JMEPEG (1993) 2:651-658

Nitrogen Concentration in Fe-Cr-Mn Alloys

J.C. Rawers and M. Kikuchi

Nitrogen addition to iron alloys improves mechanical properties. The composition of the alloy as well as the melt pressure influences nitrogen concentration. In this US Bureau of Mines study, nitrogen concentrations in Fe-Cr-Mn alloys were determined. New thermodynamic expressions were derived to relate nitrogen concentration to alloy composition and melt pressure. These expressions included nonlinear terms, such as pressure-concentration and Cr-Mn terms.

Keywords
Fe-Cr-Mn steels, nitrogen, Sieverts' law, steel, thermodynamics

1. Introduction

NITROGEN, unlike carbon, is not easily alloyed with iron. Nitrogen solubility in iron at 1 atm is very limited, approximately 0.04 wt% for bcc alloys and 0.40 wt% for Fe-Cr-Ni fcc alloys.[1] For Fe-Cr-Mn alloys, the nitrogen concentration can reach 0.60 wt% when melted under nitrogen at 1 atm.[1] Several high-nitrogen stainless steels are currently being produced with all or part of their nickel alloy concentration replaced by manganese.[1]

Addition of nitrogen to austenitic stainless steels enhances mechanical and physical properties.[2] Unlike carbon alloying, which forms chromium carbides at carbon levels as low as 0.1 wt%, nitrogen remains in solid solution until the nitrogen concentration level exceeds 1.0 wt%.[3] Recently, it was shown that the nitrogen concentration in iron alloys can be increased significantly by melting under elevated nitrogen pressure.[4,5] The higher level of nitrogen in these alloys results in improved wear, fatigue, creep resistance, and tensile strength.

In an extended series of thermodynamic studies during the late 1960s and early 1970s, the concentration of nitrogen was determined for numerous iron alloys.[6-8] The majority of these alloys were Fe-*X* binary or Fe-Cr-Ni-*X* alloys (where *X* = Mn, Mo, V, etc.). Nitrogen concentration in these iron alloys was shown to be a function of alloying composition, crystal phase, and nitrogen pressure used during fabrication. It has been demonstrated in these studies that nickel decreases nitrogen concentration and manganese increases nitrogen concentration. Only a few commercial austenitic stainless steel alloys are produced with manganese.

Recently, a thermodynamic study of nitrogen concentration in binary iron alloys has been extended to determine the effect of melting under elevated pressure.[9] In this study, it was shown that the thermodynamic coefficients determined for iron-nitrogen alloys prepared at atmospheric pressure are similar to those determined for pressures as high as 10 MPa.

To date, there have been few studies that would allow researchers to predict nitrogen solubility in Fe-Cr-Mn alloys.[9,10] Thus, it has not been possible to generate phase diagrams describing the development of second-phase precipitates. Without phase diagrams, it is not possible to develop heat treatment processes similar to those currently available that improve mechanical properties of carbon steel.

This study was designed to extend previous nitrogen concentration studies to include nitrogen high-pressure melting of Fe-Cr-Mn alloys. Research is part of the US Bureau of Mines Advance Alloy Development Program, in which high-pressure melting is used to increase nitrogen concentation levels.[5]

2. Experimentation

Iron-chromium-manganese alloys were melted in a nitrogen-pressurized furnace. After cooling, nitrogen concentrations in the solids were measured.

A series of 150-g iron and iron alloy buttons (iron-chromium, iron-manganese, and iron-chromium-manganese) were arc melted in an inert, reduced pressure atmosphere (Table 1). The buttons were partitioned into thirds. One piece of each alloy was placed in an alumina crucible and melted in a hot isostatic pressure (HIP) furnace at 1650 °C under a nitrogen atmosphere of 0.1, 10, or 200 MPa. Temperature and pressure were simultaneously raised and held for 1 h. The melt pressure was maintained while the temperature was reduced to well below solidification temperature, approximately 1000 °C, after which the temperature and pressure were simultaneously reduced.

After cooling, the nitrogenated alloys were sectioned for microscopic examination and for nitrogen concentration determination. Nitrogen analyses were obtained from several different regions throughout each sample. Total nitrogen concentrations were obtained by inert gas fusion and thermal conductivity using a LECO TC-436 Nitrogen/Oxygen Determinator.[1] Metal matrix crystal phase and nitride precipitates were determined on prepared metallurgical mounts using X-ray diffraction. Nitride morphologies were determined by scanning electron microscope (SEM) examination of the metallographic surfaces.

