Met. Mater. Int., Vol. 19, No. 5 (2013), pp. 1077~1081
doi: 10.1007/s12540-013-5024-0

Nitrogen Solubility in High Manganese-Aluminum Alloyed Liquid Steels

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(received date: 23 January 2013 / accepted date: 1 April 2013)

The nitrogen solubility in liquid Fe-Mn and Fe-Mn-Al alloys has been measured by the gas-liquid metal equilibration technique utilizing a high frequency induction furnace under the nitrogen partial pressures of 0.1 to 0.8 atm in the temperature range of 1773 to 1873 K. The variation of the nitrogen solubility with the addition of manganese was measured by sampling and *in-situ* analysis of nitrogen content. Manganese significantly increased nitrogen solubility in liquid Fe-Mn and Fe-Mn-Al alloys. The nitrogen dissolution followed the Sieverts' law for liquid Fe-Mn alloys contained manganese up to 26 mass%. Using the Wagner's interaction parameter formalism, the experimental results were thermodynamically analyzed to determine the first- and second-order interaction parameters of manganese and aluminum on nitrogen in high Mn-Al alloyed liquid steels. No temperature dependence of these values was observed in the temperature range of 1773 to 1873 K. $e_N^{Mn} = -0.023, r_N^{Mn} = 0 \;\; r_N^{Mn,Al} = 0$ (Mn≤26 mass%, Al≤0.4 mass%, 1773-1873 K).

Key words: metals, thermodynamic properties, high manganese steel, nitrogen solubility, interaction parameter

1. INTRODUCTION

Recently, high manganese steels such as Twinning Induced Plasticity (TWIP) steels have been developed as next generation steels because of their high formability as well as excellent strength and ductility [1-3]. In these steel grades, a large amount of manganese (15-20 mass%) and aluminum (1-2 mass%) are added to liquid steels [4], and such high manganese and aluminum concentrations bring the great challenges to the steelmaking and casting processes. Manganese significantly increases the nitrogen solubility in liquid iron [5-9] and the AlN inclusions can be easily formed at such high aluminum concentrations [10-11]. In order to control the nitrogen content and the formation of AlN inclusions in these steel grades during the steelmaking process, it is important to understand the thermodynamic interactions of manganese and aluminum on nitrogen in liquid Fe-Mn-Al-N alloys.

Nitrogen solubility in Fe-Mn alloy melts has been measured using the Sieverts' method [5] and the sampling method [6-9]. In the authors' recent study [12,13], nitrogen solubility in Fe-Al alloy melts was measured using the sampling method in the temperature range of 1823 to 1973 K. However, the simultaneous effect of manganese and aluminum at high concentrations on nitrogen in liquid Fe-Mn-Al-N alloys is still not known. Also, there remains uncertainty about the temperature dependence of the interaction parameter of manganese on nitrogen in liquid Fe-Mn alloys [9]. Therefore, it is worthwhile to check the temperature dependence of this parameter at a low temperature near the melting point of Fe-Mn alloys.

In the present study, the effect of manganese on nitrogen solubility in Fe-Mn alloy melts containing manganese up to 26 mass% was measured in the temperature range of 1773 to 1873 K at a reduced nitrogen partial pressure of 0.3 atm. The simultaneous effect of manganese and aluminum on nitrogen solubility was also measured in the temperature range of 1823 to 1873 K. Using Wagner's formalism [14], the present results were thermodynamically analyzed to determine the interaction parameters of manganese and aluminum on nitrogen in liquid Fe-Mn-Al-N alloys over a wide range of melt compositions and temperatures.

2. EXPERIMENTAL

2.1. Experimental procedures

The gas-liquid metal equilibration experiments were carried out to measure nitrogen solubility in Fe-Mn and Fe-Mn-Al melts. Detailed descriptions of the experimental apparatus and procedure are available in the authors' recent studies on Fe-Al-N and Fe-Cr-N systems [13,15].

