Thermodynamics of Nitrogen in Fe-Mn-Al-Si-C Alloy Melts

MIN-KYU PAEK, SAIKAT CHATTERJEE, JONG-JIN PAK, and IN-HO JUNG

Thermodynamic behavior of nitrogen in the entire range of the Fe-Mn-Al-Si-C liquid solution was modeled based on the critical evaluation and optimization of all available experimental data. The Gibbs energy of liquid solution was described using the Modified Quasichemical Model (MQM) in the pair approximation, instead of classical Wagner Interaction Parameter Formalism, to consider the strong interactions between species in liquid state. In particular, the dissolution behavior of N and formation of AlN in the entire ternary and higher order liquids were accurately predicted from the MQM only with binary model parameters of N.

DOI: 10.1007/s11663-016-0588-y

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I. INTRODUCTION

RECENTLY, high alloy steels such as high Mn-Si steel, high Al and TWIP (TWining Induced Plasticity) steels have been developed as next generation advanced high strength steels for automotive applications. High amounts of alloying elements bring great challenges to steelmaking and casting processes; significant corrosion of refractories, new types of non-metallic inclusion formation, high solubility of gas species, and long solidification range. For example, TWIP steel shows an excellent combination of high strength, ductility, and formability over conventional steels by alloying a large amount of Mn (15 to 20 wt pct), Al (1 to 3 wt pct), Si (~0.3 wt pct), and C (0.4 to 0.6 wt pct).^[1–3] However, Mn significantly increases the N solubility in liquid iron, while decreases the melting temperature of the steels down to near 1723 K (1450 °C).^[4] In addition, the aluminum nitride, AlN, can be easily formed by the strong affinity of Al with N in the high-Mn and high-Al alloyed liquid steels.^[5] Although the AlN inclusion is considered as a detrimental phase for the surface quality as well as the mechanical property of the final steel product, the critical N content for the AlN formation during cooling and solidification of high alloyed steels is less predictable due to the lack of the thermodynamic information.

So far, the most commonly used thermodynamic model to describe the N solubility in molten steel is the Wagner interaction parameter formalism.^[6] But this model is limited only for specific alloy composition such as low carbon steel. The other model used in the commercial steel databases such as FactSage FSSel database^[7] and Thermo-Calc TCFE database^[8] is the Bragg–Williams random mixing model with regular or subregular parameters. However, the available models and parameters are insufficient to reproduce the thermodynamic behavior of N in high alloy melts.

The purpose of this study is to develop a new thermodynamic database accurately describing the thermodynamic behavior of N in molten steel. In order to keep a pace with the development of high alloy steels, the database has been developed to describe entire composition range of liquid alloys in Fe-Al-Mn-Si-C system. In the present study, all the available experimental data related to the N solubility in unary, binary, ternary, and high order liquid were reviewed. Using the Modified Quasichemical Model with binary interaction model parameters between N and alloying elements, all available experimental data in ternary and higher order liquid systems were accurately predicted.

II. THERMODYNAMIC MODEL

A. Limitations of Previous Thermodynamic Models

1. Wagner interaction parameter formalism

The Wagner Interaction Parameter Formalism (WIPF)^[6] is the most common model used for the description of the thermodynamics of dilute solution. In order to overcome the thermodynamic inconsistency of this classical formalism and obey the Gibbs–Duhem relationship in non-dilute solution, Pelton and Bale^[9,10] introduced the Unified Interaction Parameter Formalism (UIPF) containing the correction term in the activity coefficient of solvent. For example, the molar Gibbs energy, g , of the Fe-M-N system (M = alloying element such as Al, Mn, Si, C, and N = nitrogen) can be described by the UIPF as follows:

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Manuscript submitted March 13, 2015.

Article published online February 1, 2016.

$$g = (X_{\text{Fe}}g_{\text{Fe}}^{\circ} + X_{\text{M}}g_{\text{M}}^{\circ} + X_{\text{N}}g_{\text{N}}^{\circ}) + RT(X_{\text{Fe}} \ln X_{\text{Fe}} + X_{\text{M}} \ln X_{\text{M}} + X_{\text{N}} \ln X_{\text{N}}) + RT(X_{\text{Fe}} \ln \gamma_{\text{Fe}} + X_{\text{M}} \ln \gamma_{\text{M}} + X_{\text{N}} \ln \gamma_{\text{N}}) \quad [1]$$

where g_i° is the molar Gibbs energy of the i element in the Raoultian standard state, γ_i is the activity coefficients. When the standard states of M and N are changed to their infinite dilution standard states,

$$g = (X_{\text{Fe}}g_{\text{Fe}}^{\circ} + X_{\text{M}}g_{\text{M}}^{\circ} + X_{\text{N}}g_{\text{N}}^{\circ}) + RT(X_{\text{Fe}} \ln X_{\text{Fe}} + X_{\text{M}} \ln X_{\text{M}} + X_{\text{N}} \ln X_{\text{N}}) + RT(X_{\text{Fe}} \ln f_{\text{Fe}} + X_{\text{M}} \ln f_{\text{M}} + X_{\text{N}} \ln f_{\text{N}}) \quad [2]$$

where $g_i^{\circ} (= g_i^{\circ} + RT \ln \gamma_i^{\circ})$ is the molar Gibbs energy of i element in its infinite dilution (Henrian) standard state, and f_{M} and f_{N} are the activity coefficients relative to the infinite dilution standard state:

$$\ln f_{\text{M}} = \sum_{i=\text{M},\text{N}} \varepsilon_{\text{Mi}} X_i + \sum_{i,j=\text{M},\text{N}} \varepsilon_{\text{Mij}} X_i X_j + \ln f_{\text{Fe}} \quad [3]$$

$$\ln f_{\text{N}} = \sum_{i=\text{M},\text{N}} \varepsilon_{\text{Ni}} X_i + \sum_{i,j=\text{M},\text{N}} \varepsilon_{\text{Nij}} X_i X_j + \ln f_{\text{Fe}} \quad [4]$$

$$\ln f_{\text{Fe}} = -\frac{1}{2} \sum_{i,j=\text{M},\text{N}} \varepsilon_{ij} X_i X_j - \frac{2}{3} \sum_{i,j,k=\text{M},\text{N}} \varepsilon_{ijk} X_i X_j X_k \quad [5]$$

The $\ln f_{\text{Fe}}$ term is the correction term in UIPF, which is set to be zero in the classical WIPF. Of course, the 1 wt pct standard state with Fe as a solvent can be also used, but then the validity of thermodynamic parameters (Henrian activity coefficients and interaction parameters) can be limited in Fe-rich solution rather than in wide range of solution.

Among the numerous studies, the compilations of the interaction parameters by Japanese Society for the Promotion of Science (JSPS)^[11] and Sigworth and Elliott^[12] are the most well accepted one so far. However, this WIPF has two inherent limitations. The first limitation results from the assumption of ideal random entropy regardless of the interactions between solvent and solute and between solutes themselves. Although it may not be well-noticed in the calculations of activity or chemical reaction using interaction parameters, the overall Gibbs energy of solution expressed by the WIPF in Eqs. [1] or [2] clearly shows the ideal entropy of mixing. This is less realistic to describe the mixing entropy especially when there is highly negative interaction between species in solution. Typically, in the interaction parameter, $\varepsilon = A/T + B$, of WIPF, a large negative A term (enthalpic term) requires a large B term (entropic term). In order to overcome this limitation, Jung *et al.*^[13] introduced the Associate model for deoxidation equilibria. As the WIPF is originally designed for the description of dilute solution, there is no interpolation technique integrated in the Gibbs

energy formalism. When the model is applied to non-dilute solution, there is always additional interaction terms required to correct the activity coefficients of solutes (in the end, the Gibbs energy of solution). Therefore, this model is unrealistic choice to describe liquid solution covering a wide range of composition.