3. Thermodynamic Analysis

Thermodynamic calculations for nitrogen concentration in iron and iron alloys have been made at or near atmospheric pressure.[6-8] There have been a limited number of studies that incorporate the effects of pressure on nitrogen solubility in metal alloys.[6,9] In the analysis below, thermodynamic expres-

---

J.C. Rawers, U.S. Bureau of Mines, Albany Research Center, Albany, Oregon, and **M. Kikuchi,** Tokyo Institute of Technology, Tokyo, Japan.

Table 1 Alloy composition, total nitrogen concentration (wt%), metal matrix phase(a), and nitride precipitate(b)

Composition, wt%			Nitrogen melt pressure		
Fe	**Cr**	**Mn**	**0.1 MPa**	**10 MPa**	**200 MPa**
100	...	...	0.042 α(a)	0.32 α(a,b)	1.69 α(a, b)
			0.025 α	0.27 α(b)	1.58 α(b)
			0.031 α	0.29 α(b)	1.74 α(b)
98	2	...	0.05 α	0.40 α	...
96	4	...	0.07 α	0.61 α	...
95	5	...	0.07 α	0.67 α(b)	2.51 α(b)
90	10	...	0.09 α	1.43 α (b)	3.55 α(b)
85	15	...	0.15 α	1.88 α(b)	4.15 α(b)
80	20	...	0.22 α	2.08 α(b)	4.35 α(b)
70	33	...	0.26 α (b)	2.42 α(b)	6.60 α(b)
97	...	3	0.05 α	0.38 α	1.44 α/δ
95	...	5	0.09 α	0.46 α	...
92	...	8	0.10 α	0.54 α/δ	2.04 δ
85	...	15	0.13 δ	0.81 δ(b)	2.81 δ(b)
82	...	18	0.16 δ	1.03 δ(b)	3.11 δ(b)
70	...	30	0.29 δ	1.82 δ(b)	4.31 δ(b)
95	2	3	0.06 α	0.50 α	...
91	4	5	0.13 α	0.58 α	...
90	5	5	0.17 α/δ	0.89 δ/α(b)	2.50 δ(b)
80	10	10	0.39 α/δ	1.02 δ/α(b)	3.67 δ(b)
70	10	20	0.42 δ	2.32 δ(b)	4.72 δ(b)
70	15	15	0.60 δ(b)	2.16 δ(b)	5.26 δ(b)
70	20	10	0.81 δ(b)	2.65 δ(b)	5.76 δ(b)
65	21	14	0.63 δ(b)	2.09 δ(b)	6.29 δ(b)
62	23	15	0.78 δ(b)	2.02 δ(b)	6.21 δ(b)
60	19	20	0.79 δ(b)	3.13 δ(b)	6.68 δ(b)
55	30	14	0.87 δ(b)	3.07 δ(b)	7.33 δ(b)
55	15	30	0.93 δ(b)	3.26 δ(b)	6.24 δ(b)
40	30	30	2.00 δ(b)	5.33 δ(b)	8.37 δ(b)

(a) α = bcc, δ = fcc. (b) X-Ray diffraction showed the presence of second-phase nitride precipitates $(Fe, Mn, Cr)_xN_y$.

sions were developed that account for variation of both alloy composition and for pressures up to 200 MPa and the effects on the nitrogen concentration on iron alloy microstructure. The derivations presented below are similar to recently published studies for nitrogen pressures up to 10 MPa.[9]

Thermodynamic principles, in particular Gibbs equation, can be used to predict the nitrogen concentration in liquid or solids:

$$\Delta G^0 = -R*T*\ln(K_{sp}) \qquad [1]$$

where G^0 is the Gibbs free energy; R is the universal gas constant; T is absolute temperature; K_{sp} is the solubility constant, which is equal to $[N]/\sqrt{P_N}$ (Sieverts' law), where [N] is the total nitrogen concentration, wt%; and P_N is the nitrogen pressure applied on the liquid in MPa.

Gibbs relationship requires that, for pure iron and for all nitrogen melt pressures, the solubility product, K_{sp}, should be constant. The pressure term, P, in Eq 1 is the gas activity coefficient, which for a nonideal gas requires corrections for temperature and pressure.

Nitrogen analysis of nitrogen high-pressure melted (N-HPM) pure iron shows that Sieverts' law (total nitrogen concentration is proportional to the square root of the nitrogen pressure) was valid over the pressure range 0.1 to 200 MPa:

$$[N] = 0.116*\sqrt{P_N} \qquad [2]$$

where the correlation coefficient $(R^2) = 0.995$.

