Aluminum Deoxidation Equilibrium of Fe-Ni Alloy at 1773 and 1873 K

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Abstract

The aluminum deoxidation equilibrium in molten Fe-36 mass%Ni and Fe-46 mass%Ni alloys was experimentally determined at 1773 and 1873 K to obtain the thermodynamic parameters around the liquidus temperature, which is required to predict the deoxidation reaction for the ingot casting process. Automatic SEM-EDS inclusion analysis was performed to estimate the undissolved oxygen content. Thermodynamics analysis on the Al deoxidation has been carried out by using Miki and Hino's formula, which is based on Darken's quadratic formalism and Redlich-Kister Polynomial. From the composition dependence of the apparent equilibrium constant in Fe-Ni alloy, the necessity of the third order interaction parameter of Ni-Al was found. Then, the interaction parameters of Fe-Al, Al-O and Ni-Al were evaluated.

1. Introduction

To produce high quality steel, control of the oxygen content in steel is one of the most important technical issues in the steelmaking process. Due to the strong affinity with oxygen, aluminum is commonly used as deoxidizing agent in the process. Therefore, the thermodynamics of aluminum deoxidation in the steel melt have been intensively studied since the 1950's by many researchers.

To describe the Al deoxidation equilibrium in low alloy steel, the first-order interaction parameter formalism of Wagner^[1] (Wagner's formula) has been used for practical engineering purposes due to its simple equation and easy application in multi-component systems. However, since this Wagner's formula was inherently derived from the Taylor expansion at infinitely dilute solution, there are many difficulties to apply Wagner's formula to high-alloy steel and steel with high Al levels.

Miki and Hino^[2] have developed Darken's quadratic formalism^[3, 4] and a Redlich-Kister type polynomial^[5, 6] to calculate the deoxidation equilibrium in non-dilute alloys. Their formula enables calculating the deoxidation equilibrium in high-alloy steels such as stainless steel.

Even though there have been many studies performed on the Al deoxidation equilibrium in a steel melt, most of these studies were carried out around a typical steel refining temperature (i.e. 1873 K). These studies were intended to describe and/or predict the deoxidation reaction during the steel refining process.

However, for large ingot casting, the solidification takes a long time. Especially for extremely large ingots, it takes several days to complete the solidification after pouring, which is much longer than the refining time. After pouring the steel melt into the ingot case, the temperature of the steel melt decreases to the liquidus temperature and then the liquid steel gradually solidifies from the ingot surface to its center. Due to the temperature drop and deoxidizing or oxidizing reactions during casting, the equilibrium state between inclusions and steel melt after pouring might differ from that in the refining process. During the long solidification period, the chemistry of the inclusions in the steel melt might evolve towards the new equilibrium state in the ingot case. Therefore, thermodynamic parameters applicable at solidification temperatures (about 1773 K) are required to describe or predict

the deoxidation reactions during solidification for large ingots.

In 2002, C. H. Rhee *et al*^[7] carried out an experimental study on the Al deoxidation equilibrium in Fe-36 mass%Ni alloy at 1773 K using a levitation furnace to obtain the interaction parameters for Wagner's formula. As their parameters were only valid for Al deoxidation in an Fe-36 mass%Ni alloy at 1773 K, the aim of this study is to extend these data to Fe-Ni alloys with Ni between 36 and 46 mass% and for temperatures of both 1773 and 1873 K. Based on the experimentally determined Al deoxidation equilibrium data, the thermodynamics analysis was carried out by using Miki and Hino's formula to obtain the thermodynamics parameters applicable for large ingot solidification.

2. Experiments

2.1. Experimental setup and procedure

The experiments were conducted with a vertical heat resistance furnace at purified Ar atmosphere. **Fig. 1(a)** shows a diagram of the experimental set-up. The furnace consists of an Al₂O₃ working tube, MoSi₂ heating elements, an Al₂O₃ gas inlet tube, a Al₂O₃ support tube, an Al₂O₃ outer protective crucible, an Al₂O₃ inner crucible (OD=24 mm, ID=20 mm, H=60 mm), an Al₂O₃ brick to fix the inner crucible in the outer crucible and an oxygen sensor which measures the oxygen partial pressure at the gas outlet.

