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Thermodynamic Properties of Ni Nitrides and Phase Stability in the Ni–N System

A. Fernández Guillermet[1] and K. Frisk[2]

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The thermodynamics of the Ni–N system is poorly known from experiments, and there is a need of information on the stability of the various nitride phases and the Ni–N phase diagram. This kind of information has been obtained by us, by combining the few measurements available with predictions, based on recently reported regularities in bonding properties and vibrational entropy of 3d transition metal compounds. A calculated Ni–N phase diagram is presented. A certain range of homogeneity for the hexagonal nitride phase is obtained, which is comparable to that of other 3d transition metal–nitrogen systems. The question of the possible existence of a stable "Ni_4N" phase is examined. According to our results, Ni_4N is metastable in the Ni–N system.

KEY WORDS: enthalpy; entropy; metastable phases; nickel compounds; nitrides; phase diagrams; phase stability.

1. INTRODUCTION

1.1. Background

The study of the thermodynamic properties of transition metal systems is a subject of considerable practical and theoretical interest. Accurate thermodynamic information forms the basis of the so-called CALPHAD (i.e., Calculation of Phase Diagrams) approach to phase diagrams of multicomponent alloy systems. In this approach, pioneered by Kaufman [1, 2], one searches for a consistent description of the thermodynamics of the system,

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[1] Consejo Nacional de Investigaciones Científicas y Técnicas, Centro Atómico Bariloche, 8400 San Carlos de Bariloche, Argentina.

[2] Division of Physical Metallurgy, The Royal Institute of Technology, S-10044 Stockholm, Sweden.

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based on constructing Gibbs energy (G) functions for the various phases in the multicomponent system, making use of the descriptions of the lower-order systems, e.g., binaries and ternaries. Since the experimental information on the binary systems may sometimes be uncertain, scarce or lacking, there is a strong interest in the developement of methods for predicting thermodynamic quantities and judging available information.

1.2. Recent Work

Miedema's formula [3] has been very successful in accounting for the enthalpy of formation of various groups of compounds, but it does not treat the temperature dependence of G. The problem of estimating G at high temperatures has led Fernández Guillermet and Grimvall [4] to a systematic study of the thermodynamic properties of various 3d transition metal compounds. They have reported various correlations which allowed the estimation of, e.g., the room-temperature entropy and the enthalpy of formation of various carbides, nitrides, and oxides. They have also used the correlations for analyzing the stability of metastable phases, e.g., a phase with the NaCl structure in the Cr–C system [5].

1.3. The Present Work

The purpose of the present work is to couple the results of Ref. 4 with thermodynamic calculations in order to gain information on the properties of a system which is poorly known from experiments, the Ni–N system. This study is part of a research project aimed at treating the Cr–Fe–Mo–Ni–N system, which is currently carried out by one of us (KF). Previous reports by Frisk have dealt with the thermodynamics of transition metal–nitrogen binary (e.g., Cr–N, Fe–N, Mo–N [6]) and ternary (e.g., Cr–Mo–N [6] and Cr–Fe–N [7]) systems. The present paper is organized as follows. In Section 2 we present the models for the Gibbs energy of the various phases in the Ni–N system, and in Section 3 we explain the evaluation of model parameters. Section 4 is devoted to the phase stability of Ni nitrides and in Section 5 we give a discussion of our results. In Section 6 we summarize the work and present the conclusions.

2. THERMODYNAMIC MODELING

2.1. Phases and Structures

The experimental information on the Ni–N system has been compiled by Wriedt [8]. In addition to the fcc, Ni-rich solution, he included the following phases in the stable Ni–N diagram:

(i) An hexagonal nitride with an unknown homogeneity range, which has been represented by the ideal formula "Ni_3N" (hP8).

(ii) A cubic nitride which has been represented by the ideal formula Ni_4N. Its homogeneity range, or stability relative to fcc and the hexagonal nitride, is not known. The nitride has been observed in another form, a tetragonal one. However, in view of the lack of information, only the cubic (cP5) form, isomorphous with the Fe_4N phase of the Fe–N system, is treated here.

Ni azide NiN_6 or $Ni(N_3)_2$, with an unknown crystal structure or homogeneity range, was excluded from the present study.

2.2. Gibbs Energy of Solid Phases

The Gibbs energy of the solid phases was described by resolving it into a magnetic (ΔG_m^{mg}) and a nonmagnetic contribution. The magnetic contribution was described by Hillert and Jarl's [9] modification of the model proposed by Inden [10], whereas the nonmagnetic contribution was described by a two-sublattice model [11]. Ni atoms were assumed to occupy the first sublattice, whereas N atoms and vacant (Va) interstitial sites were assumed to substitute for each other on the second one. The phases were described by the two-sublattice model $(Ni)_1\,(N, Va)_c$, and the Gibbs energy per mole of formula units was represented by the expression:

$$G_m^\alpha = y_N\,{}^\circ G_{Ni:N}^\alpha + y_{Va}\,{}^\circ G_{Ni:Va}^\alpha + cRT(y_N \ln y_N + y_{Va} \ln y_{Va}) + {}^E G_m^\alpha + \Delta G_m^{mg,\alpha} \quad (1)$$

The variable y_i ($i = N, Va$) is the so-called [12] site fraction of the component "i" on the second sublattice. The parameter c represents the number of interstitial sites per metal atom. The parameter ${}^\circ G_{Ni:Va}^\alpha$ is the Gibbs energy of Ni in a hypothetical nonmagnetic state with the structure α, and ${}^\circ G_{Ni:N}^\alpha$ is the Gibbs energy of a hypothetical state where all interstitial sites are filled with N. All ${}^\circ G$ values were referred to the enthalpy of a special standard state recommended by SGTE (Scientific Group Thermodata Europe) [13]. This state, denoted by the superscript SER (Stable Element Reference), is defined as the stable state at 298.15 K and 0.1 MPa. The term ${}^E G_m^\alpha$ in Eq. (1) represents the excess Gibbs energy, whereas $\Delta G_m^{mg,\alpha}$ is the magnetic contribution, which is described for each phase in Table I.