The excellent linear fit of these data to Sieverts' law suggests that there was no need to apply fugacity corrections at elevated pressures and temperatures. Similar results have been observed in other studies for pressures to 10 MPa.[9]

For iron alloys, Eq 1 is used as the starting point for thermodynamic analyses. Variation in the nitrogen concentration due to alloy composition is accounted for by a Taylor series expansion in elemental composition about the pure iron nitrogen value:

$$\ln(K_{sp}) = \ln([N]_{Fe}/\sqrt{P_N}) \text{ for pure iron} \qquad [3]$$

$$\ln(K_{sp}) = \ln(f\,[N]_{alloy}/\sqrt{P_N}) \text{ for iron alloys} \qquad [4]$$

where f is the activity coefficient and $([N]_{Fe}/[N]_{alloy})_{P,T}$.

Correlation 1. The activity coefficient is a function of temperature and pressure, as well as alloy composition. For each temperature and pressure, the pure iron nitrogen concentration must be divided by the corresponding alloy nitrogen concentration at the same pressure and temperature. As a result of this

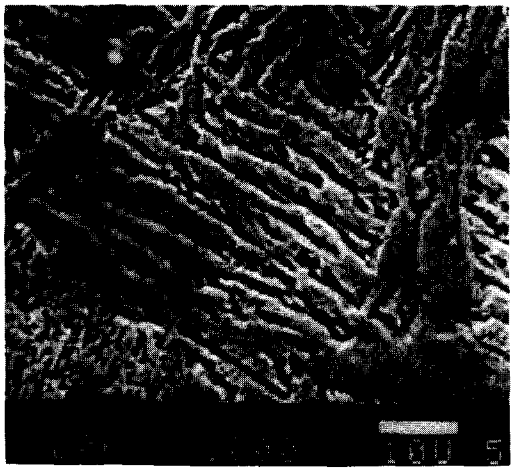

Fig. 1 Scanning electron micrograph of pure iron melted under 200 MPa nitrogen. The second-phase precipitate was determined by X-ray diffraction to be Fe_4N.

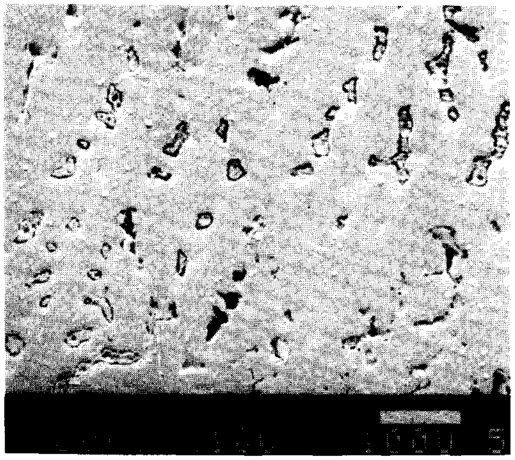

Fig. 2 Scanning electron micrograph of Fe-30Mn alloy melted under 200 MPa nitrogen. The second-phase precipitate was determined by X-ray diffraction to be Mn_2N.

pressure and temperature correction, the relationship between measured nitrogen concentration and alloy composition should produce a universal relationship independent of temperature and pressure.

To determine the elemental concentration effects of each alloy, the activity coefficient is expressed in a Taylor series:

$$\ln(f) = \Sigma\, E_i{*}[X_i] \qquad [5]$$

where E_i is the interaction coefficient which is equal to $\delta(\ln[\mathrm{N}]/\delta[X_i]$, where $[X_i]$ is alloy i concentration, wt%.

For Fe-Cr-Mn alloys, this reduces to:

$$\begin{aligned}\ln(f)_P = {} & E_0 + E_1{*}[\mathrm{Cr}] + E_2{*}[\mathrm{Cr{*}Cr}] + \\ & E_3{*}[\mathrm{Mn}] + E_4[\mathrm{Mn{*}Mn}] + \ldots \\ & E_5{*}[\mathrm{Cr{*}Mn}] + \ldots \end{aligned} \qquad [6]$$

Results from these studies will show that the above approach is not valid when the pressure is increased to 200 MPa. Two new derivations that account for pressure effects to be addressed and still maintain the general theoretical approach described above are presented below.