2. Bragg Williams random mixing model

The Bragg Williams Random Mixing Model (BWRMM) is used for describing the Gibbs energy of liquid solution in a current commercial thermodynamic database like Thermo-Calc TCFE and FactSage FSSel. The Gibbs energy of solution Fe-M-N system can be expressed by the BWRMM as below:

$$g = (X_{\text{Fe}}g_{\text{Fe}}^{\circ} + X_{\text{M}}g_{\text{M}}^{\circ} + X_{\text{N}}g_{\text{N}}^{\circ}) + RT(X_{\text{Fe}} \ln X_{\text{Fe}} + X_{\text{M}} \ln X_{\text{M}} + X_{\text{N}} \ln X_{\text{N}}) + \sum_{i,j} {}^m L_{ij} X_i X_j (X_j - X_i)^m \quad [6]$$

where ${}^m L_{ij}$ are excess parameters between binary i and j species in solution (i and $j = \text{Fe}, \text{M}$ and N), which are expressed in the form of the Redlich–Kister polynomial. Due to the simplicity of the model equation, this has been widely used for the description of liquid alloy in the CALculation of PHase Diagram (CALPHAD) method. The same model has been used by Miki and Hino for Fe-Ni-based alloy description.^[14] Like the WIPF, the random mixing entropy is also assumed in this model, and an intrinsic Muggianu interpolation technique^[15] is used to predict the Gibbs energy of ternary solution from binary excess model parameters, which are the limitations of the this model. As mentioned above, if the interaction between species is very negative, the entropy of solution would deviate from ideal entropy. In order to compensate this entropic limitation, large temperature-dependent parameters^[13] can be often introduced which influence to non-configurational entropy of solution. In addition, the Muggianu interpolation technique is less satisfactory for the prediction of the Gibbs energy of dilute solution as pointed out by Pelton and Chartrand.^[16]

B. Modified Quasichemical Model: Present Study

The Modified Quasichemical Model (MQM)^[16,17] in the pair approximation was used in order to take into account the short-range-ordering (SRO) exhibited in the Fe-Mn-Al-Si-C-N liquid solution. In comparison to the WIPF and BWRMM, the advantages of the MQM are (i) the intrinsic description of non-ideal mixing entropy of solution depending on the interaction of solution species and (ii) flexible choice of interpolation techniques for each ternary system. The detailed development of the MQM for binary^[17] and for multicomponent^[16] solutions can be found elsewhere. A brief description of the model will be presented here.

In the pair approximation of the MQM, the A and B atoms or molecules are assumed to be distributed on a quasi-lattice, and the following pair exchange reaction is considered:

$$(A-A) + (B-B) = 2(A-B); \quad \Delta g_{AB} \quad [7]$$

where $(i-j)$ represents the first-nearest neighbor (FNN) pair in metallic solution. The non-configurational Gibbs energy change for the formation of two moles of $(A-B)$ pairs is Δg_{AB} . Let n_A and n_B be the number of moles of A and B , n_{ij} be the number of moles of $(i-j)$ pairs, and Z_A and Z_B be the coordination numbers of A and B . Then, the following mass balance equations for the pairs are obtained.

$$Z_A n_A = 2n_{AA} + n_{AB} \quad [8]$$

$$Z_B n_B = 2n_{BB} + n_{AB} \quad [9]$$

The pair fractions, mole fractions, and “coordination-equivalent” fractions in the model are defined respectively as

$$X_{ij} = n_{ij} / (n_{AA} + n_{BB} + n_{AB}) \quad [10]$$

$$X_A = n_A / (n_A + n_B) = 1 - X_B \quad [11]$$

$$\begin{aligned} Y_A &= Z_A n_A / (Z_A n_A + Z_B n_B) \\ &= Z_A X_A / (Z_A X_A + Z_B X_B) = 1 - Y_B \end{aligned} \quad [12]$$

Then, the Gibbs energy of the $A-B$ binary solution is given by

$$G = (n_A g_A^\circ + n_B g_B^\circ) - T \Delta S^{\text{config}} + (n_{AB}/2) \Delta g_{AB} \quad [13]$$

where g_A° and g_B° are the molar Gibbs energies of pure components of A and B , and ΔS^{config} is an approximate expression for the configurational entropy of mixing given by randomly distributing the $(A-A)$, $(B-B)$, and $(A-B)$ pairs in the one-dimensional Ising approximation.^[17]

$$\begin{aligned} \Delta S^{\text{config}} &= -R(n_A \ln X_A + n_B \ln X_B) \\ &- R \left[n_{AA} \ln \left(\frac{X_{AA}}{Y_A^2} \right) + n_{BB} \ln \left(\frac{X_{BB}}{Y_B^2} \right) + n_{AB} \ln \left(\frac{X_{AB}}{2Y_A Y_B} \right) \right] \end{aligned} \quad [14]$$

Δg_{AB} is expanded in terms of the pair fractions:

$$\Delta g_{AB} = \Delta g_{AB}^\circ + \sum_{i \geq 1} g_{AB}^{i0} X_{AA}^i + \sum_{j \geq 1} g_{AB}^{0j} X_{BB}^j \quad [15]$$

where Δg_{AB}° , g_{AB}^{i0} and g_{AB}^{0j} are the parameters of the model which can be functions of temperature. When $\Delta g_{AB} = 0$, the ΔS^{config} becomes ideal random entropy, while it becomes close to zero when $\Delta g_{AB} \ll 0$.

The composition of maximum SRO in each binary subsystem, typically corresponding to the composition of minimum enthalpy of mixing of binary solution, is determined by ratio of the coordination numbers, Z_B/Z_A , as given each of them by the following equations:

$$\frac{1}{Z_A} = \frac{1}{Z_{AA}^A} \left(\frac{2n_{AA}}{2n_{AA} + n_{AB}} \right) + \frac{1}{Z_{AB}^A} \left(\frac{n_{AB}}{2n_{AA} + n_{AB}} \right) \quad [16]$$

$$\frac{1}{Z_B} = \frac{1}{Z_{BB}^B} \left(\frac{2n_{BB}}{2n_{BB} + n_{AB}} \right) + \frac{1}{Z_{BA}^B} \left(\frac{n_{AB}}{2n_{BB} + n_{AB}} \right) \quad [17]$$

where Z_{AA}^A and Z_{AB}^A are the values of Z_A , respectively, when all nearest neighbors of an A are A 's (that is, Z for pure element A), and when all nearest neighbors of an A are B 's, and where Z_{BB}^B and Z_{BA}^B are defined similarly. Z_{AB}^A and Z_{BA}^B represent the same quantity and can be used interchangeably. The use of the one-dimensional Ising model in Eq. [14] introduces a mathematical approximation into the model which can be partially compensated by selecting smaller coordination numbers than the actual values.^[18] For the default coordination number, Z_{ij}^i , of pure element in metallic solution is set to be ‘6’ in the FactSage metallic database. Then, binary coordination numbers, Z_{ij}^i , are used to fix the SRO composition. In the most cases, the default coordination number, ‘6’, was applied in binary solutions in the present study. The expansion of the pair formation energies in each binary solution to the ternary and multicomponent system can be done considering the interpolation technique for each ternary system and the details of the formulation were described by Pelton and Chartrand.^[16]

All binary MQM model parameters between metallic elements including C in liquid Fe-Al-Mn-Si-C solution were already optimized by the critical evaluation and optimization of all available phase diagram and thermodynamic properties data of liquid as well as solid phases.^[19–27] In the description of the Gibbs energy of liquid solution of Fe-Al-Mn-Si-C system, no ternary excess parameters were needed for liquid solution except for the Fe-Al-Mn solution.^[27] All these parameters were taken in the present study without any modification. The interpolation technique for each ternary system was determined based on the thermochemical properties of constituent sub-binary solutions. In the present study, all ternary systems containing nitrogen were treated by the Toop interpolation technique^[28] considering N as an asymmetric component.