Five hundred grams of high purity electrolytic iron contained in an Al_2O_3 crucible (outer diameter (OD): 56 mm, inner diameter (ID): 50 mm, height (H): 96 mm) was melted using a 15 kW/30 kHz high frequency induction furnace as

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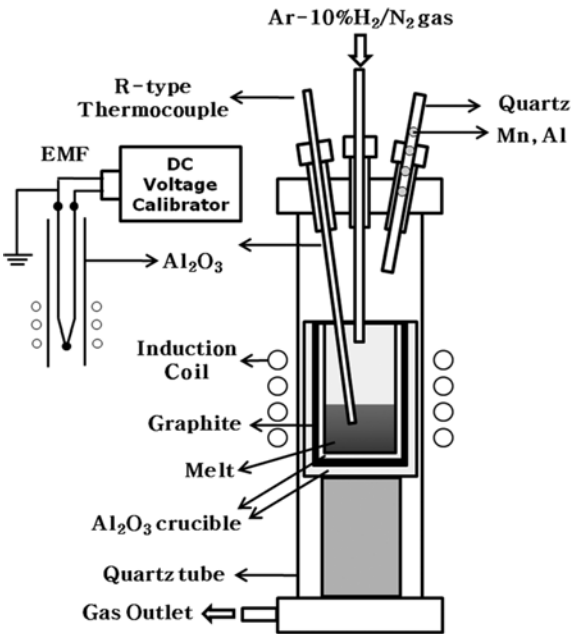

Fig. 1. Schematic diagram of experimental system.

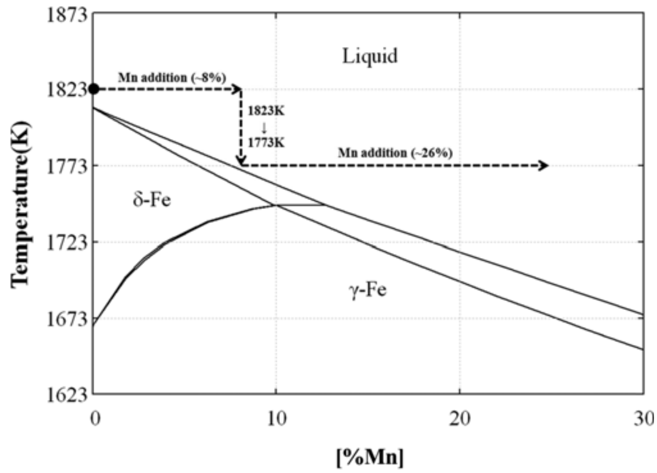

Fig. 2. Fe-Mn binary phase diagram [16].

shown in Fig. 1. After melting the iron, the melt temperature was directly measured using a Pt/Pt-13 mass%Rh thermocouple sheathed with an 8 mm OD alumina tube immersed in the melt; the temperature was accurately controlled within 2 K during the experiment using the proportional-integral-derivative (PID) controller of the induction furnace. After the melt temperature reached the desired value, Ar-10%H_2 gas was blown onto the melt surface at a high flow rate of ~5000 ml/min for 2 h to deoxidize the iron melt. The oxygen content in the melt decreased to a value of less than 20 mass ppm. Then, the gas was switched to a mixture of Ar-10%H_2 and N_2 gases to yield nitrogen partial pressures from 0.1 to 0.8 atm. The flow rate of the gas mixture was controlled using a mass flow controller in the range of 1000-2000 ml/min depending on nitrogen partial pressures in the gas. Strong agitation of the melt by the induction furnace resulted in a fast attainment of equilibrium nitrogen solubility in liquid iron under nitrogen partial pressure within 1 hour.

2.2. Nitrogen solubility measurements

In order to measure nitrogen solubility in Fe-Mn-N melts, manganese pellets (99.99% purity) were added to liquid iron through an 18 mm OD quartz tube after confirming the equilibrium nitrogen solubility in pure liquid iron under a nitrogen partial pressure of 0.3 atm. Figure 2 provides a phase diagram of the Fe-Mn alloy system calculated using the Factsage program [16]. For an experimental run at 1773 K for the Fe-Mn-N melt, high purity electrolytic iron was melted at 1823 K and manganese pellets were added up to 8 mass%. Then, the melt temperature was decreased to 1773 K as shown in Fig. 2. After each manganese addition, a new level of nitrogen solubility was attained within 1 hour; this level was confirmed by sampling and *in situ* analysis of nitrogen at 30 minutes intervals. For nitrogen solubility in Fe-Mn-Al-N melts, pre-melted Mn-1 mass%Al alloys were added to liquid iron under various nitrogen partial pressures in the range of 0.1-0.8 atm. Manganese addition was repeated up to 26 mass%Mn in liquid iron.