Correlation 2. Pressure correction can be introduced into the nitrogen determination by using Eq 3 and expanding about the measured nitrogen concentration:

$$\ln([\mathrm{N}]_{\mathrm{Fe}}/\sqrt{P_{\mathrm{N}}}) = \ln[\mathrm{N}]_{\mathrm{Fe}} - \ln\sqrt{P_{\mathrm{N}}} \text{ for pure iron} \qquad [7]$$

The alloy correction is again made as a series expansion:

$$\ln[\mathrm{N}]_{\mathrm{alloy}} = \mathrm{fnc.}([\mathrm{N}]_{\mathrm{Fe}}, [X_i], \ln\sqrt{P_{\mathrm{N}}} \qquad [8]$$

For Fe-Cr-Mn alloys, this reduces to:

$$\begin{aligned}\ln[\mathrm{N}]_{\mathrm{alloy}} = {} & E_0 + E_1{*}[\mathrm{Cr}] + E_2{*}[\mathrm{Cr{*}Cr}] + \ldots \\ & E_3{*}[\mathrm{Mn}] + E_4{*}[\mathrm{Mn{*}Mn}] + \ldots \\ & E_5{*}[\mathrm{Cr{*}Mn}] + \ldots \\ & E_6{*}\ln\sqrt{P_{\mathrm{N}}} + E_7{*}\mathrm{Cr}{*}\ln\sqrt{P_{\mathrm{N}}} + \ldots \\ & E_8{*}\mathrm{Mn}{*}\ln\sqrt{P_{\mathrm{N}}} + \ldots \end{aligned} \qquad [9]$$

where E_0 is the nitrogen concentration of pure iron, which is equal to $\ln[\mathrm{N}]_{\mathrm{Fe}}$.

This expression allows not only for determination of alloy composition and pressure effects, but also for interaction effects between alloying elements and pressure.

Correlation 3. Pressure correction can also be expressed by expansion of the solubility coefficient, K_{sp}:

$$K_{sp} = [\mathrm{N}]_{\mathrm{Fe}}/\sqrt{P_{\mathrm{N}}}, \text{ for pure iron} \qquad [10]$$

The alloy correction is again made in terms of a series expansion:

$$[\mathrm{N}]_{\mathrm{alloy}} = \mathrm{fnc.}([\mathrm{N}]_{\mathrm{Fe}}, [X_i], \sqrt{P_{\mathrm{N}}} \qquad [11]$$

For Fe-Cr-Mn alloys, this reduces to:

$$\begin{aligned}[\mathrm{N}]_{\mathrm{alloy}} = {} & E_0 + E_1{*}[\mathrm{Cr}] + E_2{*}[\mathrm{Cr{*}Cr}] + \ldots \\ & E_3{*}[\mathrm{Mn}] + E_4{*}[\mathrm{Mn{*}Mn}] + \ldots \\ & E_5{*}[\mathrm{Cr{*}Mn}] + \ldots \\ & E_6{*}\sqrt{P_{\mathrm{N}}} + E_7{*}\mathrm{Cr}{*}\sqrt{P_{\mathrm{N}}} + \ldots \\ & E_8{*}\mathrm{Mn}{*}\sqrt{P_{\mathrm{N}}} + \ldots \end{aligned} \qquad [12]$$

This expression is similar to Eq 9 in that it allows for higher order interactions between alloying elements and/or between alloying elements and pressure.

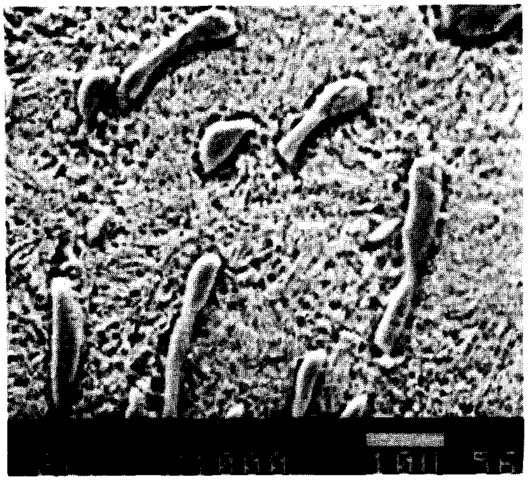

Fig. 3 Scanning electron micrograph of Fe-30Cr alloy melted under 200 MPa nitrogen. The second-phase precipitate was determined by X-ray diffraction to be CrN.

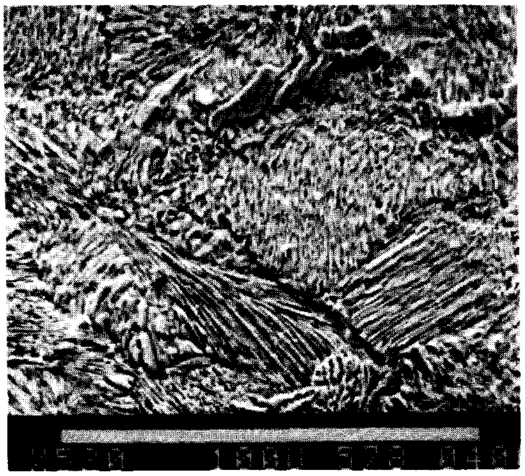

Fig. 4 Scanning electron micrograph of Fe-30Cr-15Mn alloy melted under 10 MPa nitrogen. Two different chromium nitrides were produced: (a) pearlite Cr_2N fcc iron and (b) eutectoid CrN.