2.3. Fcc Phase

When α is fcc, $c = 1$, and we have the two-sublattice model $(Ni)_1\,(N, Va)_1$. In this case Eq. (1) involves the parameters ${}^\circ G_{Ni:Va}^{fcc}$ and

Table I. Summary of Parameters Describing the Thermodynamic Properties of the Ni–N System (Values Are Given in SI Units)[a]

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fcc and "NiN"

$^{\circ}G^{\mathrm{fcc}}_{\mathrm{Ni:N}} = {}^{\circ}G^{\mathrm{fcc}}_{\mathrm{Ni:Va}} + {}^{\circ}G^{\mathrm{gas}}_{\mathrm{N}} + 38680 + 143.09\ T - 10.9\ T \ln T + 0.00438\ T^2$

$298.15 < T < 1728.00$:

$^{\circ}G^{\mathrm{fcc}}_{\mathrm{Ni:Va}} - 1\ H^{\mathrm{SER}}_{\mathrm{Ni}} = -5179.159 + 117.854\ T - 22.096\ T \ln T - 0.0048407\ T^2$

$1728.00 < T < 6000.00$:

$^{\circ}G^{\mathrm{fcc}}_{\mathrm{Ni:Va}} - 1\ H^{\mathrm{SER}}_{\mathrm{Ni}} = -27840.655 + 279.135\ T - 43.1\ T \ln T + 1.12754\ 10^{31}\ T^{-9}$

hcp and ε

$^{\circ}G^{\mathrm{hcp}}_{\mathrm{Ni:N}} = {}^{\circ}G^{\mathrm{fcc}}_{\mathrm{Ni:Va}} + 1/2\, {}^{\circ}G^{\mathrm{gas}}_{\mathrm{N}} - 4409.6 + 72.93\ T - 7.36\ T \ln T + 0.00614\ T^2$

$^{\circ}G^{\mathrm{hcp}}_{\mathrm{Ni:Va}} = {}^{\circ}G^{\mathrm{fcc}}_{\mathrm{Ni:Va}} + 1046 + 1.255\ T$

Liquid

$^{\circ}G^{\mathrm{liquid}}_{\mathrm{Ni}} = {}^{\circ}G^{\mathrm{gas}}_{\mathrm{N}} + 29950 + 59.02\ T$

$298.15 < T < 1728.00$: $^{\circ}G^{\mathrm{liquid}}_{\mathrm{Ni}} = {}^{\circ}G^{\mathrm{fcc}}_{\mathrm{Ni:Va}} + 16414.686 - 9.397\ T - 3.82318\ 10^{-21}\ T^7$

$1728.00 < T < 6000.00$: $^{\circ}G^{\mathrm{liquid}}_{\mathrm{Ni}} = {}^{\circ}G^{\mathrm{fcc}}_{\mathrm{Ni:Va}} + 18290.88 - 10.537\ T + 1.12754\ 10^{31}\ T^{-9}$

$^{\circ}L^{\mathrm{liquid}}_{\mathrm{N,Ni}} = 14{,}981$

N_2 Gas

$298.15 < T < 950.00$:

$^{\circ}G^{\mathrm{gas}}_{\mathrm{N}} - 1\ H^{\mathrm{SER}}_{\mathrm{N}} = -3750.675 - 9.45425\ T - 12.7819\ T \ln T - 0.00176686\ T^2$
$+ 2.680735\ 10^{-9}\ T^3 - 32{,}374\ T^{-1}$

$950.00 < T < 3350.00$:

$^{\circ}G^{\mathrm{gas}}_{\mathrm{N}} - 1\ H^{\mathrm{SER}}_{\mathrm{N}} = -7358.85 + 17.2003\ T - 16.3699\ T \ln T - 6.5107\ 10^{-4}\ T^2$
$+ 3.0097\ 10^{-8}\ T^3 + 563{,}070\ T^{-1}$

$3350.00 < T < 6000.00$:

$^{\circ}G^{\mathrm{gas}}_{\mathrm{N}} - 1\ H^{\mathrm{SER}}_{\mathrm{N}} = -16392.8 + 50.26\ T - 20.4695\ T \ln T + 2.397545\ 10^{-4}\ T^2$
$- 8.3331\ 10^{-9}\ T^3 + 4{,}596{,}375\ T^{-1}$

Ni_4N

$^{\circ}G^{\mathrm{Ni_4N}}_{\mathrm{Ni:N}} = +4\,{}^{\circ}G^{\mathrm{fcc}}_{\mathrm{Ni:Va}} + {}^{\circ}G^{\mathrm{gas}}_{\mathrm{N}} - 5393 + 142.97\ T - 15.65\ T \ln T + 0.0154\ T^2$

