{,}000 + 1.88T$
$oG^{\gamma}_{\mathrm{Mn:C}}$	${}^{o}G^{\gamma}_{\mathrm{Mn}} + {}^{o}G_{\mathrm{Gr}} + 16{,}000$
${}^{o}G^{\gamma}_{\mathrm{Fe:C}}$	${}^{o}G^{\gamma}_{\mathrm{Fe}} + {}^{o}G_{\mathrm{Gr}} + 77{,}207 - 15.877T$
${}^{o}G^{\gamma}_{\mathrm{Co:C}}$	${}^{o}G^{\gamma}_{\mathrm{Co}} + {}^{o}G_{\mathrm{Gr}} + 50{,}036.2 - 6.234T$
$L^{\gamma}_{\mathrm{Ni:C,\,Va}}$	0
$L^{\gamma}_{\mathrm{Mn:C,\,Va}}$	$-52{,}000 + 8T$
$L^{\gamma}_{\mathrm{Fe:C,\,Va}}$	$-34{,}671$
$L^{\gamma}_{\mathrm{Co:C,\,Va}}$	0
$L^{\gamma}_{\mathrm{Fe,\,Mn}}$	$-13{,}701 + 12T + x_{\mathrm{Mn}}(-8150 + 6.87T)$
$L^{\gamma}_{\mathrm{Ni,\,Mn}}$	$(-51{,}882 + 10.878T)\, x_{\mathrm{Mn}} + (-64{,}434 + 10.878T)\, x_{\mathrm{Ni}}$
$L^{\gamma}_{\mathrm{Ni,\,Fe}}$	$-12{,}054.355 + 3.27413T + (x_{\mathrm{Ni}} - x_{\mathrm{Fe}})(11082.1315 - 4.45077T)$ $-725.805174(x_{\mathrm{Ni}} - x_{\mathrm{Fe}})^{2}$
$L^{\gamma}_{\mathrm{Co,\,Fe}}$	$-8{,}471 + (1{,}181 - 1.6544T)(x_{\mathrm{Co}} - x_{\mathrm{Fe}})$
	Graphite ($\mathrm{J \cdot mol^{-1}}$)
${}^{o}G_{\mathrm{Gr}}$	$-17{,}369 + 170.73T - 24.3T \ln T - 4.723 \times 10^{-4}T^{2} + 2{,}562{,}600T^{-1}$ $-2.643 \times 10^{8}T^{-2} + 1.2 \times 10^{10}T^{-3}$

Table II. Enthalpy and Entropy of Melting of Binary 3d Transition Metals and Carbon Alloys Having Eutectic Compositions and of Alloys at Compositions that Correspond to the Minimum Melting Temperatures

System (composition)	Enthalpy of melting ($kJ \cdot mol^{-1}$) Calc.	Enthalpy of melting ($kJ \cdot mol^{-1}$) Expt.	Entropy of melting ($J \cdot mol^{-1} \cdot K^{-1}$) Calc.	Entropy of melting ($J \cdot mol^{-1} \cdot K^{-1}$) Expt.
Fe–Ni (66 at% Ni, 34 at% Fe)	14.8	14.7	8.65	8.59
Fe–Co (68 at% Co, 32 at% Fe)	15.2	15.0	8.65	8.54
Mn–Ni (40 at% Ni, 60 at% Mn)	12.0	12.0	9.23	9.23
Mn–C (7 at% C, 93 at% Mn)	18.5	18.0	12.5	12.1
Co–C (11.5 at% C, 88.5 at% Co)	15.6	15.0	8.64	8.53
Fe–C (17 at% C, 83 at% Fe)	11.2	11.0	7.94	7.8
Ni–C (9 at% C, 91 at% Ni)	15.8	16.0	9.93	10.1

where $T_L = T_S$ is the melting temperature of an alloy having the eutectic composition or the composition that corresponds to the temperature of the minimum of the diagram, i.e., an alloy that melts invariantly. Table II presents the calculated and experimental values of melting enthalpies and entropies for the alloys under study. The discrepancies between the calculated and the experimental values are within the limits of experimental uncertainty.

An alloy whose temperature is above the solidus and below the liquidus is a closed thermodynamic system, in which two phases—solid and liquid—coexist at the equilibrium state. The Gibbs energy for such a system is defined by the relation:

$$\hat{G} = G_S \frac{x - x_L}{x_S - x_L} + G_L \frac{x_S - x}{x_S - x_L} \tag{7}$$

where G_S and G_L are the Gibbs energies of phases having a concentration of one of the components x_S and x_L, respectively; x is the alloy concentration. The molar heat capacity of a binary system in the melting temperature range, which is defined as the heat energy spent to raise the temperature of 1 mol by 1 K can be calculated by

$$\hat{C}_p = \frac{dH}{dT} = -T \frac{d^2\hat{G}}{dT^2} \tag{8}$$

The calculations were made for alloys of the systems under study having the following compositions: 20 at% C, 80 at% Fe; 10 at% C, 90 at% Ni; 14 at% C, 86 at% Co; 75 at% Fe, 25 at% Mn; 75 at% Ni, 25 at% Mn; and 75 at% Fe, 25 at% Ni (Table III). Calculated results for the alloys of the Ni–C and Mn–Ni systems are given in Fig. 1. Experimental data on heat capacity are indicated by open diamonds.