2.3. Chemical analysis

The metal sample was extracted using a 6 mm OD quartz tube; sample was quenched rapidly in water within 2 seconds. The metal samples were carefully cut for the chemical analysis. Four specimens of each metal sample were prepared for the analysis of nitrogen and oxygen. The nitrogen and oxygen contents in the metal sample were measured using the inert gas fusion-infrared absorptiometry technique (LECO TC-600 apparatus; LECO Corporation, St. Joseph, MI), which has an accuracy of ±2 mass ppm. For the analysis of manganese and aluminum, the metal sample (0.2 g) was dissolved in 20 mL of HCl (1+1) in a glass beaker of 50 mL capacity heated in a water bath for 2 h and analyzed using the inductively coupled plasma atomic emission spectroscopy (ICP-AES, SPECTRO ARCOS apparatus, manufactured by Spectro Analytical Instruments, Kleve, Germany); appropriate standard solutions containing the same amount of Fe (2000 mass ppm) were used as sample solutions. The analytical limit for manganese and aluminum in the metal sample was 5±1 mass ppm.

3. RESULTS AND DISCUSSION

The equilibrium nitrogen solubility in Fe-Mn containing manganese up to 26 mass% was measured to determine the effect of manganese on nitrogen solubility in liquid iron. The experimental results are summarized in Table 1. Figure 3

Table 1. Nitrogen Solubility in Fe-Mn and Fe-Mn-Al melts

Temperature (K)	P_{N_2} (atm)	[%Mn]	[%N]
		0	0.0249
		3.30	0.0308
		8.06	0.0391
1873	0.3	11.65	0.0463
		15.74	0.0542
		17.99	0.0632
		21.08	0.0730
		0	0.0248
		4.17	0.0308
		8.31	0.0378
1823	0.3	12.04	0.0459
		15.47	0.0538
		18.80	0.0638
		22.29	0.0748
		8.60	0.0395
		11.11	0.0452
		13.68	0.0514
1773	0.3	16.41	0.0571
		18.56	0.0641
		21.07	0.0736
		23.69	0.0824
		25.63	0.0933

shows the nitrogen solubility in Fe-Mn melts under a nitrogen partial pressure of 0.3 atm at 1773, 1823, and 1873 K. Manganese significantly increases nitrogen solubility in liquid iron.

The dissolution of nitrogen in liquid iron alloys can be expressed as

$$\frac{1}{2}N_2(g) = \underline{N} \tag{1}$$

$$\Delta G_1^o = 3,598 + 23.89T \quad \text{J/g}\cdot\text{atom}^{[5]}$$

$$K_N = \frac{f_N[\%N]}{P_{N_2}^{1/2}} \tag{2}$$

where K_N is the equilibrium constant for Reaction (1), [%N] is the equilibrium nitrogen content in mass% and, f_N is the Henrian activity coefficient of nitrogen, for which the reference state is the infinitely dilute solution, i.e., $f_N \rightarrow 1$ when [%N]→0. P_{N_2} is the nitrogen partial pressure in atm over the melt surface.

Using Wagner's formalism [14], the activity coefficient of nitrogen can be expressed as the following relation using the interaction parameters:

$$\log f_N = (e_N^N[\%N] + r_N^N[\%N]^2 + e_N^{Mn}[\%Mn] + r_N^{Mn}[\%Mn]^2) \tag{3}$$

where e_N^i and r_N^i, respectively, are the first- and second-order interaction parameters of elements on nitrogen in liquid iron. As mentioned earlier, the oxygen content was very