Fig. 5 Scanning electron micrograph of Fe-30Cr-15Mn alloy melted under 200 MPa nitrogen. Two different CrN morphologies were produced: (a) eutectoid and (b) primary dendrite.

4. Microstructural Analysis

X-ray diffraction analysis of the Fe-Cr-Mn-N alloys shows that both bcc and fcc metal matrix phases, as well as metal nitride precipitates, can be present (Table 1). As the pressure increases, the nitrogen concentration increases, eventually reaching solubility limits and with increasing nitrogen concentration in the formation of metal nitrides. The nitride phase and microstructure that forms depend on alloy composition and nitrogen level.[11,12]

Micrographs of several different alloys are shown in Fig. 1 to 5. The principal goal of this study was to determine thermodynamic coefficients; microstructural analysis was conducted only to determine if and which precipitates form. Nitride precipitates that form in pure iron, Fe-Mn alloys, and Fe-Cr alloys are shown in Fig. 1, 2, and 3. Different chromium nitrides that form in Fe-Cr-Mn alloys as a function of nitrogen pressure during melting are shown in Fig. 4 and 5. For intermediate nitrogen concentrations, two different nitride phases were observed: (1) Cr_2N-fcc iron eutectoid pearlite and (2) CrN eutectic (Fig. 4). For higher nitrogen concentrations, two different CrN microstructures formed: (1) eutectic and (2) primary equiaxed structures (Fig. 5).

It is not the intent of this article to discuss the formation, chemistry, or development of nitride precipitates. Precipitate phases and microstructure will be discussed in an upcoming paper.[13] The precipitates and metal matrix phases are mentioned here only to show that determination of thermodynamic coefficients does not depend on which matrix phase is present or if precipitates are present.

5. Discussion

Before evaluating the differences between the different thermodynamic expressions, it is important to determine exactly what nitrogen concentration is being determined. The ability of only one expression to characterize nitrogen concentration in both fcc and bcc metal matrix is consistent with the interpretation that the derived thermodynamic coefficients are the same as those of the high-pressure melt conditions at 1650 °C. If the determined coefficients were a measure of the solid phase nitrogen concentration, then two different equations would be needed, one for the lower nitrogen solubility of bcc iron and one for the higher nitrogen solubility of fcc iron.

Four other observations are important before discussing the thermodynamic results. First, the fugacity correction for nitrogen gas at the pressures and temperatures used in this study is assumed to be 1.0, and therefore, no corrective term or expression is needed.[9,14,15] Second, chromium nitrides develop in Fe-Cr-Mn alloys at nitrogen concentration levels similar to levels where they develop in Fe-Cr-Ni alloys and have no effect on the derivation of the activity coefficients.[6] Third, the thermodynamic relationship between pure iron and the nitrogen concentration is linear with respect to nitrogen melt pressure.

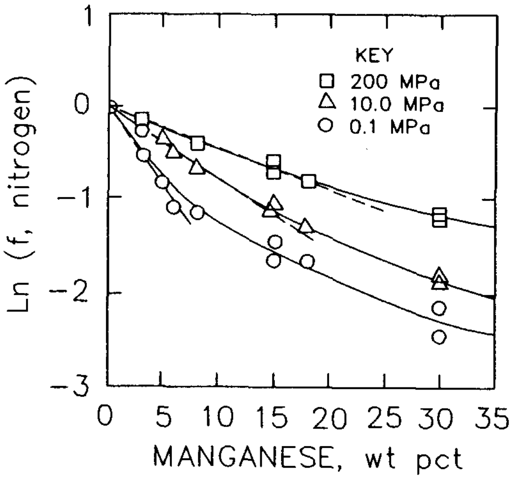

Fig. 6 Plot of ln(f) versus Mn for 0.1, 10, and 200 MPa melt pressure. If the pressure compensation had been achieved through use of the interaction coefficient, one line would explain all three pressures.

