Effect of Carbon on Nitrogen Solubility and AlN Formation in High Al Alloyed Liquid Steels

Jung-Mock JANG, Seok-Hyo SEO, Young-Dae KIM, Hyo-Jong AN and Jong-Jin PAK*

Department of Materials Engineering, Hanyang University, Ansan, 426-791 Korea.

(Received on February 8, 2014; accepted on April 10, 2014)

The nitrogen solubility and the AlN solubility product in liquid Fe–C–Al–N alloys containing a wide composition range of carbon and aluminum were measured in the temperature range of 1773–1873 K. Aluminum and carbon both decreased the nitrogen solubility in liquid iron. The simultaneous effect of aluminum and carbon on nitrogen solubility in liquid iron was determined. The AlN solubility product in liquid iron decreased significantly with carbon addition primarily due to the large effect of carbon on nitrogen solubility. Using the Wagner's formalism, the experimental results were thermodynamically analyzed to determine the interaction parameters among carbon, aluminum and nitrogen in liquid iron as follows:

\[ \ln C = 0.038 \pm 0.0006 \quad (I_C): 0.39 - 2.03 \text{ mass} \%, [Al] \leq 0.91 \text{ mass} \%, 1773 - 1873 \text{ K} \]

\[ \varepsilon_{\text{AlN}} = 0.03 \pm 0.0005, \quad \varepsilon_{\text{Al}} = 0 \quad ([C] \leq 3.9 \text{ mass} \%, [Al]: 1.2 - 2.45 \text{ mass} \%, 1773 - 1873 \text{ K}) \]

KEY WORDS: TRIP steels; aluminum; carbon; nitrogen solubility; interaction parameter.

1. Introduction

Recently, a series of new advanced high strength steels (AHSS) have been developed for the future automotive industry. Among these steel grades, transformation induced plasticity (TRIP) and twinning induced plasticity (TWIP) steels offer an outstanding combination of strength and ductility with very high aluminum (1.5–2 mass%) and medium carbon composition range.1–7 However, these aluminum-rich steel grades placed great challenges to steelmaking and casting processes because AlN can be easily formed in liquid steel at such high aluminum content.8 AlN is considered as a detrimental phase for the hot ductility of the steels.9 The thermodynamics of aluminum, nitrogen and AlN formation in liquid Fe–Al–N alloy is available in the authors’ recent studies,10,11 and the effect of carbon on the nitrogen solubility in liquid Fe–C–N alloy is extensively studied by various authors.12–20 However, the effect of carbon on AlN formation and the simultaneous effect of carbon and aluminum on nitrogen solubility in liquid Fe–C–Al–N alloy are not known yet.

In the present study, the effect of carbon on nitrogen solubility and AlN solubility product in liquid Fe–C–Al–N alloys were determined over a wide range of carbon content in the temperature range from 1773 to 1873 K. The experimental results were thermodynamically analyzed to determine the first- and the second-order interaction parameters among carbon, aluminum and nitrogen using available thermodynamic data of Fe–Al–N and Fe–C–N systems.11,12

2. Experimental

The nitrogen solubility and the AlN solubility product in liquid Fe–C–Al–N alloys were determined using the metal-gas and metal-nitride-gas equilibration experiments. Detailed descriptions of the experimental apparatus and procedure are available in the authors’ recent studies.10–12 Five hundred grams of high purity electrolytic iron or Fe–C alloys contained in an Al2O3 crucible (outer diameter (OD): 56 mm, inner diameter (ID): 50 mm, height (H): 96 mm) was melted in the temperature range from 1773 to 1873 K by a 15 kW/30 kHz high frequency induction furnace. After melting the iron, the melt temperature was directly measured by a Pt/Pt-13 mass%Rh thermocouple sheathed with an 8 mm OD alumina tube immersed in the melt. The temperature fluctuation of iron melt could be controlled within 2 K during experiment by the PID controller of the induction furnace.