III. CRITICAL EVALUATION AND OPTIMIZATION OF N SOLUBILITY IN BINARY AND TERNARY SYSTEMS

All experimental data related to the solubility of N in the Fe-Al-Mn-Si-C were collected, and evaluated critically and simultaneously based on experimental technique and consistency with other set of experimental data to obtain the best model parameters to describe the binary N containing solutions. Then, the N solubilities in ternary and higher order liquid metal were predicted accurately without any additional model parameters. The Gibbs energies of all elements, Fe, Mn, Al, and Si in their liquid states were taken from the SGTE pure

Table I. Optimized Model Parameters in the Present Study (J/mol)

<i>Liquid (L): MQM (Fe, Mn, Al, Si, C, N)</i>	
$Z_{\text{FeFe}}^{\text{Fe}} = Z_{\text{AlAl}}^{\text{Al}} = Z_{\text{MnMn}}^{\text{Mn}} = Z_{\text{SiSi}}^{\text{Si}} = Z_{\text{CC}}^{\text{C}} = Z_{\text{NN}}^{\text{N}} = 6^{[7]}$	
$Z_{\text{FeAl}}^{\text{Fe}} = Z_{\text{AlFe}}^{\text{Al}} = Z_{\text{AlC}}^{\text{Al}} = Z_{\text{AlC}}^{\text{C}} = 6^{[20,26]}$	
$Z_{\text{MnAl}}^{\text{Mn}} = Z_{\text{AlMn}}^{\text{Al}} = Z_{\text{FeMn}}^{\text{Fe}} = Z_{\text{FeMn}}^{\text{Mn}} = Z_{\text{FeSi}}^{\text{Fe}} = Z_{\text{FeSi}}^{\text{Si}} = 6^{[22,23,27]}$	
$Z_{\text{MnSi}}^{\text{Mn}} = Z_{\text{SiMn}}^{\text{Si}} = Z_{\text{SiC}}^{\text{Si}} = Z_{\text{SiC}}^{\text{C}} = 6^{[24]}$	
$Z_{\text{FeC}}^{\text{Fe}} = Z_{\text{MnC}}^{\text{C}} = 6, Z_{\text{FeC}}^{\text{Fe}} = Z_{\text{MnC}}^{\text{C}} = 3^{[21,24]}$	
$Z_{\text{AlSi}}^{\text{Al}} = Z_{\text{AlSi}}^{\text{Si}} = 5^{[25]}$	
$Z_{\text{FeN}}^{\text{Fe}} = Z_{\text{FeN}}^{\text{N}} = Z_{\text{MnN}}^{\text{Mn}} = Z_{\text{MnN}}^{\text{N}} = Z_{\text{AlN}}^{\text{Al}} = Z_{\text{AlN}}^{\text{N}} = Z_{\text{SiN}}^{\text{Si}} = Z_{\text{SiN}}^{\text{N}} = Z_{\text{CN}}^{\text{C}} = Z_{\text{CN}}^{\text{N}} = 6$	
$g_{\text{Fe}}^{\circ}, g_{\text{Mn}}^{\circ}, g_{\text{Al}}^{\circ}, g_{\text{Si}}^{\circ}, g_{\text{C}}^{\circ}$	
$g_{\text{N(l)}}^{\circ}$	From ^[29] $8893.2 + 36.4856T - 12.7819T\ln T - 1.7669 \times 10^{-3}T^2$ $+ 2.6810 \times 10^{-9}T^3 - 32374.0T^{-1}$ (298 K to 1496 K (25 °C to 1223 °C)) $5285.1 + 63.1401T - 16.3699T\ln T - 6.5107 \times 10^{-4}T^2 + 3.0097 \times 10^{-8}T^3$ $+ 563070.0T^{-1}$ (1496 K to 3896 K (1223 °C to 3623 °C)) $- 3748.9 + 96.1997T - 20.4695T\ln T + 2.3975 \times 10^{-4}T^2 - 8.3330 \times 10^{-9}T^3$ $+ 4596375.0T^{-1}$ (3896 K to 6546 K (3623 °C to 6273 °C))
Δg_{FeN}	0
Δg_{AlN}	0
Δg_{MnN}	$-29,560 + 5.31T$
Δg_{SiN}	83,680
Δg_{CN}	125,520
Δg_{FeAl}	$-20,292.4 + 3.347T - (1673.6 + 1.255T)X_{\text{FeFe}}^{\text{FeFe}}$ $- 1046X_{\text{FeFe}}^2 - (10,460 - 4.184T)X_{\text{AlAl}}^{[20]}$
Δg_{FeMn}	$-1338.9 + 0.1674T + 418.4X_{\text{FeFe}}^{\text{FeFe}} - 334.7X_{\text{MnMn}}^{[27]}$
Δg_{FeSi}	$-33,710.5 + 2.259T - (12,522 + 5.021T)X_{\text{FeFe}}^{\text{FeFe}}$ $- (8368 - 4.812T)X_{\text{AlFe}}^2 - (3054.3 - 6.485T)X_{\text{SiSi}}^{[22]}$
Δg_{FeC}	$-30,459.5 + 3.138T - 1129.7X_{\text{FeFe}}^{\text{FeFe}}$
Δg_{MnAl}	$-16,945.2 + 3.012T - (1673.6 - 2.761T)X_{\text{MnMn}} - (5857.6 - 0.418T)X_{\text{AlAl}}^{[23]}$
Δg_{MnSi}	$33,053.6 + 6.694T - 20,920X_{\text{MnMn}} + (11,715.2 - 0.8368T)X_{\text{MnMn}}^2 + 1.674TX_{\text{SiSi}}^{[24]}$
Δg_{MnC}	$-42,676.8 + 4.502T + (2092 + 1.751T)X_{\text{MnMn}}^{[24]}$
Δg_{AlSi}	$-4622.3 - 0.03T + (836.8 - 1.172T)X_{\text{AlAl}}^{[25]}$
Δg_{AlC}	$-13,897.8 + 1.674T^{[26]}$
Δg_{SiC}	4184 ^[24]
$g_{\text{FeAl(Mn)}}^{\circ}$	$-6276^{[27]}$
<i>Stoichiometric compound</i>	
AlN	$G = -316999.5 + 322.6T - 50.4T\ln T + 832748.2T^{-1}$ $- 929.1T^{0.5} - 50107966.0T^{-2} - 7862.0\ln T$

Table II. Interpolation Method for Each Ternary Liquid Systems Used in the Present Study

System	Method*	Asymmetric Component	Refs.
Fe-Mn-Al	T	Al	27
Fe-Mn-Si	M	—	7
Fe-Mn-C	T	C	19
Fe-Mn-N	T	N	present study
Fe-Al-Si	K	—	7
Fe-Al-C	T	Al	20
Fe-Al-N	T	N	present study
Fe-Si-C	T	Fe	19
Fe-Si-N	T	N	present study
Fe-C-N	T	N	present study
Mn-Al-Si	K	—	7
Mn-Al-C	T	Al	19
Mn-Al-N	T	N	present study
Mn-Si-C	T	Mn	24
Mn-Si-N	T	N	present study
Mn-C-N	T	N	present study
Al-Si-C	T	Al	19
Al-Si-N	T	N	present study
Al-C-N	T	N	present study
Si-C-N	T	N	present study

*T, M, and K represent Toop, Muggianu, and Kohler interpolation technique, respectively.

substance database.^[29] Although solid carbon can be used as the reference state for conventional Wagner or Unified Interaction Parameter Formalism, liquid carbon Gibbs energy is required to describe liquid solution containing C for the MQM. Its Gibbs energy was originally evaluated by Gustafson^[30] to reproduce the phase diagram of Fe-C system and activity of C in liquid Fe-C solution. As liquid N does not exist as a stable elemental phase, it is impossible to measure the Gibbs energy of liquid N. In the course of this study, we found that the Gibbs energy of liquid N adopted in TCFe database and FSSTel database could be unsatisfactory for the description of steel containing high amount of N. Therefore, the Gibbs energy of liquid N was reevaluated, as described in Section III-A. All optimized model parameters determined in the present study are listed in Table I and the applied interpolation methods for each ternary system are listed in Table II.