The Ar gas was purified by a Mg furnace and silica gel. A feeding chamber was installed at the top of the gas inlet tube, which allows the deoxidizing agent to be added into the crucible without any contamination of the atmosphere. The melt temperature was calibrated by a thermocouple (Type S) with Al₂O₃ shielding and controlled within ± 2 °C during experiments.

To obtain a homogeneous experimental condition, a Fe-Ni alloy prepared from electrolytic iron (99.99%) and nickel (99.99%) was used for the deoxidation experiments as a master alloy. About 60 g of the Fe-Ni master alloy was placed in the inner crucible and set into the furnace. After the gas atmosphere was changed to the purified Ar, the Fe-Ni alloy was heated and melted completely at 1873 K. High purity Al as a deoxidizing agent was added to the melt from the feeding chamber through

the gas inlet tube. The temperature was controlled at the temperature of interest (1773, 1873 K) for more than 8 hours. Then the melt with inner crucible was picked up from the furnace and rapidly water quenched.

2.2. Chemical analysis of metal and characterization of inclusion

The quenched samples were analyzed by the following techniques. **Figs. 1(b) and 1(c)** shows a diagram of the extraction of the quenched sample for steel composition analysis (ICP-AES, LECO) and SEM-EDS inclusion characterization. Ni and Al contents were analyzed by using Inductively Coupled Plasma Optical Emission Spectroscopy (Varian 720ES, Agilent Technology Co, USA). Sample solutions for Ni measurement were prepared by dissolving 1.0 g metal sample in HNO₃ (1:1) and filling the 100 ml flask with deionized water. Sample solutions for Al measurement were obtained by diluting the Ni measurement solutions to 1/100. Because the concentrations of Fe and Ni in the sample solutions were much higher than these of Al, the Al spectrum might be affected by Fe and Ni. To minimize the effect of Fe and Ni as background elements in the sample solutions, standard solutions containing the same amount of Fe and Ni were used for Al measurement. The total O content was analyzed by using inert gas infrared fusion spectroscopy (TC-436, LECO Co, USA). Each specimen was cleaned by using ultrasonic cleaning in methanol after grinding by SiC abrasive paper. Each sample was analyzed at least 3 times to confirm the reliability of the analysis.

SEM-EDS (JSM-6610LA, JEOL Co, Japan) and Particle Finder (JEOL ENGINEERING Co, Japan) was employed for the inclusion analysis. Horizontal cross sections of the Fe-Ni samples at 5 mm from the bottom of the crucible were cut, grinded by SiC abrasive paper and polished prior to the inclusion characterization by SEM-EDS with Particle Finder. As shown in **Fig. 1(c)**, an area of 19.66 mm² was scanned and backscattered electron (BSE) images were recorded. Due to the difference in average atomic number between the metal matrix phase and the oxide inclusions, all inclusions larger than 0.1 μm² are detected automatically by the contrast in the BSE image. The chemical composition of the detected inclusions were simultaneously analyzed by EDS. Since the inclusions

sizes were very small, the results of EDS analysis might be affected by the Fe-Ni metallic matrix phase. To eliminate this background effect, peaks of Fe and Ni in EDS spectra have been ignored in quantitative composition analysis of inclusions. By using this technique, information about all detected inclusions such as size, shape, distribution and composition were obtained.