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[a] The magnetic contribution to Gibbs energy is described by $\Delta G^{\mathrm{mg}}_{\mathrm{m}} = \mathrm{RT} \ln(\beta + 1)\, f(\tau)$, $\tau = T/T_{\mathrm{c}}$. For $\tau < 1$,

$$f(\tau) = 1 - \left[\frac{79\tau^{-1}}{140} + \frac{474}{497}\left(\frac{1}{p} - 1\right)\left(\frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600}\right)\right] \Big/ A$$

and for $\tau > 1$,

$$f(\tau) = -\left(\frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500}\right) \Big/ A$$

where

$$A = \left(\frac{518}{1125}\right) + \left(\frac{11692}{15975}\right)\left[\left(\frac{1}{p}\right) - 1\right]$$

and p depends on the structure, p is 0.28 for fcc and hcp. $Tc^{\mathrm{fcc}}_{\mathrm{Ni}} = Tc^{\mathrm{hcp}}_{\mathrm{Ni}} = 633$. $\beta^{\mathrm{fcc}}_{\mathrm{Ni}} = \beta^{\mathrm{hcp}}_{\mathrm{Ni}} = 0.52$.

${}^{\circ}G^{\text{fcc}}_{\text{Ni:N}}$, which were treated as follows. ${}^{\circ}G^{\text{fcc}}_{\text{Ni:Va}}$, the nonmagnetic Gibbs energy of fcc Ni, was taken from the assessment by Dinsdale [14]. ${}^{\circ}G^{\text{fcc}}_{\text{Ni:N}}$ represents the Gibbs energy of a nonmagnetic nitride with the formula "NiN," Since all interstitial sites in this fcc phase are filled with N, NiN is a nitride with the NaCl (cF8) structure. As a consequence, the problem of determining this ${}^{\circ}G$ parameter for the fcc structure has been considered by us to be equivalent to evaluating the Gibbs energy of an NaCl-structure phase in the Ni-N system, i.e., the kind of problem which has been discussed in Refs. 4 and 5. ${}^{\circ}G^{\text{fcc}}_{\text{Ni:N}}$ was expressed as

$$
{}^{\circ}G^{\text{fcc}}_{\text{Ni:N}} = {}^{\circ}G^{\text{fcc}}_{\text{Ni:Va}} + {}^{\circ}G^{\text{gas}}_{\text{N}} + \Delta{}^{\circ}G^{\text{fcc}}_{\text{Ni:N}} \tag{2}
$$

${}^{\circ}G^{\text{gas}}_{\text{N}}$ was described as in Ref. 15, whereas $\Delta{}^{\circ}G^{\text{fcc}}_{\text{Ni:N}}$ is a function of temperature, which is presented in Section 4. The excess Gibbs energy term ${}^{\text{E}}G^{\text{fcc}}_{\text{m}}$ was expressed as

$$
{}^{\text{E}}G^{\text{fcc}}_{\text{m}} = y_{\text{N}}\, y_{\text{Va}} L^{\text{fcc}}_{\text{Ni:N,Va}} \tag{3}
$$

where the constant $L^{\text{fcc}}_{\text{Ni:N,Va}}$ is discussed in Section 5.

2.4. Hexagonal (ε) Nitride Phase

The range of stability of the hexagonal nitride phase in the Ni–N system is not known, and Wriedt [8] represented it using the formula Ni_3N. On the other hand, the range of homogeneity of the hexagonal (ε) nitride is appreciable in other 3d transition metal–nitrogen systems. In particular, it increases [6] when moving from the Cr–N to the Fe–N system, and it seems natural to expect a certain homogeneity range in the Ni–N system as well. An attempt to predict that range was made by us, based on adopting for the hexagonal nitride in the Ni–N system the same model as used for the ε nitride in the Fe–N and Cr–N systems, which is as follows. The metal atom arrangement of the ε phase is close-packed hexagonal, and there is one octahedral interstitial site per atom. However, it was assumed that two neighboring interstitial sites in the hexagonal c-direction are never simultaneously occupied. This phase was thus approximated with the model $(\text{Ni})_1\,(\text{N, Va})_{0.5}$, and its Gibbs energy was described with Eq. (1) with $c = 0.5$. The model parameter ${}^{\circ}G^{\text{hcp}}_{\text{Ni:Va}}$ coincides with the nonmagnetic Gibbs energy of hcp Ni. Although this modification is metastable, it has been proposed [16] to treat it as ferromagnetic, and this has recently been supported by band-structure calculations [17]. The nonmagnetic Gibbs energy values according to Dinsdale [14] were used by us. ${}^{\circ}G^{\text{hcp}}_{\text{Ni:N}}$ represents the Gibbs energy of an hypothetical nonmagnetic nitride with formula $\text{NiN}_{0.5}$. There is no information on its properties, but there is some information on the nitride composition $NiN_{0.33}$, which was used by us to evaluate the properties of $NiN_{0.5}$, as described in Section 4. The parameter $^{\circ}G^{hcp}_{Ni:N}$ was represented as

$$^{\circ}G^{hcp}_{Ni:N} = {}^{\circ}G^{fcc}_{Ni:Va} + 0.5\,{}^{\circ}G^{gas}_{N} + \Delta{}^{\circ}G^{hcp}_{Ni:N} \tag{4}$$

and $\Delta{}^{\circ}G^{hcp}_{Ni:N}$ was evaluated from information on $NiN_{0.33}$ using an optimization procedure where the excess Gibbs energy (${}^{E}G^{hcp}_{m}$) was set equal to zero.