A. Re-assessment of the Gibbs Energy of Liquid Nitrogen

The Gibbs free energy of pure liquid N, $g_{N(l)}^\circ$, is the one of the decisive factors to describe the Gibbs energy of liquid steel containing N. There is no definitive Gibbs energy of hypothetical liquid monoatomic N, N(l). In the WIPF for dilute solution, the Henrian activity coefficient of N is determined after assuming $g_{N(l)}^\circ = 1/2g_{N_2(g)}^\circ$ to describe the N solubility in pure liquid Fe. In the CALPHAD community, the Gibbs energy of N was determined to describe the phase diagram and other thermodynamic properties of N-containing system in a wide range of composition and temperature.^[31,32] During the first thermodynamic assessment of the Fe-N

system, Frisk^[31] proposed the $g_{N(l)}^\circ = 1/2g_{N_2(g)}^\circ - 711 + 70.2 T$ to reproduce the phase diagram of the Fe-N system. Later, he realized that the original $g_{N(l)}^\circ$ proposed for Fe-N system was not sufficient to describe other N containing systems such as Cr-N and Mo-N system. So he revised the value as $g_{N(l)}^\circ = 1/2g_{N_2(g)}^\circ + 29950 + 59.02 T$.^[32] In the both cases, he further added regular or sub-regular interaction parameters to describe the binary liquid solutions containing N. Although his thermodynamic descriptions of the binary systems are accurate enough under normal nitrogen pressures, certain potential problems were raised when the N₂ gas phase is suppressed in the thermodynamic calculations during the evaluation of the data in the present study. For example, under suppression of nitrogen gas phase formation, FCC phase is calculated to reappear at high N content about 0.4 to 0.5 X_N below 743 K (470 °C) in the Fe-N system and more critically BCC phase is stable again above the liquidus temperature in the Cr-N systems (a wide range of BCC phase can be calculated above 2473 K (2200 °C) in the Cr-N system). The similar problem can be found in Mo-N system.

These problems result from the relative less stable Gibbs energy of liquid monoatomic N, $g_{N(l)}^\circ$. Therefore, we reassessed $g_{N(l)}^\circ$ not only for the solubility of nitrogen gas in liquid alloy but also for the phase diagram calculations for all binary and high order systems containing N. There are no definitive ways to determine the Gibbs energy of hypothetical liquid N. In this study, we determined the values of $g_{N(l)}^\circ$ by assuming that the binary Fe-N liquid is an ideal solution. That is, the $g_{N(l)}^\circ$ was adjusted to reproduce the solubility of nitrogen in the binary Fe-N liquid without any additional interaction parameters (strictly speaking, $\Delta g_{FeN} = 0$ in this study). Our preliminary tests for the optimizations of phase diagrams and thermodynamic properties of various binary N systems show no strange phase diagram results with this new $g_{N(l)}^\circ = 1/2g_{N_2(g)}^\circ + 12643.9 + 45.939T$.

B. Evaluation and Optimization of Binary Systems

The thermodynamic model parameters were determined based on the critically evaluated experimental data in the literature on the N solubility and AlN solubility product measured in liquid iron containing Mn, Al, Si, C, and N. In general, the effects of alloying elements on the N solubility and the AlN formation in liquid iron have been measured by the Sieverts' method, levitation melting technique, and the sampling method. However, the Sieverts' method causes an error by the vaporization and condensation of metal as well as the side-chemical reactions.^[33] In case of levitation melting technique designed to eliminate the interaction between liquid solution and crucible materials, the presence of a film of metallic vapor near melt surface can cause an error in the temperature measurement by an optical pyrometer, and the equilibrium time is typically limited within 1 minute to avoid the evaporation of alloying

elements at relatively higher operating temperature.^[34] With the sampling technique, the equilibrium N solubility can be underestimated by desorption of N (nitrogen gas formation) during quenching,^[35] but it was found that the quenching the samples in water within 3 seconds can be sufficient to keep original N content for most cases.^[36] Recent sampling experiments under reduced partial pressures of N₂ can especially reduce the chance of a loss of N during the quenching, which provides very reliable and consistent results. All these possible experimental and analytical advantage and disadvantage of each experimental technique were taken into account in the evaluation of the experimental data.

1. Fe-N system

The experimental N solubilities in molten Fe at 1 atm N₂ pressure are plotted in Figure 1. The N solubility in liquid iron has been measured by the Sieverts' method,^[33,37,38] the levitation melting technique,^[39–42] and the sampling method.^[43–46] The reported data of the N solubility are scattered significantly, and the temperature dependences of the data are different depending on the experimental studies. The N solubility in liquid Fe increases with increasing temperature. As both levitation technique and sampling method would induce a loss of nitrogen during experiments, the experimental data with higher N content were preferred among the reported data. Evaporation of liquid Fe can be expected at high temperature. As can be seen by the experimental data of Tsu and Saito,^[41] the N solubility decreases with temperature when experiment was carried out above 2473 K (2200 °C). This can be well explained by the consideration of evaporation of Fe, which induces the decrease of N₂ pressure lower than 1 atm (due to dilution of N₂ gas by Fe gas) as shown in calculated line (dashed line). Simultaneously, all experimental data^[4,33,35,36,38,41,45–55] at high and low partial pressure of N₂ over a wide range of temperatures from 1823 K to 2173 K (1550 °C to 1900 °C), as shown in Figures 2(a) through (f), were considered in the evaluation of the

Gibbs energy of liquid Fe-N solution. It should be noted that Frisk^[51,32] selected only the results of Ishii *et al.*^[43] among all other experimental data for his description of the Fe-N system without any supporting reason.

The maximum solubility of N in liquid Fe available among all experimental results is about 0.3 wt pct N at 1873 K (1600 °C) and 50 atm P_{N₂} as shown in Figure 2(b). Up to this range of nitrogen concentration, the nitrogen solubility is increasing linearly with P_{N₂}^{1/2}. That is, the N in liquid Fe shows the Henrian solution behavior at least up to this range of solubility. As mentioned in Section III–A, the $g_{N(l)}^{\circ}$ value was determined to reproduce all N solubility data in liquid Fe without any MQM parameter, ($\Delta g_{FeN} = 0$):

$$g_{N(l)}^{\circ} = 1/2g_{N_2(g)}^{\circ} + 12643.9 + 45.939T \quad [18]$$

This means that the additional Gibbs energy term of $g_{N(l)}^{\circ}$ in Eq. [18] can be mathematically considered as the Henrian activity coefficient of N in liquid Fe in the WIPF with no interaction parameters:

$$RT \ln_N^{\circ} = 12643.9 + 45.939T \quad [19]$$

The Henrian activity coefficient derived from this study is very similar to the value suggested by the JSPS:^[11] $RT \ln_N^{\circ} = 9916 + 46.954T$.

2. Mn-N system

The Mn-N binary system was thermodynamically evaluated by Qui and Guillermet^[56] using the BWRMM for the liquid solution. By adopting the $g_{N(l)}^{\circ}$ value evaluated by Frisk,^[32] they modeled the liquid solution using the subregular parameters (composition dependent). As shown in Figure 3, the N solubility calculated from their model parameters agrees well with the lower N solubility dataset.^[57–61] On the other hand, the higher N solubility dataset such as recent experimental data measured by Kim *et al.*^[34] at low temperature and Tsu and Saito^[41] at higher temperature region were more favored in the present optimization. As pointed out by Kim *et al.*^[34] and Tsu and Saito,^[41] the relatively high vapor pressure of Mn can affect the N₂ partial pressure over the melt surface and the absorption of N by Mn vapor cannot be neglected in this system: The Mn vapor pressure is calculated to be 0.05 and 0.2 atm at 1873 K and 2073 K (1600 °C and 1800 °C), respectively. Kim *et al.*^[34] and Tsu and Saito^[41] made corrections of the equilibrium N₂ partial pressure by considering the Mn vapor pressure. The experimental data of Baratashvili *et al.*^[62] are rather scattered. Although the equilibrium N solubility increases with decreasing temperature, the N pickup during the quenching of the sample cannot be expected due to slow dissolution kinetics of N into liquid metal. These data were well reproduced by introducing a small temperature-dependent Δg_{MnN} term (independent of composition), because the N dissolution shows the opposite temperature dependence with liquid Fe.