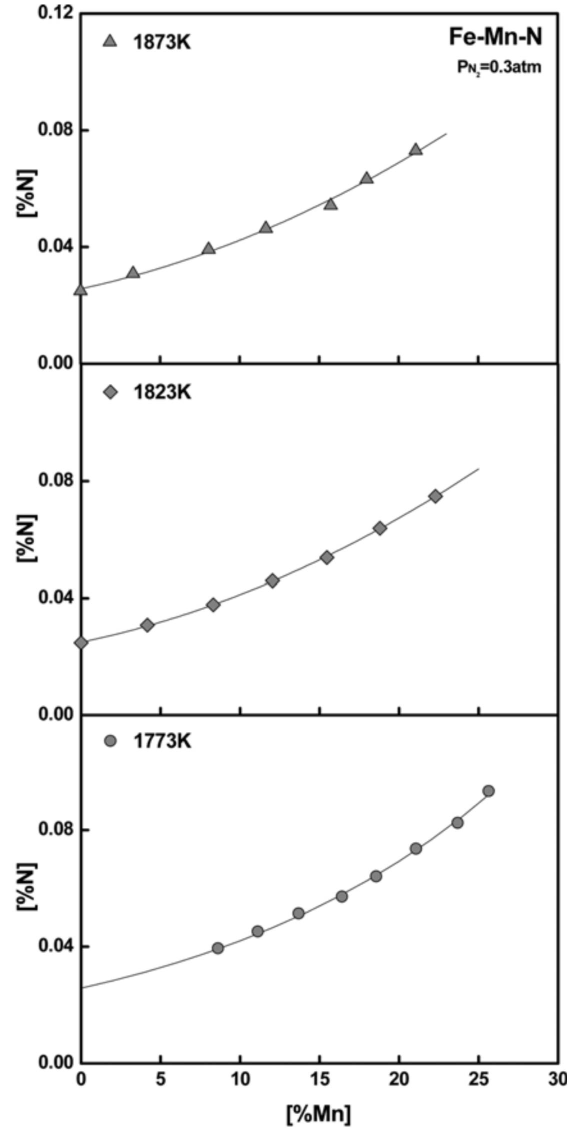

Fig. 3. Effect of manganese additions on nitrogen solubility in Fe-Mn-N melts.

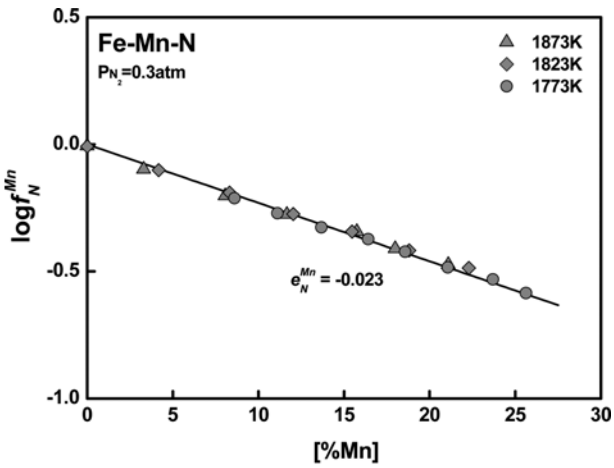

Fig. 4. Relation of $\log f_N^{Mn}$ *vs.* [%Mn] in Fe-Mn-N.

Table 2. Interaction Parameters of Mn on N in Liquid Iron

e_N^{Mn}	r_N^{Mn}	$r_N^{Mn,Al}$	Temp. range (K)	Comp. range	Method	Ref.
-0.023	0	0	1773-1873	[%Mn]≤26, [%Al]≤0.4	Sampling	Present study
-0.020			1879	[%Mn]<6	Sieverts	5
-0.020			1823-1973	[%Mn]<4	Sampling	6
-0.0245			1873-1973	[%Mn]<22.5	Sampling	7
-0.020			1813-1953	[%Mn]<9	Sampling	8
-0.0209 (-59.6/T+0.011)			1823-1923	[%Mn]<25	Sampling	9

low in the melt and the effect of oxygen on nitrogen was assumed to be negligible. The e_N^N and r_N^N values are known to be zero in the present experimental temperature range [17].

Figure 4 shows the relation of log f_N *vs.* manganese content in mass% in Fe-Mn-N melts using the relation expressed by Eq. (3). The data determined at different temperatures show an excellent linear relationship. Therefore, the values of e_N^{Mn} and r_N^{Mn} can be determined as -0.023 and 0, respectively, using a linear regression analysis of the data in the figure. No temperature dependence of these values was observed in the temperature range of 1773 to 1873 K.