After the melt temperature was reached at a desired value, the melt was deoxidized by blowing an Ar-10%H2 gas onto the melt surface at a high flow rate of ~5000 ml/min for 2 h. The oxygen content in the melt decreased to a value less than 20 mass ppm. Then, the gas was switched to a mixture of Ar-10%H2 and N2 gases to have a desired nitrogen partial pressure. The flow rate of the gas mixture was controlled by a mass flow controller in the range from 1000 to 2000 ml/min depending on nitrogen partial pressures in the gas. Strong agitation of the melt by an induction furnace resulted in a fast attainment of equilibrium nitrogen solubility in liquid

* Corresponding author: E-mail: jjpak@hanyang.ac.kr
DOI: http://dx.doi.org/10.2355/isijinternational.54.1578
iron under a nitrogen partial pressure within 1 h.

In case of the nitrogen solubility measurement in Fe–Al–N and Fe–C–Al–N melts, aluminum (99.9% purity) was added through an 18 mm OD quartz tube after confirming the equilibrium nitrogen solubility in pure liquid iron or Fe–C alloy melts under a nitrogen partial pressure. In one set of nitrogen solubility measurement experiments at 1823 K, aluminum and carbon additions (99.99% purity graphite) were made alternately. After each aluminum and carbon addition in liquid iron, the new equilibrium nitrogen solubility was attained within 30 minutes. This was confirmed by sampling and in situ nitrogen analysis with time after the additions.

In order to determine the effect of carbon on the AlN solubility product in liquid iron, aluminum was added in pure liquid iron or Fe–C alloy melts until an AlN layer was formed on the surface of the melts under a given nitrogen partial pressure, and then carbon was added up to 3.9 mass%. The formation of AlN in the melts could be also confirmed by a sharp decrease in nitrogen content checked by the analysis of metal samples during the experiment. After each carbon addition, a new AlN solubility equilibrium was attained within 1 h.

The metal sample of about 10 g was extracted by a 4 mm ID quartz tube connected to a syringe (10 ml), and it was quenched rapidly in water within 2 s. The metal samples were carefully cut for the chemical analysis. The nitrogen and oxygen contents in the metal sample were analyzed by the nitrogen/oxygen analyzer (LECO TC-600 apparatus; LECO Corporation, St. Joseph, MI) with an accuracy of ±2 mass ppm, and the carbon content was analyzed by the carbon/sulfur analyzer (CS-800, Eltra, Neuss, Germany) within an error range of 1%. Aluminum in the metal sample was analyzed by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, SPECTRO ARCOS apparatus, manufactured by Spectro Analytical Instruments, Kleve, Germany) using appropriate standard solutions containing the same amount of Fe (2000 mass ppm) as the sample solutions. The analytical limit for aluminum in the metal sample was ±1 mass ppm.

After each AlN solubility experiment, the melt remained in the crucible was quenched by blowing helium gas onto the melt surface. In order to check the presence of inclusions including AlN in the quenched melts, about 10 g of metal sampled near the upper surface of the melt was dissolved in dilute HCl (1+1) solution heated in a water bath for 72 h. After the complete dissolution of metallic portion, the residue was filtrated and analyzed by the X-ray diffraction analysis (XRD, High power X-ray Diffractometer System, Rigaku D/MAX-2500/PC).

3. Results and Discussion

3.1. Effect of Carbon and Aluminum on Nitrogen Solubility in Liquid Fe–C–Al–N Melt

The experimental results of nitrogen solubility and AlN solubility measurements for Fe–Al–N and Fe–C–Al–N melts are summarized in Table 1. Figure 1 shows the variations of equilibrium nitrogen solubility in Fe–Al–N and Fe–C–Al–N melts with aluminum additions under various nitrogen partial pressures of 0.19–0.8 atm in the temperature range of 1823–1873 K.