As mentioned in the Fe-N system, the evaporation of metallic element can affect the nitrogen partial pressure at high temperature. In particular, as Mn has much

Fig. 1—N solubility in liquid Fe at 1 atm N₂ gas pressure^[33,37–46] along with the present optimization result and previous modeling result.^[32]

Fig. 2—Calculated N solubility in liquid Fe depending on the partial pressures of N_2 along with experimental data.^[4,33,35,36,38,41,45–55]

higher vapor pressure than Fe, this should be taken into account in thermodynamic analysis. Dashed line in Figure 3 shows the calculated N solubility considering the Mn evaporation. In comparison to the calculated N solubility at 1 atm N_2 pressure, the noticeable difference can be already found above 1873 K (1600°C).

Figure 4 shows the effect of N_2 partial pressure on the N solubility in liquid Mn. The solubility of N in liquid Mn is much higher than that in liquid Fe at the same partial pressure of N_2 . As clearly shown in Figure 4, the N dissolution in liquid Mn does not follow the Sieverts' law. There are quite scatter in the experimental data in

Fig. 3—N solubility in liquid Mn at 1 atm N_2 pressure^[34,41,57–62] along with the present optimization and previous modeling results.^[56]

Fig. 4—Calculated N solubility in liquid Mn depending on the partial pressures of N_2 along with experimental data.^[34,41,57,59–61, 63]

Figure 4, but present optimization agrees very well with the recent experimental results measured by Jang *et al.*^[63] and Kim *et al.*^[34] at low temperature

(Figure 4(a)) and Tsu and Saito^[41]'s results at high temperature up to 2273 K (2000 °C) (Figure 4(b)). The results by Perepelkin^[59] which were measured under higher N_2 partial pressures up to 9 atm were very scattered. The samples equilibrated under high pressures might lose significant amount of N during quenching if the pressure of N_2 was not kept the same during the quenching.

3. Al-N system

Several experimental studies^[64–66] are available on the N solubility in liquid Al, and they are well reviewed by Wriedt.^[67] Figure 5 shows the experimental results of Iwase^[64] and Schweighofer and Kúdela.^[65,66] Iwase^[64] used the Sieverts' method in the temperature range from 973 K to 1203 K (700 °C to 930 °C). Schweighofer and Kúdela^[65,66] analyzed the amount of AlN in the quenched Al samples after equilibrating liquid Al with N_2 gas of 20 to 50 atm using an induction melting apparatus, and then they calculated the N solubility under 1 atm N_2 pressure using the Sieverts' law with the assumption that analyzed AlN in quenched sample was all soluble N state in liquid Al. In both studies, they could not find any detectable soluble N in Al and assumed that all AlN in Al was originally soluble N. Theoretically, AlN is very stable so it should be formed under their experimental conditions. For example, as pointed out by Wriedt^[67], the equilibrium N_2 gas pressure for 'liquid Al + AlN' assemblage at about 1273 K (1000 °C) is about 10^{-16} atm and the equilibrium amount of N in liquid Al should be less than ppm level, which is not detectable using common analytical tools. Although Iwase^[64] and Schweighofer and Kúdela^[65,66] claimed that the formation of AlN was very sluggish so they could effectively reach the metastable equilibration between Al and N_2 gas, their results are doubtful. Several other experimental studies^[68,69] reported nearly no solubility of N in liquid Al up to 1773 K (1500 °C). In particular, Czochralski^[68] and Claus^[69] used the Sieverts' method but they reported no detectable N in liquid Al, which cast the doubt about the Iwase's results.

In the present study, the MQM parameter for Al-N was set to be zero: $\Delta G_{AlN} = 0$. In order to compare the metastable nitrogen dissolution into liquid Al claimed by Iwase^[64] and Schweighofer and Kúdela,^[65,66] we calculated the metastable equilibration between liquid Al and 1 atm N_2 gas with suppression of AlN formation. As can be seen in Figure 5, the calculated solubility from the present model is about twice higher than the experimental data by Iwase and Schweighofer and Kúdela. In order to reproduce these experimental data, a temperature-independent negative parameter of ΔG_{AlN} would be necessary. It should be noted that the calculated results and experimental data in Figure 5 are metastable and in reality stable solid AlN should form during the dissolution of N in liquid Al under equilibrium condition. In the course of the thermodynamic modeling of the ternary Fe-Al-N solution, it was found that zero ΔG_{AlN} parameter is more suitable to predict the nitrogen solubility in Fe-Al melt (see in Section III-C-2). Therefore, considering that the

Fig. 5—Solubility of N in liquid Al under 1 atm pressure: metastable equilibrium assuming no AlN formation (see text for more explanation).

experimental results by Iwase^[64] and Schweighofer and Kúdela^[65,66] in Figure 5 were obtained in metastable condition, it was decided to keep the $\Delta g_{\text{AlN}} = 0$ for more accurate predictions in higher order system.

4. Si-N and C-N systems

No solubility of N in liquid Si has been determined experimentally. Due to high melting temperature of C, no experiments for the solubility of N in liquid C have been attempted. The temperature for the three phase equilibria of ‘liquid Si + solid Si_3N_4 + gas N_2 (1 atm)’ was predicted as part of evaluation of the Gibbs energy of Si_3N_4 ,^[70] but the predicted solubility of nitrogen in liquid Si, 723 wt ppm N at 2150 K (1877 °C), in this condition is not supported by any experimental results. Therefore, the model parameter for each system, Δg_{SiN} and Δg_{CN} , cannot be determined from the binary systems. In the present study, they were determined to reproduce the experimental data for ternary Fe-Si-N and Fe-C-N systems, as will be discussed in Sections III-C-3 and III-C-4. The calculated solubilities of nitrogen in liquid Si at 1773 K (1500 °C) and 1873 K (1600 °C) from the present model parameters are 0.034, and 0.088 wt ppb, respectively. In the case of the three phase equilibration of ‘liquid Si + solid Si_3N_4 + gas N_2 (1 atm)’, the solubility is 0.75 wt ppb at 2144 K (1871 °C).

C. Evaluation and Optimization of Ternary Systems

All the experimental data in ternary alloy melts were well predicted from the MQM using only binary model parameters with the Toop interpolation technique where N was considered as an asymmetric component.

1. Fe-Mn-N system

The N solubilities in liquid Fe-Mn alloy have been measured over wide composition and temperature ranges under various N_2 partial pressures. Figure 6

Fig. 6—Comparison between experiments^[4,33,71–74] and model calculations for N solubility in Fe-Mn melts at Fe-rich region under the N_2 partial pressure of (a) 1 and (b) 0.3 atm.

shows the N solubility in liquid Fe-Mn alloys measured by various investigators^[4,33,71–74] at the temperatures from about 1823 K to 1923 K (1550 °C to 1650 °C) under (a) 1 and (b) 0.3 atm N_2 partial pressures. As shown in the figure, the N solubility significantly increases with increasing Mn content. The temperature dependence of the solubility changes from positive to negative at about 8.5 wt pct of Mn in this temperature range. Shin *et al.*^[71]’s results measured by N_2 bubbling and sampling method clearly showed the effect of Mn on the N solubility in liquid iron and its temperature dependence. The predicted N solubility from the present model is compared to more experimental data in Figure 7. As discussed in binary Mn-N system (see Section III-B-2), many previous experimental data on the N solubility in liquid Mn are lower than the calculated solubility from the present optimization, but the present modeling was based on the more recent experimental data and the data including the correction of Mn partial pressure. As can be seen in Figure 7(a), the recent measurements by Jang *et al.*^[75] up to 55 wt pct of Mn and by Kim *et al.*^[34] from 75 to 100 wt pct Mn at N_2 partial pressure of 0.2 atm are well predicted, while the other experimental results in

Fig. 7—Comparison between experiments^[34,57,61,74–77] and model calculations for N solubility in Fe-Mn melts at 1823 K (1550 °C) under (a) 0.2 atm, and at (b) 1823 K (1550 °C), (c) 1923 K (1650 °C), and (d) 1973 K (1700 °C) under 1 atm N₂ pressure.