2.5. The Ni_4N Phase

Since the range of homogeneity of this phase is not known [8], we have treated it as a stoichiometric compound of the ideal composition Ni_4N. Its Gibbs energy was described as

$$^{\circ}G^{Ni4N}_{Ni:N} = 4\,{}^{\circ}G^{fcc}_{Ni:Va} + {}^{\circ}G^{gas}_{N} + \Delta{}^{\circ}G^{Ni4N}_{Ni:N} \tag{5}$$

The term $\Delta{}^{\circ}G^{Ni4N}_{Ni:N}$ is considered later in this work.

2.6. Liquid Phase

The liquid phase was treated with a substitutional solution model,

$$G^{liq}_{m} = x_N\,{}^{\circ}G^{liq}_{N} + x_{Ni}\,{}^{\circ}G^{liq}_{Ni} + RT(x_N \ln x_N + x_{Ni} \ln x_{Ni}) + x_N x_{Ni} L^{liq}_{N,Ni} \tag{6}$$

The quantities $^{\circ}G^{liq}_{N}$ and $^{\circ}G^{liq}_{Ni}$ were taken from Refs. 6 and 14, respectively, whereas the regular solution parameter $L^{liq}_{N,Ni}$ was treated as a constant and evaluated from experimental data; see Section 5.

2.7. N_2 Gas

The N_2 gas was treated as an ideal gas in the present work. The Gibbs energy for N_2 gas was taken from the JANAF Thermochemical Tables [18].

3. PARAMETER EVALUATION PROCEDURE

Four thermodynamic model parameters were determined in the present work, $\Delta{}^{\circ}G^{fcc}_{Ni:N}$, $\Delta{}^{\circ}G^{hcp}_{Ni:N}$, $\Delta{}^{\circ}G^{Ni4N}_{Ni:N}$, and $L^{liq}_{Ni,N}$. The evaluation was made by analyzing experimental and estimated quantities by means of PARROT, a computer program for the optimization of thermodynamic parameters developed by Jansson [19]. The constant $L^{liq}_{N,Ni}$ was directly determined from the measured solubility of N in liquid Ni. The other parameters, which represent Gibbs energy differences, so-called lattice stabilities [1], of the nitrides "NiN," $NiN_{0.5}$, and Ni_4N, respectively, were treated as functions of temperature and determined by combining experimental or estimated enthalpy of formation values with our estimates of their entropy at high temperature. The estimation procedure is presented in the next section.

4. METHOD FOR ESTIMATING THE LATTICE STABILITIES

4.1. Regularities in Thermodynamic Properties of 3d Transition Metal Compounds

In Ref. 4 Fernández Guillermet and Grimvall reported various correlations between quantities related to the strength of bonding in 3d transition metal carbides and nitrides, and the average number of valence electrons per atom, n_e. Of particular relevance for the present study is the correlation between the room-temperature enthalpy of formation per atom, $(\Delta^\circ H)$ and n_e, and the correlation involving the characteristic energy, E_S. This quantity, introduced in Ref. 4, was defined as

$$E_S(\mathrm{Ry}) = k_S \Omega^{2/3} \tag{7}$$

where Ω is the average volume per atom, and k_S is a quantity with the dimension of a force constant (i.e., force per length), which is related to the vibrational properties of the compound as follows:

$$k_S = M_{\mathrm{eff}}(k_B \theta_S/\hbar)^2 \tag{8}$$

M_{eff} is the logarithmic average of the atomic masses, k_B is Boltzmann's constant, $\hbar = h/2\pi$, where h is Planck's constant, and θ_S is an "entropy Debye temperature," defined [20–23] as the θ value which gives the experimental vibrational entropy per mole of atoms, S^{vib}, when inserted in the Debye model expression for the entropy, S_D.

$$S^{\mathrm{vib}}(T) = S_D(\theta_S/T) \tag{9}$$

Previous analyses based on k_S of the vibrational entropy of transition metals [24] and their combinations with C, N, and B [20–22] revealed remarkable regularities. The new correlations involving $\Delta^\circ H$ [kJ $\cdot$ (mol of atoms)$^{-1}$] and E_S(Ry) ($1\ \mathrm{Ry} \cdot \mathrm{atom}^{-1} = 1312.8\ \mathrm{kJ} \cdot \mathrm{mol}^{-1}$) for 3d transition metal carbides and nitrides are given in Fig. 1 and Fig. 2, respectively. References to the sources of enthalpy and entropy data, and a discussion of the data points for Mn compounds, which deviate from the general trend in Figs. 1b and 2b have been given in Ref. 4 and are not repeated here. The experimental data points in Fig. 2a are too few to firmly establish the E_S vs n_e relation at large n_e. However, the better-founded and analogous trends of other plots and the general relationship observed in the E_S vs n_e and $-\Delta^\circ H$ vs n_e plots lends support to the tentative, dashed line in Fig. 2a.