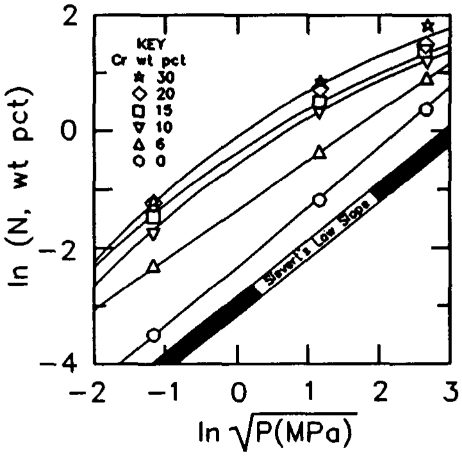

Fig. 7 Plot of the ln[N] versus ln($\sqrt{P}$) for different manganese concentrations. As the manganese concentration increases, there is an increasing loss of linearity.

Table 2 Statistically determined thermodynamic coefficients

Coefficients	Ref(a)	Correlation 1 ln(f_N)		Correlation 2 ln[N] Coefficient	Correlation 3 [N], Coefficient
		0.1	All		
Constant		−0.130	0.18	−2.20	−0.045
[Cr]	−0.104 to 0.131[6]	−0.140	−0.12	0.14	0.052
[Cr*Cr]	0.0024[8]	0.0024	0.0021	−0.0024	...
				ln$\sqrt{P}$ 1.01	$\sqrt{P}$0.260
				Cr*ln$\sqrt{P}$ −0.0076	Cr*$\sqrt{P}$ 0.0085
R^2 (34 samples)		0.97	0.81	0.99	0.97
Constant		−0.121	−0.081	−2.259	−0.058
[Mn]	−0.087[16,17]	−0.130	−0.087	0.097	0.018
[Mn*Mn]	0.0041[7]	0.0019	0.0010	−0.0010	...
				ln$\sqrt{P}$ 0.91	$\sqrt{P}$ 0.091
				Mn*ln$\sqrt{P}$ −0.0074	Mn*$\sqrt{P}$ 0.006
R^2 (39 samples)		0.96	0.74	0.98	0.98
Constant		−0.141	−0.149	−2.162	−0.127
[Cr]	−0.104 to 0.131[6]	−0.135	−0.104	0.121	0.025
[Cr*Cr]	0.0024	0.0022	0.0016	−0.0018	...
[Mn]	−0.087[16,17]	−0.133	−0.073	0.085	0.024
[Mn*Mn]	0.0041[7]	0.0020	0.00072	−0.00062	...
[Cr*Mn]	0.0014[7]	0.0005	0.00081	−0.00093	0.0009
				ln$\sqrt{P}$ 0.98	$\sqrt{P}$ 0.124
				Cr*ln$\sqrt{P}$ −0.0093	Cr*$\sqrt{P}$ 0.0082
				Mn*ln$\sqrt{P}$ −0.012	Mn*$\sqrt{P}$ 0.0044
R^2 (120 samples)		0.97	0.70	0.99	0.97

Sieverts' law is thus assumed to be valid over the melt pressure range 0.1 to 200 MPa. Similar results have recently been observed for nitrogen concentrations in iron melted under pressures as high as 10.0 MPa.[9] Thus, any nonlinear effects in the nitrogen-pressure relationship resulting from alloying are not attributable to the nitrogen departure from behavior as an ideal gas. Fourth, the measured nitrogen concentration in the solid is that of the liquid state. If nitrogen were being emitted from the melt during solidification, then there should be a porous region below the skull which is the first region to solidify.

In this study, low-pressure (0.1 MPa) thermodynamic calculated coefficients are consistent with previously determined values (Table 2, Correlation 1). Previous studies have also shown that determinations of the nitrogen activity coefficients often require first order, second order, and nonlinear terms.[7,16] In addition, one of the authors has shown that Fe-Mn[17-19] and Fe-Cr-Ni[15] alloys prepared at atmospheric pressure using the high-pressure melting technique (described in the experimental section) have thermodynamic coefficients that are consistent with those determined by other techniques,

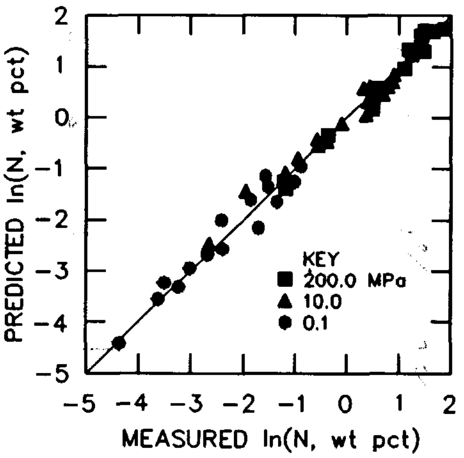

Fig. 8 Plot of the ln[N] (Eq 9) versus experimentally determined ln[N].