Figures 7(b) through (d) under 1 atm N₂ pressure^[57,61,74,76,77] show systemically lower than the predictions particularly at high Mn concentration region. This could result from the interference of high vapor pressure of Mn to partial pressure of N₂, and also a loss of N during the quenching/cooling of samples when N₂ gas pressure was not kept isobaric.

Grigorenko *et al.*^[61] and Beer^[57] determined the solubility of N with the variation of partial pressure of N₂. As shown in Figures 8(a) and (b), the N solubility is well predicted at low partial pressure of N₂ but the deviation becomes noticeable at high N₂ pressures and high Mn concentration region. The similar trend can be found for the experimental results from Satir-Kolorz and Fechtner^[50] and Rawers and Gokcen^[78] under higher N₂ pressures up to 99 and 1974 atm, respectively, as shown in Figures 8(c) and (d). The calculated results are consistently higher than the experimental results. This discrepancy can be due to the loss of nitrogen during the quenching of the samples.

2. Fe-Al-N system

This system has been extensively investigated experimentally^[5,33,45,46,73,79–83] and theoretically^[84,85].

However, there are still disagreements among the studies. In particular, there are considerable discrepancies in the Gibbs energy of formation of AlN.^[45,80,81,84–86] The effect of Al on the activity coefficient of N in liquid iron recommended by the JSPS^[11] is positive whereas that by the previous CALPHAD-type optimizations is negative.^[84,85] This can cause significant difference in the prediction of the solubility of N and the formation of AlN in liquid Fe containing a large amount of Al.

The standard Gibbs energy of formation of AlN from Al(l) and ½ N₂(g) was determined from the sublimation behavior of AlN^[87–89] and the carbothermal nitridation method.^[90] The standard Gibbs energy data of AlN derived from the experiments are plotted in Figure 9. By adopting the sublimation coefficient value from Hildenbrand and Hall,^[87] we calculated the Gibbs energies of formation of AlN from the experimental sublimation studies by Bolgar *et al.*^[88] and Dreger *et al.*^[89] As can be seen in Figure 9, the experimental data are very scattered.

The Gibbs free energy of AlN in the JANAF tables^[86] was determined mainly based on the results of Hildenbrand and Hall.^[87] However, it was found that the

Fig. 8—Calculated N solubility in liquid Fe-Mn alloys depending on the partial pressure of N_2 along with experimental results from (a) Grigorenko *et al.*,^[61] (b) Beer,^[57] (c) Satir-Kolorz and Feichtinger,^[50] and (d) Rawers and Gokcen.^[78]

Fig. 9—Standard Gibbs free energy of formation of AlN^[81,87–91] from liquid Al and N_2 gas.

Gibbs free energy from JANAF tables was rather positive to reproduce the AlN solubility product data in liquid iron.^[5,45,46,73,79–82] For example, the Gibbs

energy of formation of AlN was calculated from AlN solubility product data by Paek *et al.*^[91] and Evans and Pehlke^[81] using the activity coefficient of Al and N in this study, and plotted in Figure 9. The standard enthalpy of formation of AlN from Al(l) and $\frac{1}{2} N_2(g)$ was determined by the direct nitridation (-320.0 ± 0.8 kJ/mol)^[92] and the combustion calorimetry (-316.3 ± 1.7 kJ/mol).^[93] The enthalpy can be also indirectly determined from the Gibbs energy plotted in Figure 9 by assuming the linear temperature dependence of the standard Gibbs energy of formation: -312.9 to -329.7 kJ/mol from the AlN sublimation experiments,^[87–89] and -308.2 kJ/mol from the carbothermal nitridation method.^[90] In order to reproduce the AlN solubility data in liquid Fe, in the present study, the standard entropy of formation and heat capacity of AlN were taken from the JANAF tables and then standard enthalpy of formation of AlN of the JANAF tables was modified from -318.0 to -327.0 kJ/mol.

Figure 10 shows the calculated phase diagrams of the Fe-Al-N system at various temperatures under different partial pressures of N_2 . All available experimental data

Fig. 10—Comparison between experiments^[5,33,45,46,73,79–82] and model calculations for equilibrium Al-N relation in liquid iron.

in literatures were also plotted to test the accuracy of the calculated diagrams. The solubility limit of N in liquid Fe can be determined by two types of phase equilibria with N₂(g) and solid AlN. At low Al concentration, the solubility of N is determined directly by the N₂(g) formation and thus dependent on the partial pressure of N₂(g). Recent experimental data by Jang *et al.*,^[79] Kim

et al.,^[46] and Kim *et al.*,^[45] and the previous data by Ishii *et al.*,^[73] and Pehlke and Elliott^[33] show that the N solubility in liquid Fe in equilibrium with N₂ gas is decreasing with increasing Al content which is very well predicted in the present calculations. Regarding the solubility limit of AlN (that is, liquidus of AlN) in liquid Fe, the experimental data are rather scattered. In

Fig. 11—Comparison of the calculated N solubility in the Fe-Al melt at 1873 K (1600 °C) from various thermodynamic assessments.

Fig. 12—Comparison between experiments^[33,54,55,73,75,94] and model calculations for N solubility in Fe-Si melts at (a) 1873 K (1600 °C) under 1 atm N₂ pressure and (b) 1823 K to 1873 K (1550 °C to 1600 °C) under reduced N₂ partial pressures.

general, recent results using sampling technique^[5,45,46,73,79] show lower solubility limit than the earlier works based on the Sieverts' method.^[80–82] In the recent sampling experiments,^[5,45,46,79] the authors

checked the samples very carefully using SEM to demonstrate that their liquid Fe was really saturated with solid AlN and no solid AlN is entrained in liquid metal sample for the analyses of soluble Al and N. Unfortunately, it is difficult to find such details of analysis in the previous works using Sieverts' method. Therefore, the recent experimental works were more favored in the present thermodynamic modeling. It should be noted that this solubility limit of AlN is already taken into account in the determination of the Gibbs energy of solid AlN as described above.

Figure 11 shows the comparison of the calculated phase diagrams of the Fe-Al-N system at 1873 K (1600 °C) from various thermodynamic assessments. The solubility limit of AlN in molten iron is highly dependent on the Gibbs energy of AlN used in each assessment. The present modeling work puts more weight on the recent experimental data while the JSPS evaluation was based on Wada *et al.*^[80]'s experimental results using the Sieverts' method. Therefore, there is noticeable difference in the solubility limit of AlN in the calculated diagrams. The calculated N solubility results from Hillert and Jonsson^[84] and Miettinen^[85] are much higher than the experimental data. The slope of the phase boundary against N₂(g) from the present work and JSPS is slightly negative and agrees with experimental data, while the results from the classical CALPHAD-type assessments with BWRMM^[84,85] show slight positive slope. This difference results from the parameter used for liquid Al-N solution. In the present MQM description, no parameter for the Al-N interaction ($\Delta g_{\text{AlN}} = 0$) was used, and the WIPF description by JSPS used positive interaction parameter between Al and N. While, negative interaction parameters were introduced in the BWRMM description.

3. Fe-Si-N system

The N solubility in the Fe-Si melts was measured by the Sieverts' method^[33,94] and the sampling method.^[54,55,73,75] All the literature data for N solubility in liquid Fe equilibrated with N₂ gas at 1 atm and less than 1 atm pressures are plotted together in Figure 12. Although the experimental data by Vaughan and Chipman^[94] using the Sieverts' method indicated a maximum N solubility at low Si concentration region due to unknown reason, later studies^[33,54,55,73,75] confirmed that the N solubility continuously decreases with increasing Si. The interaction parameter between Si and N in the WIPF was determined based on the experimental data in this Fe-Si-N system. The present MQM parameter of Δg_{SiN} was determined to reproduce the experimental data in Figure 12. A slightly positive but constant Δg_{SiN} can reproduce the solubility data of N in the Fe-Si melts.