4.2. Application to the Ni–N System

The correlations in Fig. 2 are applied to predict the properties of Ni nitrides which are not known from experiments. Our procedure is

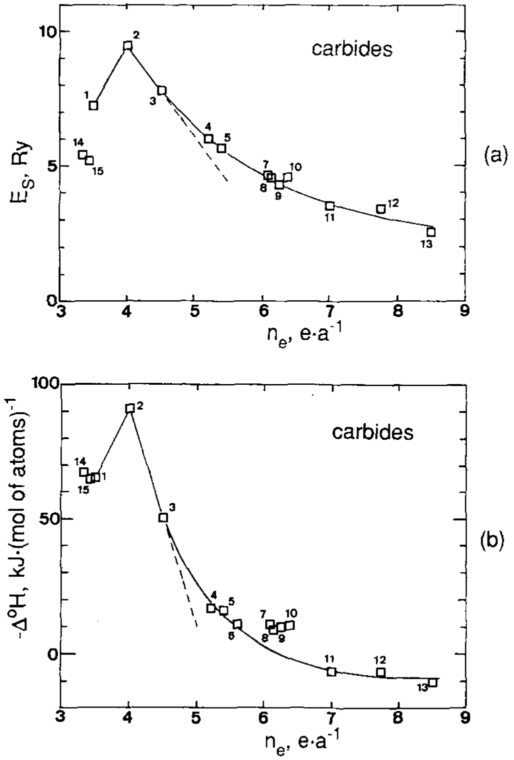

Fig. 1. (a) E_S and (b) $\Delta^\circ H$ of carbides, as functions of n_e. The numbers refer to ScC (1), TiC (2), VC (3), Cr_3C_2(4), Cr_7C_3 (5), $Cr_{23}C_6$ (6), Mn_7C_3 (7), Mn_5C_2 (8), Mn_3C (9), $Mn_{23}C_6$ (10), Fe_3C (11), Co_3C (12), Ni_3C (13), Sc_2C (14), and Sc_4C_3 (15), with identical indentification for the E_S values at the same n_e. The dashed lines refer to the (cF8) structure. From Fernández Guillermet and Grimvall [4].

as follows. From the number of valence electrons of Ni, $n_{\mathrm{Ni}} = 10\,\mathrm{e}\cdot\mathrm{a}^{-1}$, and of N, $n_{\mathrm{N}} = 5\,\mathrm{e}\cdot\mathrm{a}^{-1}$, we calculate n_e. For a nitride NiN_c, $n_\mathrm{e} = (n_{\mathrm{Ni}} + cn_{\mathrm{N}})/(1+c)$. Then, from Figs. 2a and b we get E_S and $\Delta^\circ H$, respectively. From E_S and the experimental [25] Ω, we get k_S and θ_S. If experimental information of Ω of a compound is not available, we estimate it by relying on interpolations in Ω vs n_e plots, as explained in Ref. 4.

Anharmonicity makes θ_S temperature dependent. When the vibrational entropy at high temperatures was needed in Ref. 5, one let θ_S decrease with T, relying on the known behavior of the temperature dependence of θ_S for similar compounds. Because of the lack of information on θ_S for 3d transition metal nitrides at large n_e values, we have here

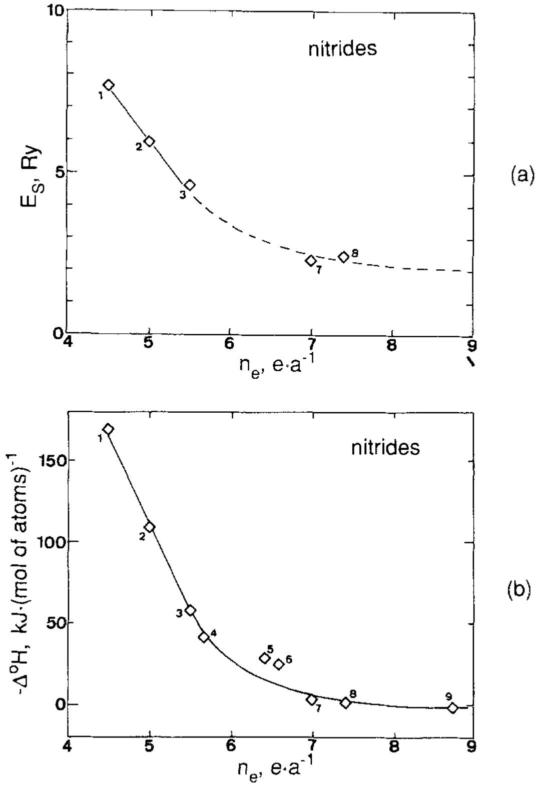

Fig. 2. (a) E_S and (b) $\Delta^\circ H$ of nitrides, as in Fig. 1. The numbers refer to TiN (1), VN (2), CrN(3), $\mathrm{Cr_2N}$ (4), $\mathrm{Mn_5N_2}$ (5), $\mathrm{Mn_4N}$ (6), $\mathrm{Fe_2N}$ (7), $\mathrm{Fe_4N}$ (8), and $\mathrm{Ni_3N}$ (9). The E_S–n_e relation is only tentative. From Fernández Guillermet and Grimvall [4].

neglected such corrections. We have also neglected nonvibrational contributions. Then the entropy values calculated from Eq. (9) were combined with experimental or estimated values for $\Delta^{\circ}H$ (see below) and the Gibbs energy differences $\Delta^{\circ}G^{\beta}_{\mathrm{Ni:N}}$ ($\beta = $ fcc, hcp, Ni_4N) were fitted to the following type of expression

$$\Delta^{\circ}G^{\beta}_{\mathrm{Ni:N}} = a^{\beta} + b^{\beta}T + c^{\beta}T\ln T + d^{\beta}T^{2} \tag{10}$$

Equation (10) has previously been found to provide a satisfactory representation of Gibbs energy values predicted from θ_{S} of various substances [4, 5, 26].