Several groups, including Pehlke and Elliott [5], Maekawa and Nakagawa [6], Wentrup and Reif [7], Ishii *et al*. [8] and Shin *et al*. [9] measured nitrogen solubility in Fe-Mn melts at 1 atm nitrogen pressure. They reported e_N^{Mn} values in the range of -0.02 ~ -0.0245 in the temperature range of 1813-1973 K; these data are shown in Table 2 for comparison. The e_N^{Mn} value determined in the present study is in good agreement with the values shown in Table 2. Shin *et al*. [9] reported a slight temperature dependence of e_N^{Mn} values of -59.6/T + 0.011 in the temperature range of 1823-1923 K. In the present study, however, the temperature dependency of this parameter was negligible within the experimental uncertainty.

The simultaneous effect of manganese and aluminum on nitrogen solubility was also measured in Fe-Mn-Al melts. The experimental results are summarized in Table 3. Figure 5 shows the nitrogen solubility in Fe-Mn-Al melts under various nitrogen partial pressures at 1823, 1848, and 1873 K.

For an Fe-Mn-Al-N alloy, the activity coefficient of nitrogen can be expressed as

$$\log f_N = e_N^{Mn}[\%Mn] + r_N^{Mn}[\%Mn]^2 + e_N^{Al}[\%Al] + r_N^{Al}[\%Al]^2 + r_N^{Mn,Al}[\%Mn][\%Al] \quad (4)$$

where the values of e_N^{Mn} and r_N^{Mn} were determined as -0.023 and 0, respectively, at 1773-1873 K in liquid Fe-Mn-N alloy in the present study, and the values of e_N^{Al} and r_N^{Al} were previously determined as 0.017 and 0, respectively, at 1823-1973 K in liquid Fe-Al-N alloy in the authors' recent study [13].

Figure 6 shows the relation of Eq. (4) to determine the value of $r_N^{Mn,Al}$ using the nitrogen solubility data for Fe-Mn-Al melts in Table 3. From the slope of the straight line shown in the figure, the value of $r_N^{Mn,Al}$ can be shown to be zero in the temperature range of 1823 to 1873 K.

Table 3. Nitrogen Solubility in Fe-Mn-Al Melts

Temp. (K)	P_{N_2} (atm)	[%Mn]	[%Al]	[%N]
1873	0.7	0	0	0.0372
		0.54	0.01	0.0386
		1.54	0.02	0.0401
		1.94	0.03	0.0414
		5.91	0.06	0.0520
		9.65	0.07	0.0623
		13.45	0.22	0.0750
		16.68	0.28	0.0872
	0.3	0	0	0.0320
		0.78	0.11	0.0336
		1.49	0.17	0.0355
		1.99	0.17	0.0366
		5.09	0.19	0.0414
		9.21	0.21	0.0525
		13.33	0.29	0.0643
		17.59	0.32	0.0773
		20.26	0.38	0.0939
	0.1	0	0	0.0142
		0.38	0.01	0.0146
		1.80	0.03	0.0156
		4.72	0.08	0.0184
		8.17	0.14	0.0221
		11.57	0.20	0.0263
		14.46	0.26	0.0306
1848	0.8	0	0	0.0404
		0.52	0.01	0.0416
		1.63	0.02	0.0442
		2.13	0.03	0.0460
		5.40	0.10	0.0544
		9.68	0.15	0.0676
		12.77	0.23	0.0814
		16.59	0.27	0.0950
1823	0.4	0	0	0.0283
		0.51	0.01	0.0292
		1.59	0.02	0.0313
		2.14	0.03	0.0327
		6.49	0.08	0.0413
		10.04	0.15	0.0497
		13.56	0.22	0.0595
		16.88	0.26	0.0699