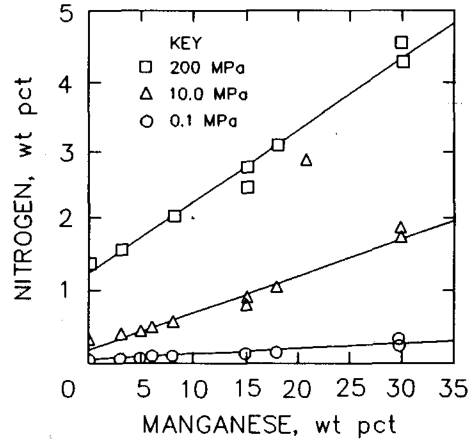

Fig. 9 Plot of nitrogen concentration versus manganese alloy concentration of Fe-Mn alloys for three different pressures.

such as Sieverts' apparatus, for determination of nitrogen concentration in liquid metal.[1,6]

For Fe-Cr alloys, the Cr and Cr*Cr coefficients determined in this study are in agreement with the range of previously determined values.[6,8] Furthermore, there is little difference between the reported values and the values obtained in either Correlation 1 or Correlation 2. Similarity of results is to be expected due to the similarity of the theoretical approach used in deriving Correlations 1 and 2.

For Fe-Mn alloys, the Mn coefficient determined in this study is approximately the same as that previously measured.[17,18] However, values for the higher order Mn*Mn coefficients are different from those determined previously.[7] One possible explanation for this is the extended range of manganese concentrations used in this study.

For Fe-Cr-Mn alloys, there is little difference between the values of elemental coefficients determined for Fe-Cr-Mn alloys and those for Fe-Cr and Fe-Mn alloys.

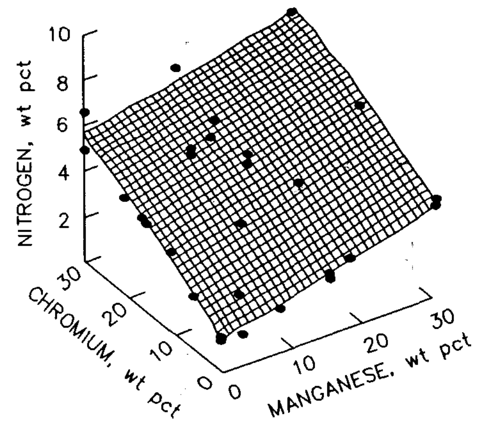

Fig. 10 Three-dimensional plot of nitrogen for different chromium and manganese concentrations for Fe-Cr-Mn alloys melted under 200 MPa.

There are considerable differences in statistical reliability of results among the different analytical techniques when data of all pressure melts are combined. When the data from all three different pressures are combined and the statistical analysis is applied to determine thermodynamic coefficients, the statistical fit becomes tenuous for Correlation 1 (Table 2). Figure 6 is a plot of ln(f) versus [Mn] for the three different pressures used in this experiment. As the manganese concentration increases, the ln(f) relationship becomes nonlinear, and pressure dependent. Similar results have previously been observed for Fe-Cr and Fe-Cr-Ni alloys.[12,20] It is evident from Fig. 6 that there remains a significant pressure effect in the Correlation 1 analysis and that pressure correction terms must be included in any thermodynamic expression.

Because it is difficult to visualize the four dimensional relationships among Fe, Cr, Mn, and N, the following discussion on the determination of thermodynamic coefficients will be limited to Fe-Mn and Fe-Cr alloys. Results for the Fe-Cr-Mn-N alloys are consistent with Fe-Mn-N and Fe-Cr-N analysis and are presented in Table 2.

Incorporating the pressure term into the thermodynamic analysis (Correlation 2, Eq 7, and Correlation 3, Eq 9) significantly improves the statistical correlation. Correlation coefficients for linear and higher order terms in Correlation 2 are very similar to those determined by Correlation 1 for 0.1 MPa (atmospheric pressure) data only and to the reference values. Coefficients for the pressure term are consistent with the hypothesis that the pressure dependence follows Sieverts' law.

The correlation between ln[N] and $\ln\sqrt{P}$ for Fe-Cr alloys in Fig. 7 shows the linear relationship (Sieverts' law) between pressure and nitrogen for pure iron. As the chromium concentration is increased, an increasing nonlinear dependence of the nitrogen concentration is observed. Addition of the pressure concentration term accounts for this nonlinearity and significantly increases the statistical correlation. The relationship between nitrogen concentration predicted by Eq 9 for all Fe-Cr-Mn alloys and nitrogen concentration measured at different pressures in this study is shown in Fig. 8. There is considerable overlap between different pressures and alloy concentration, and there is no observed scatter due to the presence of precipitates or to different metal matrix phases.