5. RESULTS AND DISCUSSION

5.1. "NiN" Nitride and the fcc Phase

As explained in Section 2.3 our treatment of the fcc phase was based on determining the parameter $\Delta^{\circ}G^{\mathrm{fcc}}_{\mathrm{Ni:N}}$, which, in our thermodynamic model [11], represents the properties of the hypothetical "NiN" (NaCl) nitride. $\Delta^{\circ}G^{\mathrm{fcc}}_{\mathrm{Ni:N}}$ was determined from a consideration of the correlations reviewed in Section 4.1. Experimental information on NaCl structure nitrides is available only for $n_{\mathrm{e}} \leqslant 5.5\ \mathrm{e \cdot a^{-1}}$ (i.e., the linear part of the solid lines in Figs. 2a and b), and the question has been considered [4] how the properties of this phase should be estimated at larger n_{e}. Some information on carbides suggested a linear extrapolation (e.g., the dashed lines in Figs. 1a and b), but for larger n_{e} the possibility was considered [4] of nonlinear plots with a positive deviation. The study of this question for E_{S} of "NiN" is hampered by the lack of entropy information. Therefore we relied, as an approximation, on the dashed line in Fig. 2a and estimated for "NiN" ($n_{\mathrm{e}} = 7.5$) $E_{\mathrm{S}} = 2.3$ Ry. Combining this with our own estimate $\Omega = 8.6\ 10^{-30}\ \mathrm{m^3 \cdot atom^{-1}}$, we get $k_{\mathrm{S}} = 119\ \mathrm{N \cdot m^{-1}}$ and $\theta_{\mathrm{S}} = 382$ K, which was used to determine the entropy of "NiN," as explained in Section 4.2. If, as suggested in Ref. 4, the E_{S} vs n_{e} curve for NaCl compounds at large n_{e} falls under that for complex nitrides (i.e., the dashed line in Fig. 2a), we are overestimating E_{S} and θ_{S} for "NiN," i.e., underestimating its entropy. Fortunately, data on the solubility of N in fcc at high temperatures and in equilibrium with N_2 gas or $NH_3 + H_2$ mixtures, reviewed in Ref. 8, are available. This solubility is very low, almost nil, and in the present work data from Ref. 27 were analyzed in an attempt to gain information on $\Delta^{\circ}H$ for "NiN." We performed a series of calculations where the entropy of "NiN" was the predicted one, but the $\Delta^{\circ}H$ value was varied so that the experimental solubility of N in fcc was reproduced. Because these calculations involved the properties of the fcc phase over a large composition range, we also tested various possible assumptions about the excess Gibbs energy term, Eq. (3). In particular, we varied $L^{\rm fcc}_{\rm Ni:N,Va}$ from $+20$ to $-30\ \rm kJ \cdot mol^{-1}$, which covers the range of interaction parameters which have been evaluated for the fcc phase in other 3d transition metal–nitrogen systems [6]. The results are given in Table II, where we also present the enthalpy of formation of an "NiN" compound according to the predictions of Miedema's formula [3]. It is evident that interaction parameters comparable to those for the Cr–N and Fe–N systems [6] lead to $\Delta^\circ H$ values falling under the solid line in Fig. 2b [which gives $\Delta^\circ H = -2\ \rm kJ \cdot (mol\ of\ atoms)^{-1}$ at $n_e = 7.5\ \rm e \cdot a^{-1}$] but well above the prediction of a linear extrapolation of the line from the range $n_e < 5.5\ \rm e \cdot a^{-1}$ [which gives $\Delta^\circ H = 160\ \rm kJ \cdot (mol\ of\ atoms)^{-1}$]. Lacking information to decide on the most probable $L^{\rm fcc}$ value, we chose $L^{\rm fcc} = 0$ and adopted $\Delta^\circ H = 21.6(\pm 10)\ \rm kJ \cdot (mol\ of\ atoms)^{-1}$. However, in view of our possible underestimation of the high-temperature entropy of "NiN" (see above), we regarded this value only as an approximation of the lowest limit for $\Delta^\circ H$ of "NiN." In line with this expectation, the enthalpy estimate based on Miedema's formula [3], $36\ \rm kJ \cdot (mol\ of\ atoms)^{-1}$, is larger.

5.2. "Ni_3N," $NiN_{0.5}$, and the Hexagonal Phase

Our treatment of the hexagonal phase was based on determining the properties of the hypothetical $NiN_{0.5}$ nitride. This was made by including

Table II. The parameter $L^{\rm fcc}_{\rm Ni:N,Va}$ Describing the Excess Gibbs Energy of the fcc Phase, and the Enthalpy of Formation of the Hypothetical "NiN" (NaCl) Nitride Phase Optimized in the Present Work, as Described in Section 5.1[a]

$L^{\rm fcc}_{\rm Ni:N,Va}$ $(\rm kJ \cdot mol^{-1})$	$\Delta^\circ H$ for "NiN" $[\rm kJ \cdot (mol\ of\ atoms)^{-1}]$	Comments
20.0	11.8	
0.0	21.6	Adopted in the present work
−20.0	31.2	
−25.0	34.1	
−30.0	36.6	
—	36.0	$\Delta^\circ H$ for an "NiN" compound, according to Miedema's formula (3)

[a] The enthalpy value for an "NiN" compound (unspecified structure) according to Miedema's formula is also given.

in the optimization procedure information on the $NiN_{0.33}$ composition (i.e., on the "Ni_3N" nitride) and assuming that the mixing of N atoms and vacancies on the second sublattice is ideal. The enthalpy of formation of Ni_3N has been determined by reaction calorimetry [28] and DTA experiments [29]. The results from [28], already adopted in Ref. 4, were used in the present optimization. The vibrational entropy was estimated by using Fig. 2a. From the value $E_S = 2.05$ Ry for $NiN_{0.33}$ ($n_e = 8.75\ e \cdot a^{-1}$) and the experimental [25] value $\Omega = 9.889\ 10^{-30}\ m^3 \cdot atom^{-1}$, we get $k_S = 97\ N \cdot m^{-1}$ and $\theta_S = 288$ K. The total entropy of $NiN_{0.33}$ was estimated by adding to the vibrational contribution the (ideal) configurational contribution (corresponding to $y_N = 0.33/0.50 = 0.66$) and neglecting other contributions.