<table>
<thead>
<tr>
<th>Temp. (°K)</th>
<th>(P_{N_2}) (atm)</th>
<th>[% C]</th>
<th>[% Al]</th>
<th>Observed [% N]</th>
<th>Calculated [% N]</th>
<th>AlN saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1823</td>
<td>0.19</td>
<td>0.39</td>
<td>0.19</td>
<td>0.0132</td>
<td>0.0127</td>
<td>sat.</td>
</tr>
<tr>
<td>1873</td>
<td>0.5</td>
<td>0.39</td>
<td>0.19</td>
<td>0.0132</td>
<td>0.0127</td>
<td>sat.</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>0.39</td>
<td>0.19</td>
<td>0.0132</td>
<td>0.0127</td>
<td>sat.</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.39</td>
<td>0.19</td>
<td>0.0132</td>
<td>0.0127</td>
<td>sat.</td>
</tr>
</tbody>
</table>
range from 1 773 to 1 873 K.

The nitrogen solubility decreases linearly as the aluminum content increases in liquid iron when the melt is not saturated with AlN as shown as open symbols in Fig. 1. When AlN is formed at higher Al contents, the nitrogen solubility decreased along the solubility product lines for the reaction equilibrium of \( \text{AlN(s)} = \text{Al}^{+} + \text{N}^{-} \) as shown as solid symbols in the figure. In an experiment at 1 823 K under a nitrogen partial pressure of 0.19 atm, aluminum and carbon additions were made alternately. As shown in Fig. 1(b), aluminum was first added up to 0.58 mass% in Fe-0.39 %C melt, then carbon was increased to 2.03 mass% and aluminum was added again until an AlN layer was formed on the surface of the melt.

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

\[
\frac{1}{2} N_2(g) = N \quad \Delta G_{i}^{\circ} = 3 598 + 23.89T \quad \text{J/g \cdot atom}^{21)} \\
K_N = \frac{f_N[N]}{P_N} \quad \text{.......................... (2)}
\]

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, \( \text{i.e.,} f_N \rightarrow 1 \) when \([% N] \rightarrow 0 \). \( P_{N_2} \) is the nitrogen partial pressure in atm over the melt surface.

In Fe–C–Al–N alloy melts, the activity coefficient of nitrogen, \( f_N \) can be determined from the following equation.

\[
\log f_{N} = e_{N}^{C}[%C] + r_{N}^{C}[%C]^{2} + r_{N}^{CAl}[%Al][%C] \quad \text{......... (3)}
\]

where \( e_{N}^{C} \) and \( r_{N}^{C} \) are the first- and the second-order interaction parameters of elements on nitrogen in liquid iron. In the authors’ recent studies, the thermodynamics of nitrogen and AlN formation in Fe–Al–N melt\(^{11)}\) and the interaction parameter of carbon on nitrogen in Fe–C–N melt\(^{12)}\) were determined. Thermodynamic parameters used in the present study are summarized in Table 2. As mentioned earlier, the oxygen content was less than 20 mass ppm in the melt. Therefore, the effect of oxygen on nitrogen was assumed to

<table>
<thead>
<tr>
<th>Table 1. Continued.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. ((^\circ \text{K}))</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td>2.03 0.58 0.0103 0.0103</td>
</tr>
<tr>
<td>0.81 0.0 0.0167 0.0167</td>
</tr>
<tr>
<td>0.80 0.99 0.0081 0.0081 sat.</td>
</tr>
<tr>
<td>0.80 0.81 0.0167 0.0167</td>
</tr>
</tbody>
</table>

Fig. 1. Equilibrium relations between [%Al] and [%N] in Fe–Al–N and Fe–C–Al–N melts: (a) 1 873 K, (b) 1 823 K and (c) 1 773 K.
be negligible.

Figure 2 shows the relation to determine the value of \( r_{N}^{\text{C-Al}} \) in Eq. (3) using the nitrogen solubility data for Fe–C–Al–N melts not saturated with AlN in Table 1. The value of \( r_{N}^{\text{C-Al}} \) can be determined as 0.038 ± 0.0006 from the slope of a straight line obtained by the regression analysis of the data in Fig. 2. The temperature dependence of \( r_{N}^{\text{C-Al}} \) value was negligible in the temperature range from 1 773 to 1 873 K.