3. Results and discussion

3.1. Methodology to evaluate the dissolved and undissolved oxygen

One of the possible reasons for the large deviation in the Al-O relation in previous studies on the Al deoxidation equilibrium is the influence of oxide inclusions on the oxygen analysis (i.e. the undissolved oxygen). A reliable analysis of the dissolved oxygen content is required for the determination of the deoxidation equilibrium. However, if the metal sample for the oxygen analysis contains some oxide inclusions, the results of Al-O equilibrium will be affected by the oxygen in these inclusions. Especially for experiments conducted in a heat resistance furnace, the force to separate inclusions from the melt is smaller than in an induction furnace, as the latter has a pinch effect which ejects inclusions from the melt. In spite of the long holding time, some inclusions might remain in the metal phase, specifically the tiny inclusions. In this study, the results of the inert gas infrared fusion spectroscopy (LECO) are assumed to be the total oxygen content (O_{Tot}), expressed in Eq. [1].

$$O_{Tot} = O_D + O_U \quad [1]$$

where O_D and O_U mean respectively the dissolved oxygen content in the metal phase and the oxygen content in the inclusions. The oxygen content in the inclusions O_U was determined by measuring the size and composition of all inclusions using SEM-EDS. The average composition of the inclusions detected by SEM-EDS are shown in **Table 2**. Although SiO_2 , MgO , CaO and ZrO_2 were detected as minor oxides, the average composition of Al_2O_3 was more than 97%. No sulfide or any other compounds were observed in the inclusions. Al_2O_3 is therefore the dominant oxide in this work and the activity of Al_2O_3 can be considered as unity.

When the inclusion particles are distributed randomly, the area fraction of the particles in an

arbitrary section is equal to the volume fraction of the particles^[8]. Since the volume fraction of the inclusions was very small, the oxygen content of the inclusions can be calculated by Eq. [2]

$$O_U = \frac{\rho_{Al_2O_3} \sum S_{Inclusion}}{\rho_{Fe-Ni} (S_{Total} - \sum S_{Inclusion}) + \rho_{Al_2O_3} \sum S_{Inclusion}} \left(\frac{3M_O}{M_{Al_2O_3}} \right) \times 100$$

$$= \frac{\rho_{Al_2O_3} \sum S_{Inclusion}}{\rho_{Fe-Ni} S_{Total}} \left(\frac{3M_O}{M_{Al_2O_3}} \right) \times 100 \quad (\because S_{Total} \gg \sum S_{Inclusion}) \quad [2]$$

where ρ_i , $\sum S_{Inclusion}$, S_{Total} and M_i are respectively the density of component i , the sum of the inclusions area, the total investigated area (19.66 mm²) and the molecular and/or atomic weight of component i . O_D is then obtained by combining Eqs. [1] and [2].

3.2. Experimental results

Table 2 shows the results of the ICP-AES, the total oxygen and the SEM-EDS inclusion analysis. **Fig. 2** shows the Al-O relation of this work. For comparison, the results of the previous studies^[7, 9-11] are also plotted in the figure on Al deoxidation in Fe-36 and 46 mass%Ni alloy at 1773 to 1973 K. The area fraction of the inclusions is proportional to the undissolved oxygen content (**Table 2**). Although the undissolved oxygen content was mostly lower than 1 ppm, a maximum of 5.2 ppm was found. The effect of the undissolved oxygen content is not negligible in the high Al range and at lower temperature to calculate the deoxidation equilibrium and/or to determine the thermodynamic parameters, as the dissolved O content has the same order of magnitude as the O content in the inclusions. This may explain the deviation between the present study and the investigation by C. H. Rhee *et al*^[7]. In the low Al range (<0.5 mass%Al), the present results for Fe-36 mass%Ni at 1773 K are in a good accordance with C. H. Rhee's results, except for the data point with the lowest Al content (No.1). However, in the high Al range (>0.5 mass% Al), the equilibrated oxygen contents in the present work are smaller than those in C. H. Rhee's experiment. This indicates that the determination of the oxygen content in the inclusions by using SEM-EDS inclusion analysis enables to obtain more accurate equilibrium data for

the high Al content steel. The dissolved oxygen contents in the metal matrix phase are used for the numerical analysis in this study.