5.3. Ni_4N Nitride

The following properties of Ni_4N (cP5), which has $n_e = 9\ e \cdot a^{-1}$, were estimated in Ref. 4 by combining Figs. 2a and b with the experimental value [25] $\Omega = 10.463\ 10^{-30}\ m^3 \cdot atom^{-1}$: $E_S = 2.05$ Ry, $k_S = 93\ N \cdot m^{-1}$, $\theta_S = 272$ K, and $\Delta^\circ H = 1\ kJ \cdot (mol\ of\ atoms)^{-1}$.

5.4. The Liquid Phase

The properties of the liquid phase were determined by evaluating a constant regular solution parameter $L^{liq}_{N,Ni}$ from N solubility data. In Fig. 3

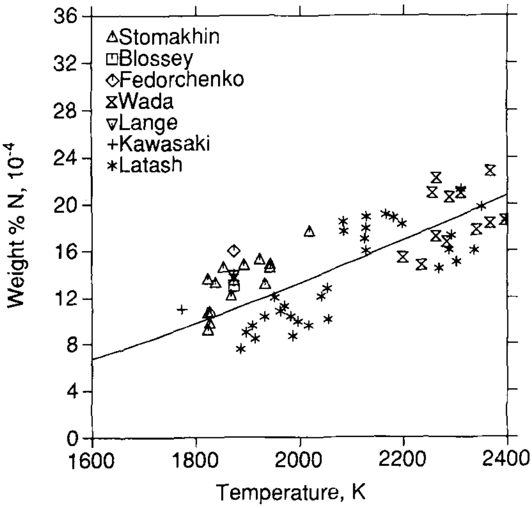

Fig. 3. The calculated solubility of N in liquid Ni in equilibrium with 1 atm N_2 gas, compared with experimental data [30–36].

the calculated solubility values are compared with experimental data over a range of temperatures [30–36]. These data are reasonably well represented by the present description.

5.5. The Ni–N Phase Diagram

In Fig. 4 we present the Ni–N phase diagram calculated using the thermodynamic description obtained in the present work (Table I). The very low solubility of N in fcc, indicated by experiments in Ref. 27, is reproduced by the calculation. However, the range of homogeneity of the hexagonal nitride phase is not known from experiments. Our prediction, in Fig. 4, for this phase indicates an appreciable range, extending on both sides of the composition corresponding to "Ni_3N." In particular, the Ni-richest boundary of the hexagonal phase field falls at $x_N = 0.15$, which is comparable to that of the calculated Fe–N phase diagram [6]. It should be noted that there is a report [37] on the preparation from fcc Ni and NH_3 at 623 K of a nitride with the formula $Ni_3N_{1.16}$ (i.e., $x_N = 0.28$). The possibility of such large deviation from the tentative formula "Ni_3N" ($x_N = 0.25$) seems to be in line with the results of the present calculation. Although Ni_4N was included as one of the competing phases in our calculation, this phase does not appear as a stable phase in the Ni–N phase diagram (Fig. 4), i.e., Ni_4N is predicted as a metastable phase in the Ni–N

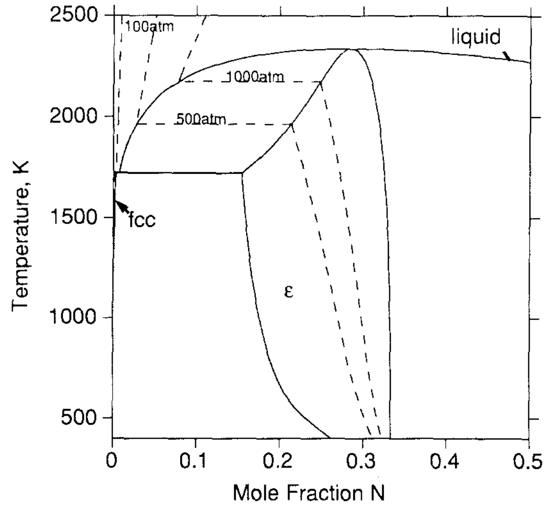

Fig. 4. The Ni–N phase diagram calculated using the thermodynamic description obtained in the present work, Table I. Dashed lines represent N isobars.

system. For temperatures higher than about 500 K, this prediction is in agreement with what was concluded in Ref. 8 from a review of the experimental data. The information at lower temperatures did not allow any firm conclusion, but Wriedt [8] tentatively suggested that Ni_4N may be stable below 523 K. In order to see how that could be accommodated in the present description, we performed a series of calculations where $\Delta^\circ H$ for Ni_4N was given values lower than $1\ \mathrm{kJ} \cdot (\mathrm{mol\ of\ atoms})^{-1}$, which is the value obtained from Fig. 2b. We found that a decrease to $0.45\ \mathrm{kJ} \cdot (\mathrm{mol\ of\ atoms})^{-1}$ is enough to bring Ni_4N in stable equilibrium with fcc and the hexagonal phase in a temperature range around 500 K. Since this enthalpy change is so close to what we obtained from Fig. 2b, we conclude that our description for Ni_4N corresponds, in fact, to a phase relatively close to being stable in the Ni–N system.