3.2. Effect of Carbon on AlN Solubility Product in Liquid Iron

The experimental results of AlN solubility measurement with carbon additions in Fe–C–Al–N melts are also summarized in Table 1. The nitride formed in the melt during the metal-nitride-gas equilibration experiments were identified as a pure solid AlN. The XRD data on the filtrated residue from the dissolved metal samples was compared with the XRD pattern of the stoichiometric AlN powder (99% purity, <10 \( \mu \text{m} \), Aldrich Chemical Co.) as shown in Fig. 3. By comparing 2\( \theta \) values of the diffraction peaks, the aluminum nitride formed in Fe–C–Al–N melt in the present study can be considered as a pure solid stoichiometric AlN.

The reaction equilibrium for the dissolution of pure solid AlN in liquid iron can be written as

\[
\text{AlN} (s) = \text{Al} (l) + \text{N} (l)
\]

where \( K_{\text{AlN}} \) is the equilibrium constant for Reaction (4), and \( h_A \) and \( h_N \) are the Henrian activities of aluminum and nitrogen relative to the 1 mass% standard state in liquid iron, and \( f_A \) and \( f_N \) are the activity coefficients of aluminum and nitrogen, respectively. The activity of AlN in Eq. (6) is unity in the present study.

In order to determine the thermodynamic relation between carbon and aluminum from the AlN solubility product data in Fe–C–Al–N melts, the equilibrium constant, \( K_{\text{AlN}} \) can be written as the following relation using the inter-
action parameters:

\[
\log K_{AN} = \log f_{Al} + \log f_{N} + \log[\% Al][\% N] \\
= e_{Al}^{C}[\% C] + r_{Al}^{C}[\% C]^{2} + e_{Al}^{AI}[\% AI] + r_{Al}^{AI}[\% AI]^{2} + e_{N}^{C}[\% N] + r_{N}^{C}[\% N]^{2} + e_{N}^{AI}[\% AI] + r_{N}^{AI}[\% AI]^{2} + r_{C,Al}^{C}[\% C][\% AI] + e_{C}^{C}[\% C] + r_{C}^{C}[\% C]^{2} + \log[\% Al][\% N]
\]

................................. (7)

where \(e_{Al}^{C}\), \(e_{Al}^{AI}\), \(r_{Al}^{C}\) and \(r_{Al}^{AI}\) are the first- and the second-order interaction parameters of elements on nitrogen and aluminum in Fe–C–Al–N melts, respectively, the value of \(r_{C,Al}^{C}\) was determined as 0.038 in the preceding section. The values of \(\log K_{AN}\) and the interaction parameters used in Eq. (7) are summarized in Table 2. As mentioned earlier, the oxygen content was very low in the melt and the effect of oxygen on aluminum and nitrogen was assumed to be negligible.

Therefore, the specific effect of carbon on aluminum can be determined from the AlN solubility product data as a function of carbon content in Fe–C–Al–N melts. Eq. (7) can be rearranged as

\[
\log f_{Al}^{C} = e_{Al}^{C}[\% C] + r_{Al}^{C}[\% C]^{2} \\
= \log K_{AN} - e_{Al}^{AI}[\% AI] - r_{Al}^{AI}[\% AI]^{2} - e_{N}^{AI}[\% N] \\
- r_{N}^{AI}[\% N]^{2} - e_{N}^{AI}[\% AI] - r_{N}^{AI}[\% AI]^{2} - e_{C}^{C}[\% C] - r_{C}^{C}[\% C]^{2} - \log[\% AI][\% N]
\]

where \(f_{Al}^{C}\) is the interaction coefficient of carbon on aluminum in liquid iron.