4. Fe-C-N system

The variation of N solubility in liquid Fe depending on carbon content was measured using the sampling method^[33,47,54,55,73] and the levitation melting technique^[39,40,95] at the temperature range between 1773 K and 2273 K (1500 °C and 2000 °C). All the experimental data are plotted in Figure 13. The Sieverts' method was

Fig. 13—Comparison between experiments^[33,39,40,47,54,55,73,75] and model calculations for N solubility in Fe-C melts at (a) 1823 K (1550 °C), (b) 1873 K (1600 °C), (c) 1923 K to 2273 K (1650 °C to 2000 °C) under 1 atm N₂ pressure, (d) 1773 K to 1873 K (1500 °C to 1600 °C) under reduced N₂ partial pressures of 0.8 and 0.3 atm.

Fig. 14—N solubility in carbon saturated liquid iron at 1 atm N₂ pressure^[75,96,98] along with the present optimization and previous modeling result.^[97]

not employed in this system because carbon monoxide gas formed by the reaction between liquid Fe-C alloy and the crucible can interfere with the gas

measurements.^[33] Except Maekawa and Nakagawa^[54] and Pehlke and Elliott^[33]'s data, other results measured by the sampling^[55,73] and levitation method^[39,40,95] under 1 atm N₂ pressure are consistent each other. Like the above Fe-Si-N system, a constant MQM parameter of Δg_{CN} was determined to reproduce the experimental N solubility. A positive parameter was optimized to reproduce the experimental data mainly from Ishii *et al.*,^[73] Gomersall *et al.*,^[39] and Schenck *et al.*^[55] at 1 atm N₂ pressure and from Jang *et al.*^[47] under reduced N₂ partial pressures of 0.3 and 0.8 atm. It should be noted that the JSPS's positive interaction parameter between C and N for the WIPF was also determined in this system mainly based on the experimental data by Ishii *et al.*^[73].

The N solubility was also measured in C saturated liquid iron as shown in Figure 14. Opravil and Pehlke^[96] measured the N solubility in Fe-C_{sat} melt in the temperature range from 1673 K to 1973 K (1400 °C to 1700 °C) using the Sieverts' method. They reported that the N solubility in C saturated melts increased with increasing temperature, and the results were in good agreement with Du and Hillert^[97] for the previous

Fig. 15—Comparison between experiments^[34,63] and model calculations for N solubility in (a) Mn-Fe, (b) Mn-C, and (c) Mn-Si alloy melts at various temperatures and N_2 partial pressures.

optimization of this ternary liquid solution using BWRMM. However, the recent measurements by Jang *et al.*^[75] using the sampling method show the opposite temperature dependence. This discrepancy in temperature dependency can be also seen in other systems like Fe-Mn-C_{sat} and Fe-Si-C_{sat} melts between these two studies. Most possible explanation of this discrepancy can be found from the experimental procedure of

Opravil and Pehlke.^[96] Opravil and Pehlke^[96] performed the continuous measurement of N solubility with increasing temperature. At starting temperature, liquid Fe would be reasonably well saturated by C from graphite crucible. But they increased the temperature continuously during the experiment and maintained only for about 15 minutes at each measurement temperature. The dissolution of graphite to liquid melts would not be fast enough for C saturation within such a short duration time; the recent experimental data by Jang *et al.*^[75] confirmed that the C saturation required at least 1 hour in the similar temperature range even when they used an induction furnace. Therefore, the liquid Fe in the experiment by Opravil and Pehlke^[96] was most probably away from the C saturation condition. If the C content in liquid Fe is fixed to be 4.88 wt pct (saturation C amount at 1673 K (1400 °C)), the N solubility in liquid Fe-C calculated from the present model increases from 76 ppm at 1400 °C to 92 ppm at 1973 K (1700 °C). On the other hand, Jang *et al.*^[75] confirmed the equilibrium of melt by C and N_2 gas at each temperature by *in situ* analyses of N and C with time using a sampling technique. The present model is well reproducing the results of Jang *et al.*^[75] without any additional parameters. The decreasing nitrogen solubility in liquid Fe-C_{sat} with increasing temperature can be caused mainly by the increasing C content in liquid Fe. As there is strong positive interaction between C and N in liquid Fe, the increasing C content in the melt can decrease the N solubility. If the results of Opravil and Pehlke^[96] were reproduced, ternary model parameters were necessary. It should be also noted that the experimental result of Chen *et al.*^[98] at 1758 K (1485 °C) is more consistent with the results of Jang *et al.*^[75]

5. Mn-Fe-N, Mn-C-N, and Mn-Si-N systems

Kim *et al.*^[34] and Jang *et al.*^[63] investigated the nitrogen solubility in the Mn-rich melt for ferro-Mn production. The experimental N solubilities in Mn-Fe, Mn-C, and Mn-Si melts were determined using the sampling technique at various temperatures under reduced N_2 partial pressures and the results are plotted in Figure 15. Without any additional ternary parameters, all the experimental data in the Mn-rich melts are also accurately predicted by the present MQM model using the optimized binary parameters.

IV. PREDICTION OF N SOLUBILITY IN MULTICOMPONENT ALLOY MELTS

In this section, the predictions of the present MQM model with binary model parameters are compared to the experimental data for multicomponent melt. In the present study, only recent experimental data in the Fe-Al-Mn-Si-C melt were collected for this comparison.

A. Fe-Mn-Si-N, Fe-Mn-C-N, and Fe-Si-C-N Systems

Recently, Jang *et al.*^[75] measured the N solubility in the Fe-Mn-Si, Fe-Mn-C, and Fe-Si-C alloy melts at

Fig. 16—Calculated N solubility in Fe-Mn-Si melts at 1873 K (1600 °C) under 0.3 atm N_2 partial pressure along with experimental data.^[75]

Fig. 17—Calculated N solubility in Fe-Mn-C melts at 1873 K (1600 °C) under 0.3 atm N_2 partial pressure along with experimental data.^[75]

1873 K (1600 °C) under reduced N_2 partial pressures in order to determine the simultaneous effects of alloying elements on the N solubility in these melts. They carried out the sampling experiment after equilibrating the melt under reduced N_2 gas pressure, which could reduce the chance of a loss of N during sampling. For the Fe-Mn-Si and Fe-Mn-C systems, they carried out the experiment with variation of Mn concentration up to 25 wt pct. Uda and Pehlke^[99] and Schenck *et al.*^[55] also investigated the N solubility in the Fe-Si-C melts under 1 atm N_2 pressure using the levitation and sampling method, respectively. All these experimental data were accurately predicted from the present model with only binary model parameters, as can be seen in Figures 16 through 18.

Figure 19 shows the N solubility in C saturated liquid iron alloys containing Mn and Si. Opravil and Pehlke^[96] and Jang *et al.*^[75] measured the N solubility in Fe-Mn- C_{sat} and Fe-Si- C_{sat} melts using the Sieverts' method and sampling method, respectively. The two

Fig. 18—Comparison between experiments^[55,99] and model calculations for N solubility in Fe-Si-C melts at 1873 K (1600 °C) under 1 atm N_2 partial pressure.

experimental studies show the opposite trend in temperature dependency. As explained above in Section III-C-4, for liquid Fe- C_{sat} (see Figure 14), because the experimental results of Opravil and Pehlke^[96] might not reach the carbon saturation condition during the progress of the experiment, their data were not considered. The present model can accurately predict the experimental results by Jang *et al.*^[75] from optimized binary parameters. Previously, Bouchard and Bale^[100] attempted to reproduce the results of Opravil and Pehlke^[96] using the UIPF. The reproduction of the experimental data required unusually many binary, ternary, and quaternary interaction parameters with temperature dependence. Compared to the calculated nitrogen solubility line for Fe- C_{sat} melt, Mn increases the nitrogen solubility while Si decreases it in Fe- C_{sat} melts as shown in Figure 19.