As previously noted, there is a linear correlation between nitrogen concentration and alloy concentration at each pressure (Fig. 9). Thermodynamic coefficients determined by Correlation 3 and Eq 10 and 12 have excellent statistical reliability. The relationship between Cr, Mn, and N at 200 MPa is shown in Fig. 10.

In comparing the different correlations, it is apparent that incorporating the pressure dependency implicitly into the activity coefficient, i.e., Correlation 1, does not provide statistically meaningful results over large pressure ranges. When pressure terms are explicitly added to the activity coefficient expansion, i.e, Correlations 2 and 3, the derived thermodynamic coefficients are consistent with Correlation 1 at 1 atm and the extra terms extend the range of validity from 0.1 to 200 MPa. Two different correlation techniques were proposed, both of which produced extremely accurate results. Both techniques are derived from similar starting points and both are consistent with Sieverts' law. The data did not allow evaluation as to which was correct. One technique, Correlation 2, has been used previously,[9] and those coefficients can be compared directly with previously published results. The other approach (Correlation 3) was proposed after examining the data and results in the use of fewer coefficients.

6. Summary

Nitrogen alloying in Fe-Cr-Mn solids prepared by high-pressure melting results in nitrogen concentrations predicted for the molten temperature. Thermodynamic expression based on concepts developed during the 1960s and 1970s are valid for atmospheric melts. However, it was not possible to combine thermodynamic results from different pressure data into the previous thermodynamic expression. To extend the thermodynamic relationships to high pressures, pressure concentration terms were needed. When these terms are incorporated into the theoretical derivation, the new expressions produce statistically meaningful results.

References

1. *Metals Handbook, Desk Edition*, H.E. Boyer and T.L. Gall, Ed., American Society for Metals, 1985
2. M.O. Spiedel, *High Nitrogen Steel—90*, Proc. Conf. 10-12 Oct 1990, G. Stein and H. Witulski, Ed., Verlag Stahleisen, Germany, 1990, p 128
3. H.A. Wriedt, N.A. Gokcen, and R.H. Nafziger, *Bull. Alloy Phase Diagrams*, Vol 8 (No. 4), 1987, p 355
4. G. Stein, J. Menzel, and H. Dorr, *High Nitrogen Steel—88*, Lille, France, J. Foct and A. Hendry, Ed., Institute of Metals, London, 1988, p 32
5. J. Rawers, J. Dunning, and R. Reed, *Adv. Mater. Proc.*, Vol 8, 1990, p 90
6. R.D. Pehlke and J.F. Elliott, *Metall. Trans. Soc. AIME*, Vol 218, 1960, p 1088
7. H. Wada and R.D. Pehlke, *Metall. Trans. B*, Vol 8 (No. 12), 1977, p 675
8. R.D. Blossy and R.D. Pehlke, *Metall. Trans. Soc. AIME*, Vol 242, 1968, p 2457
9. A.H. Satir-Kolorz and H.K. Feichtinger, *Z. Metallkunde*, Vol 82 (No. 9), 1991, p 689
10. J. Siwka and S. Tochowicz, *Arch. Metall.*, Vol 35 (No. 3), 1990, p 449
11. J. Rawers, R. Brown, and R. McCune, *High Temp. High Press.*, Vol 22, 1990, p 459
12. J.C. Rawers and L.J. Rawers, *J. Mater. Sci. Lett.*, Vol 10, 1991, p 1101
13. J. Rawers, *Scr. Metall. Mater.*, 1992, accepted for publication
14. T. Masumoto, M. Naka, and Y. Imai, *J. Jpn. Inst. Met.*, Vol 34 (No. 2), 1970, p 195
15. N.G. Shaposhnikov, Y.N. Surovoi, and Y.I. Kas'yanov, *Russ. J. Phys. Chem.*, Vol 64 (No. 1), 1990, p 110
16. S.Z. Beer, *Trans. Metall. Soc. AIME*, Vol 221, 1961, p 2
17. H. Schenek, M.G. Frohberg, and H. Heinemarn, *Arch. Eisenhutt.*, Vol 33 (No. 9), 1962, p 593
18. H. Wentrup and O. Reif, *Arch. Eisenhutt.*, Vol 20, 1949, p 359
19. G.M. Grirorienko, *Izv. SSSR Metall.*, Vol 6, 1974, p 11
20. J. Rawers, R. Pehlke, and N. Gokcen, *Metall. Trans. A*, Vol 24A, No. 1, 1993, p73