**Figure 6** shows the values of \(\log f_{Al}^{C}\) plotted vs carbon content in Fe–C–Al–N melts using the relation expressed by Eq. (8) and experimental data obtained at various nitrogen partial pressures and temperatures. The correlation shows an excellent linear relationship with carbon content up to 3.9 mass%. Therefore, the values of \(e_{Al}^{C}\) and \(r_{Al}^{C}\) can be determined as 0.03±0.0005 and 0, respectively, by a linear regression analysis of the data. The temperature dependence of \(e_{Al}^{C}\) and \(r_{Al}^{C}\) values was negligible in the temperature range from 1 773 to 1 873 K. The values of interaction parameters determined in the present study are summarized in Table 3.

The \(e_{Al}^{C}\) value determined in the present study using the metal-nitride-gas equilibration technique in Fe–C–Al–N melts is about three times lower than the \(e_{Al}^{C}\) value of 0.091 at 1 873 K reported by Wilder and Elliott.22 They estimated the \(e_{Al}^{C}\) value as 5.3 at 1 873 K in liquid Fe–C–Al alloy from the Chipman and Floridis’ aluminum distribution data23 between liquid Fe–C–Al–Ag alloys and Ag–Al melts at 1 873 K using the extrapolated Al activity data in liquid binary Ag–Al alloys at 1 223 K with an assumption that log\(\gamma_{Al}\) is inversely proportional to absolute temperature. The value of \(e_{Al}^{C}\) can be converted to the \(e_{Al}^{C}\) value as 0.091 at 1 873 K using the Lupis’ conversion relationship.24 This \(e_{Al}^{C}\) value of 0.091 at 1 873 K is the only data compiled as the recommended value by the Japan Society for the Promotion of Science (JSPS).25 However, the relatively high silver content up to 9.3 mass% in Fe–C–Al–Ag alloys equilibrated with Ag–Al alloys at 1 873 K in Chipman and Floridis’ work does not warrant the accuracy of values for \(e_{Al}^{C}\) in Fe–C–Al alloy system at 1 873 K.

The \(e_{Al}^{C}\) and \(r_{Al}^{C}\) values in aluminum-rich liquid steels are very important thermodynamic parameters to predict the formation of inclusions like AlN and Al₂O₃ in TRIP and TWIP steel grades. In the present study, these values were accurately determined by considering the first- and the sec-
The first- and second-order interaction parameters of carbon and aluminum on nitrogen in Fe–C–Al–N melts at 1773–1873 K. The main findings of this study can be summarized as follows.

4. Conclusions

Thermodynamic relations among carbon, aluminum and nitrogen were determined in liquid Fe–C–Al–N alloy melts at 1773–1873 K. The main findings of this study can be summarized as follows.

(1) From the nitrogen solubility measurement in Fe–C–Al–N melts, the second-order interaction parameter of carbon and aluminum on nitrogen was determined as

$$ r_{\text{N}}^{C, \text{Al}} = 0.038 \pm 0.0006 $$

$$ ([C]: 0.39–2.03 \text{ mass \%}, [\text{Al}] \leq 0.91 \text{ mass \%}, 1773–1873 \text{ K}) $$

(2) From the AlN solubility measurement in Fe–C–Al–N melts, the first- and second-order interaction parameters between carbon and aluminum were determined as

$$ e_{\text{Al}}^{C} = 0.03 \pm 0.0005, \quad r_{\text{Al}}^{C} = 0 $$

$$ ([C] \leq 3.9 \text{ mass \%}, [\text{Al}]: 1.2–2.45 \text{ mass \%}, 1773–1873 \text{ K}) $$

Acknowledgments

This study was supported by the R&D Center for Valuable Recycling (Global-Top R&BD Program) of the Ministry of Environment (Project No.: GT-11-C-01-220-0).

REFERENCES

9) M. Vedani, D. Dellasega and A. Mannuccii: ISIJ Int., 49 (2009), 446.
16) S. Maekawa and Y. Nakagawa: Tetsu-to-Hagané, 46 (1960), 748.