B. Fe-Si-Al-N, Fe-C-Al-N, and Fe-Mn-Al-N Systems

The effects of Si, C, and Mn on the solubility of AlN in liquid iron have been measured using the metal/AlN/gas equilibration technique.^[5,46,79,101] Kim *et al.*^[46] measured the effect of Si on the AlN solubility product in liquid Fe-Al alloy in the temperature range from 1823 K to 1923 K (1550 °C to 1650 °C). In the Fe-C-Al-N^[79] and Fe-Mn-Al-N^[5,101] systems, the experiments were carried out even below the typical steel-making temperature because C and Mn significantly decrease the melting temperature of the steels. C content was varied up to 3.9 wt pct, and Mn was added up to about 22 wt pct. It was found that both Si and C decrease the solubility of AlN in liquid iron while Mn increases it mainly due to the affinity of N with each alloying element. These experimental data were used to derive the influence of the second alloying element on the interaction parameters between the first alloying element and N in the classical WIPF description.^[5,46,79,101] That is, the WIPF needs additional correction terms (ternary interaction term) for interaction parameter. On the other hand, as can be seen in

Fig. 19—N solubility in Fe-Mn-C_{sat} and Fe-Si-C_{sat} melts at 1 atm N₂ pressure^[75,97] along with the present optimization and previous modeling result.^[100]

Figures 20 through 22, no additional parameters other than binary parameters were required in the present study using the MQM to accurately predict the nitrogen solubility in these melts.

C. Fe-Mn-Al-Si-C-N System

Although this is very important system for the TWIP steel production, very limited study has been carried out for the dissolution of N in the melt. Very recently, Jang *et al.*^[101] performed the equilibrium experiment between liquid TWIP steel and N₂ gas. They measured the critical N contents for the onset of the AlN formation and investigated the evolution of AlN inclusion in the Fe-Mn-Si-C-Al melt (Fe-23.75Mn-0.33Si-0.59C-1.3Al in wt pct) during cooling. As shown in Figure 23, the present MQM model with binary parameters can accurately predict the solubility limit of AlN in this melt at the temperatures between 1723 K and 1823 K (1450 °C and 1550 °C).

D. Mn-Based Alloy Systems

Figure 24 shows the experimental N solubility results for the Mn-Fe-C, Mn-Fe-Si, Mn-Si-C, and Mn-Fe-Si-C melts at the temperature range between 1673 K and 1773 K (1400 °C and 1500 °C) under reduced N₂ gas pressure. These experiments were carried out by Kim *et al.*^[34] and Jang *et al.*^[63] for the aiming of understanding of N dissolution in ferro-Mn melts. All these experimental data in Mn-rich melts were also well predicted by the present MQM model with the identical model parameters used for Fe-rich melt.

V. DISCUSSIONS

Although WIPF is relative simple formula to use for equilibration calculations, different sets of interaction parameters would be required depending on the target melt composition. For example, Sigworth and Elliott

Fig. 20—Calculated equilibrium solubility of AlN in Fe-Si-Al alloy melts at 1823 K to 1923 K (1550 °C to 1650 °C) along with the experimental results.^[46]

Fig. 21—Calculated equilibrium solubility of N in Fe-C-Al alloy melts at 1873 K (1600 °C) along with the experimental results^[79].

optimized the different sets of the Henrian activity coefficients and interaction parameters for different base metals like Fe,^[12] Cu,^[102] Ni,^[103] and Co-rich^[104] melts. One of the striking advantages of the present MQM approach compared to the WIPF is that the thermodynamic properties (Gibbs energy) of the entire composition range of the Fe-Al-Mn-Si-C melt can be accurately described by one set of parameter. The other big advantage of the MQM approach is that small number of model parameters is in general required in comparison to the WIPF approach. For example, in order to reproduce all N solubility in the entire Fe-Al-Mn-Si-C melts, only 3 binary N parameters were required, while the WIPF would require many folds of interaction parameters related to N to get reasonable accuracy in the same high alloy system.

Figure 25 shows the comparison between different thermodynamic assessments and databases for TWIP steel composition (Fe-20Mn-0.6C-Al in wt pct). The results from the FactSage FTmisc-FeLQ database based

Fig. 22—Calculated equilibrium solubility of AlN in Fe-Mn-Al alloy melts along with the experimental results^[5,101] at 1723 K to 1823 K (1450 °C to 1550 °C).

Fig. 23—Calculated equilibrium AlN solubility in Fe-Mn-Al-Si-C alloy melts along with the experimental results.^[101]

on the WIPF (UIPF) and FactSage FSSstel database with BWRMM were compared with the present optimization results. It should be noted that all N related parameters in the FeLQ are from the JSPS^[11] compilation, and FSSstel database contains nearly the same liquid model parameters as the Thermo-Calc TCFE database.^[8] So the results in Figure 25 show a reasonable comparison of accuracy between the most conventionally used models with optimized parameters. As can be seen in Sections III and IV, the present MQM model with optimized binary parameters is well reproducing and predicting the experimental data. Therefore, if the present model calculation is used as the reference, the calculation result from FTmisc database (WIPF; UIPF) is similar to the reference line at [wt pct Al] < 1.5, but it overestimates the N solubility at higher Al concentration. The N solubility from FSSstel (BWRMM) database is calculated to be systematically higher than the reference line by about 0.007 wt pct at low and high Al concentration region.

Fig. 24—Comparison between experiments^[34,63] and model calculations for N solubility in (a) Mn-Fe-C, (b) Mn-Fe-Si, and (c) Mn(-Fe)-Si-C alloy melts.

VI. SUMMARY

The thermodynamic behavior of N in liquid Fe-Mn-Al-Si-C solution was thermodynamically optimized using the Modified Quasichemical Model (MQM). All experimental data related to N solubility and AlN

Fig. 25—Calculated AlN saturation lines of TWIP steel (Fe-Al-20Mn-0.6C in wt pct) from different thermodynamic assessments and databases.

formation in the liquid solution were critically reviewed and optimized to obtain binary model parameters of the MQM. The use of the MQM taking into account the short-range ordering of liquid species in solution and appropriate interpolation technique can minimize the number of parameters. In particular, the nitrogen solubility in the entire compositional range of ternary and high order melt of the Fe-Mn-Al-Si-C system was accurately predicted with only three binary N model parameters. As part of the thermodynamic optimization, the Gibbs energies of liquid N and solid AlN were also reassessed. This optimized database can be used, with other thermodynamic databases like oxide and gases, to perform the complex chemical reactions related to nitrogen in high alloy steel and ferro-alloy production.

ACKNOWLEDGMENTS

Financial supports from Tata Steel Europe, POSCO, RIST, Hyundai Steel, Nucor Steel, RioTinto Iron and Titanium, Nippon Steel and Sumitomo Metals Corp., JFE Steel, Voestalpine, RHI, and the Natural Sciences and Engineering Research Council of Canada are gratefully acknowledged.

NOMENCLATURE

g_i°	Molar Gibbs energy of pure component i (J/mol)
X_i	Mole fraction of i (—)
R	Gas constant, 8.314 J/mol K
T	Absolute temperature (K)
γ_i	Raoultian activity coefficient of i (—)
g_i°	Molar Gibbs energy of pure component i in infinite dilution standard state (J/mol)
f_i°	Activity coefficient of i in infinite dilution standard state (—)

ε_{ij}	Wagner's interaction parameter between i and j (—)
${}^mL_{ij}$	Excess parameters between binary i and j (—)
Δg_{ij}	Gibbs energy change for the formation of two moles of $(i-j)$ pairs (J/mol)
n_i	Number of moles of i (mol)
n_{ij}	Number of moles of $(i-j)$ pair (mol)
X_{ij}	Pair fraction of $(i-j)$ pair (—)
Y_i	Coordination-equivalent fraction of i (—)
Z_i	Coordination number of i (—)
Z_{ij}^i	Coordination number of i in $i-j$ binary solution when all nearest neighbor of an i are j 's
ΔS^{config}	Configurational entropy of mixing (J/mol K)

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