6. SUMMARY AND CONCLUSIONS

The thermodynamic properties of the Ni–N system are poorly known from experiments and there is a need for guidelines in estimating its properties and constructing a probable diagram. In the present paper we have presented a possible approach to this problem. It was based on combining the few experiments available with predictions based on the results from Ref. 4 and using thermodynamic calculations. In this way we have been able to construct a probable phase diagram for the Ni–N system, which gave us some new insight on questions such as the existence of a range of homogeneity in the hexagonal nitride phase and the stability of Ni_4N, which have not been fully answered by the experimental studies.

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REFERENCES

1. L. Kaufman and H. Bernstein, *Computer Calculation of Phase Diagrams* (Academic Press, New York, 1970).
2. cf. the CALPHAD Journal, Pergamon Press.
3. F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema, and A. K. Niessen, *Cohesion in Metals* (North-Holland, Amsterdam, 1988).
4. A. Fernández Guillermet and G. Grimvall, *Phys. Rev. B* **40**:10582 (1989).
5. A. Fernández Guillermet and G. Grimvall, *Z. Metallkunde* **81**:521 (1990).

6. K. Frisk, Trita-Mac-0393 (The Royal Institute of Technology, Stockholm, Sweden, April 1989).
7. K. Frisk, *Metall. Trans.* **21A**:2477 (1990).
8. H. A. Wriedt, *Bull. Alloy Phase Diagrams* **6**:558 (1985).
9. M. Hillert and M. Jarl, *CALPHAD* **2**:227 (1978).
10. G. Inden, Project Meeting Calphad V, June 21–25, 1976, Max Planck Inst. Eisenforschung, GmbH, Dusseldorf, Germany, Vol. 111(4), pp. 1–13.
11. M. Hillert and L.-I. Staffansson, *Acta Chem. Scand.* **24**:3618 (1970).
12. B. Sundman and J. Ågren, *J. Phys. Chem. Solids* **42**:297 (1981).
13. M. Hillert, in *Computer Modeling of Phase Diagrams*, L. H. Bennett, ed. (The Metallurgical Society, Warrendale, 1986).
14. Scientific Group Thermodata Europe (SGTE). Data for Pure Elements, Report DMA(A)195 September 1989. Compiled by A. T. Dinsdale. National Physical Laboratory, Teddington, UK.
15. K. Frisk, *CALPHAD* **11**:127 (1987).
16. A. Fernández Guillermet, *Z. Metallkunde* **78**:639 (1987).
17. D. A. Papaconstantopoulos, J. L. Fry, and N. E. Brener, *Phys. Rev. B* **39**:2526 (1988).
18. JANAF Thermochemical Tables, 3rd ed., *J. Phys. Chem. Ref. Data* **14**:Suppl. 1 (1985).
19. B. Jansson, Ph.D. thesis (The Royal Institute of Technology, Stockholm, Sweden, 1984).
20. J. Rosén and G. Grimvall, *Phys. Rev. B* **27**:7199 (1983).
21. G. Grimvall and J. Rosén, *Int. J. Thermophys.* **4**:139 (1983).
22. G. Grimvall, *High Temp.-High Press.* **17**:491 (1985).
23. G. Grimvall, *Thermophysical Properties of Materials* (North-Holland, Amsterdam, 1986).
24. A. Fernández Guillermet and G. Grimvall, *Phys. Rev. B* **40**:1521 (1989).
25. P. V. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (American Society for Metals, Metals Park, OH, 1985).
26. A. Fernández Guillermet and G. Grimvall, *J. Less-Common Met.* **147**:195 (1989).
27. H. A. Wriedt and O. D. Gonzalez, *Trans. AIME* **221**:532 (1961).
28. H. Hahn and A. Konrad, *Z. Anorg. Allg. Chem.* **264**:181 (1951).
29. A. Baiker and M. Maciejewski, *J. Chem. Soc. Faraday Trans. 1* **80**:2331 (1984).
30. A. Y. Stomakhin, P. Bayer, and A. Y. Polyakov, *Izv. Akad. Nauk SSSR Met.* **4**:37 (1965).
31. R. G. Blossey and R. D. Pehlke, *Trans. Met. Soc. AIME* **236**:566 (1966).
32. V. I. Fedorchenko, V. V. Averin, and A. M. Samarin, *Dokl. Akad. Nauk SSSR* **183**:894 (1968).
33. H. Wada, K. Gunji, and T. Wada, *Trans. Iron Steel Inst. Jap.* **8**:329 (1968).
34. K. W. Lange and H. Schenck, *Met. Trans.* **1**:2036 (1970).
35. M. Kawasaki, M. Tokuda, and M. Ohtani, *Bull. Res. Inst. Min. Dress. Metall. Tohoku Univ.* **35**:99 (1979).
36. Y. V. Latash, G. F. Torkhov, Y. I. Kostenko, and N. N. Kalinyuk, *Advances in Special Electrometallurgy* **2**:43 (1986).
37. R. J. Arnott and A. Wold, *J. Phys. Chem. Solids* **15**:152 (1960).

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