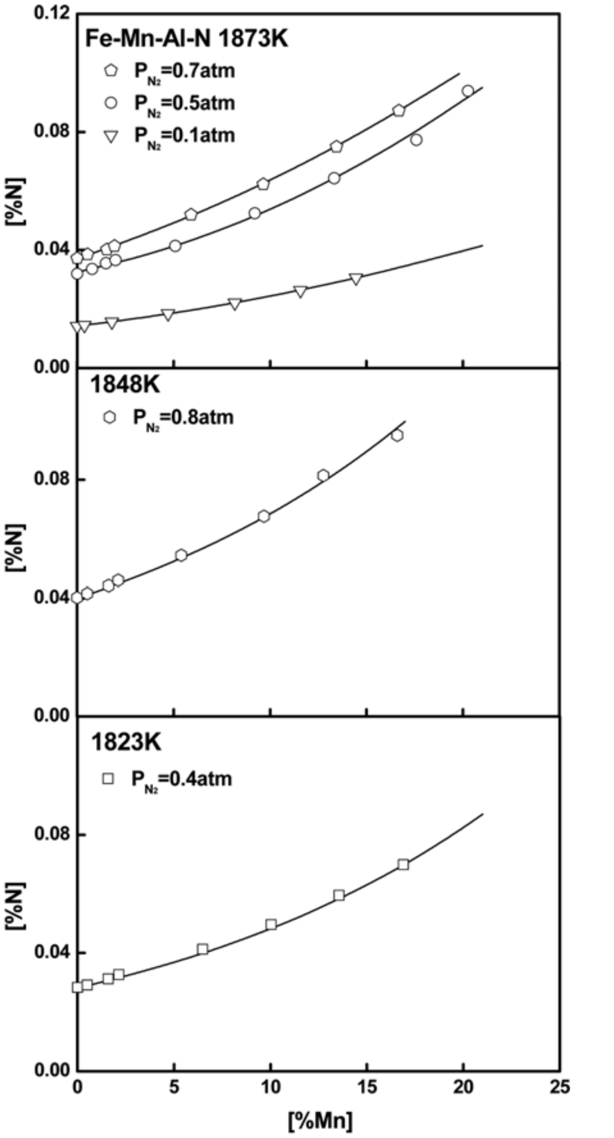

Fig. 5. Effect of manganese additions on nitrogen solubility in Fe-Mn-Al-N melts ([%Al]: 0-0.4%).

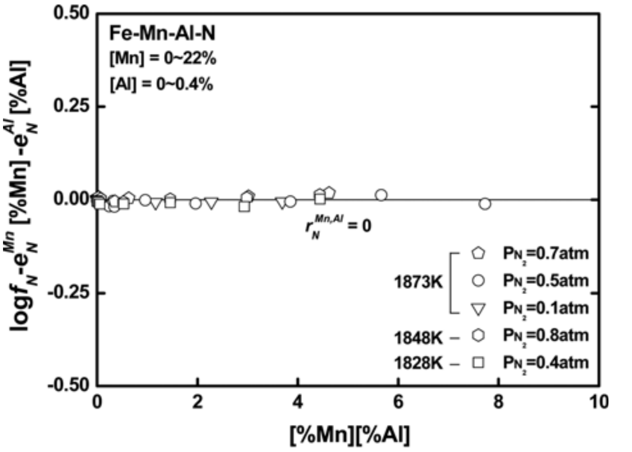

Fig. 6. Relation of $\log f_N - e_N^{Mn}$ [%Mn] $- e_N^{Al}$ [%Al] *vs.* [%Mn][%Al] in Fe-Mn-Al-N melts.

4. CONCLUSIONS

Nitrogen solubility in Fe-Mn and Fe-Mn-Al melts was measured using the gas-liquid metal equilibration technique in the temperature range of 1773 to 1873 K. The main findings of this study can be summarized as follows.

(1) Manganese significantly increases nitrogen solubility in Fe-Mn-N melts; the first- and second-order interaction parameters of manganese on nitrogen are $e_N^{Mn} = -0.023$, $r_N^{Mn} = 0$ (Mn≤26 mass%, 1773-1873 K).

(2) The second-order interaction parameter of manganese and aluminum on nitrogen in Fe-Mn-Al-N melts is $r_N^{Mn,Al}=0$ (Mn≤20 mass%, Al≤0.4 mass%, 1823-1873 K).

(3) No temperature dependence of interaction parameters was observed in the temperature range of 1773 to 1873 K.

ACKNOWLEDGMENTS

This study was supported by the R&D Center for Valuable Recycling (Global-Top Environmental Technology Development Program) funded by the Ministry of Environment (Project No.: 11-C22-ID).

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