Table III. Heat Capacity of the Binary 3d Transition Metals and Carbon Alloys in the Melting Temperature Ranges

System (composition)	Fe–C (20 at% C, 80 at% Fe)						
Temperature (K)	1320	1360	1400	1500	1600	1700	1800
Heat capacity calc./expt. (J · mol^{-1} · K^{-1})	32.7/30.5	33.0/30.6	33.3/31.0	37.3/34.1	38.8/35.9	40.7/37.1	40.4/38.1
	Ni–C(10 at% C, 90 at% Ni)						
Temperature (K)	1420	1500	1580	1620	1670	1720	1780
Heat capacity calc./expt. (J · mol^{-1} · K^{-1})	34.6/37.5	35.3/36.5	36.1/37.8	40.8/39.8	41.9/41.5	43.1/43.9	40.3/38.5
	Co–C (14 at% C, 86 at% Co)						
Temperature (K)	1510	1540	1570	1620	1680	1740	1800
Heat capacity calc./expt. (J · mol^{-1} · K^{-1})	35.5/34.0	35.7/36.2	35.9/38.0	40.9/38.5	42.1/39.0	43.4/39.1	38.2/39.0
	Fe–Mn (25 at% Mn, 75 at% Fe)						
Temperature (K)	1610	1640	1670	1690			1720
Heat capacity calc./expt. (J · mol^{-1} · K^{-1})	36.5/39.0	38.1/42.2	39.7/43.2	610/650			40.2/42.7
	Mn–Ni (75 at% Ni, 25 at% Mn)						
Temperature (K)	1410	1440	1470	1490			1530
Heat capacity calc./expt. (J · mol^{-1} · K^{-1})	33.3/35.0	34.6/37.1	35.9/34.3	420/440			39.6/38.5
	Fe–Ni (25 at% Ni, 75 at% Fe)						
Temperature (K)	1650	1680	1710	1735			1750
Heat capacity calc./expt. (J · mol^{-1} · K^{-1})	35.5/33.0	35.8/34.2	37.1/34.2	720/680			40.1/43.5

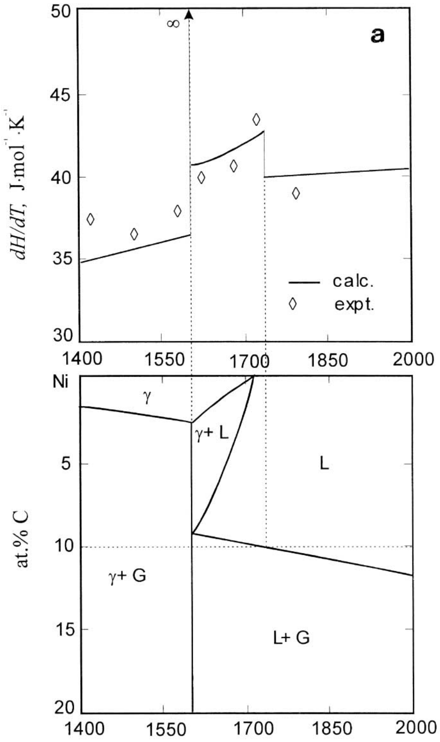

Fig. 1. Variation of heat capacity of the alloys investigated as a function of temperature: (a) 10 at% C, 90 at% Ni; (b) 75 at% Ni, 25 at% Mn.

4. CONCLUSIONS

It is shown that for two-phase samples of the considered systems both the thermodynamic calculations and the calorimetric measurements of heat capacity in the melting temperature ranges are possible. For all the samples being studied, the discrepancy between calculated and experimental data does not exceed the experimental uncertainty of melting enthalpy measurements ($\pm 10\%$). Therefore, it may be concluded that the model parameters determined with phase equilibria data allow us to describe not only phase diagrams but also thermodynamic properties of the phases.

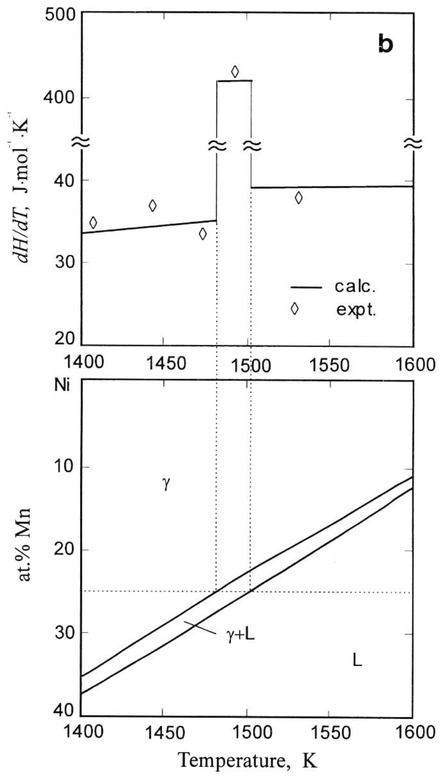

Fig. 1 *(Continued)*

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