3.3. Al deoxidation equilibrium in Fe-Ni alloys

3.3.1. Thermodynamic description of the Al deoxidation

In this study, the Redlich-Kister type polynomial proposed by Miki and Hino^[2] was used for the thermodynamic analysis of the Al deoxidation equilibrium. The pure substance was chosen as the standard state for the condensed phases (Fe, Ni and Al). Dissolved oxygen equilibrated with 1 atm (0.1 MPa) oxygen was used as the standard state for oxygen. The Al deoxidation reaction can be expressed as Eq. [3]

For the selected standard state for oxygen, the Gibbs free energy change of Eq. [3] is equal to the Gibbs free energy of Al_2O_3 formation ($\Delta G_{f, \text{Al}_2\text{O}_3}^\circ$). Therefore, the equilibrium constant K of Eq. [3] is described as Eq. [4]

$$\begin{aligned} \ln K &= -\frac{\Delta G_{f, \text{Al}_2\text{O}_3}^\circ}{RT} \\ &= \ln a_{\text{Al}_2\text{O}_3} - 2 \ln a_{\text{Al}} - 3 \ln a_{\text{O}} \\ &= -2 \ln \gamma_{\text{Al}} X_{\text{Al}} - 3 \ln \gamma_{\text{O}} X_{\text{O}} \quad (\because a_{\text{Al}_2\text{O}_3} = 1) \\ &= -2 \ln X_{\text{Al}} - 2 \ln \gamma_{\text{Al}} - 3 \ln X_{\text{O}} - 3 \ln \gamma_{\text{O}} \end{aligned} \quad [4]$$

where a_i , γ_i , X_i are respectively the activity, activity coefficient and molar fraction of component i . The excess free energy change of the Fe-Ni-Al-O system (ΔG^{ex}) can be expressed as a Redlich-Kister type polynomial using first and second order interactions (Eq. [5]). Here, since the mole fractions of Al and O are small enough, only the first order interaction parameter on Al and O is considered.

$$\begin{aligned} \Delta G^{\text{ex}} &= X_{\text{Fe}} X_{\text{Ni}} \{ {}^0\Omega_{\text{Fe-Ni}} + (X_{\text{Fe}} - X_{\text{Ni}})^1\Omega_{\text{Fe-Ni}} \} \\ &\quad + X_{\text{Fe}} X_{\text{Al}} \{ {}^0\Omega_{\text{Fe-Al}} + (X_{\text{Fe}} - X_{\text{Al}})^1\Omega_{\text{Fe-Al}} \} \end{aligned}$$

$$\begin{aligned}
& + X_{\text{Ni}} X_{\text{Al}} \{ {}^0\Omega_{\text{Ni-Al}} + (X_{\text{Ni}} - X_{\text{Al}})^1\Omega_{\text{Ni-Al}} \} \\
& + X_{\text{Ni}} X_{\text{O}} \{ {}^0\Omega_{\text{Ni-O}} + (X_{\text{Ni}} - X_{\text{O}})^1\Omega_{\text{Ni-O}} \} \\
& + X_{\text{Al}} X_{\text{O}} {}^0\Omega_{\text{Al-O}} + X_{\text{Fe}} \Delta G_{\text{fus Fe}}^\circ
\end{aligned} \tag{5}$$

Here, ${}^0\Omega_{i-j}$ and ${}^1\Omega_{i-j}$ are respectively the first and second order interaction parameters between component i and j . And $\Delta G_{\text{fus Fe}}^\circ$ is the Gibbs free energy of iron fusion. The partial molar excess free energy changes of Al and O can be expressed by Eqs. [6] and [7]:

$$\begin{aligned}
\Delta \bar{G}_{\text{Al}}^{\text{ex}} &= RT \ln \gamma_{\text{Al}} \\
&= \Delta \bar{G}^{\text{ex}} - X_{\text{Ni}} \frac{\partial \Delta \bar{G}^{\text{ex}}}{\partial X_{\text{Ni}}} + (1 - X_{\text{Al}}) \frac{\partial \Delta \bar{G}^{\text{ex}}}{\partial X_{\text{Al}}} - X_{\text{O}} \frac{\partial \Delta \bar{G}^{\text{ex}}}{\partial X_{\text{O}}} \\
&= -X_{\text{Fe}} X_{\text{Ni}} {}^0\Omega_{\text{Fe-Ni}} - 2X_{\text{Fe}} X_{\text{Ni}} (X_{\text{Fe}} - X_{\text{Ni}})^1\Omega_{\text{Fe-Ni}} \\
&\quad + X_{\text{Fe}} (1 - X_{\text{Al}}) {}^0\Omega_{\text{Fe-Al}} + X_{\text{Fe}} (X_{\text{Fe}} - 2X_{\text{Al}} - 2X_{\text{Fe}} X_{\text{Al}} + 2X_{\text{Al}}^2)^1\Omega_{\text{Fe-Al}} \\
&\quad - X_{\text{Fe}} X_{\text{O}} {}^0\Omega_{\text{Fe-O}} - 2X_{\text{Fe}} X_{\text{O}} (X_{\text{Fe}} - X_{\text{O}})^1\Omega_{\text{Fe-O}} \\
&\quad + X_{\text{Ni}} (1 - X_{\text{Al}}) {}^0\Omega_{\text{Ni-Al}} + X_{\text{Ni}} (X_{\text{Ni}} - 2X_{\text{Al}} - 2X_{\text{Ni}} X_{\text{Al}} - 2X_{\text{Al}}^2)^1\Omega_{\text{Ni-Al}} \\
&\quad - X_{\text{Ni}} X_{\text{O}} {}^0\Omega_{\text{Ni-O}} - 2X_{\text{Ni}} X_{\text{O}} (X_{\text{Ni}} - X_{\text{O}})^1\Omega_{\text{Ni-O}} \\
&\quad + X_{\text{O}} (1 - X_{\text{Al}}) {}^0\Omega_{\text{Al-O}}
\end{aligned} \tag{6}$$

$$\begin{aligned}
\Delta \bar{G}_{\text{O}}^{\text{ex}} &= RT \ln \gamma_{\text{O}} \\
&= \Delta \bar{G}^{\text{ex}} - X_{\text{Ni}} \frac{\partial \Delta \bar{G}^{\text{ex}}}{\partial X_{\text{Ni}}} + (1 - X_{\text{O}}) \frac{\partial \Delta \bar{G}^{\text{ex}}}{\partial X_{\text{O}}} - X_{\text{Al}} \frac{\partial \Delta \bar{G}^{\text{ex}}}{\partial X_{\text{Al}}} \\
&= -X_{\text{Fe}} X_{\text{Ni}} {}^0\Omega_{\text{Fe-Ni}} - 2X_{\text{Fe}} X_{\text{Ni}} (X_{\text{Fe}} - X_{\text{Ni}})^1\Omega_{\text{Fe-Ni}} \\
&\quad - X_{\text{Fe}} X_{\text{Al}} {}^0\Omega_{\text{Fe-Al}} - 2X_{\text{Fe}} X_{\text{Al}} (X_{\text{Fe}} - X_{\text{Al}})^1\Omega_{\text{Fe-Al}} \\
&\quad + X_{\text{Fe}} (1 - X_{\text{O}}) {}^0\Omega_{\text{Fe-O}} + X_{\text{Fe}} (X_{\text{Fe}} - 2X_{\text{O}} - 2X_{\text{Fe}} X_{\text{O}} + 2X_{\text{O}}^2)^1\Omega_{\text{Fe-O}} \\
&\quad - X_{\text{Ni}} X_{\text{Al}} {}^0\Omega_{\text{Ni-Al}} - 2X_{\text{Ni}} X_{\text{Al}} (X_{\text{Ni}} - X_{\text{Al}})^1\Omega_{\text{Ni-Al}} \\
&\quad + X_{\text{Ni}} (1 - X_{\text{O}}) {}^0\Omega_{\text{Ni-O}} + X_{\text{Ni}} (X_{\text{Ni}} - 2X_{\text{O}} - 2X_{\text{Ni}} X_{\text{O}} - 2X_{\text{O}}^2)^1\Omega_{\text{Ni-O}} \\
&\quad + X_{\text{Al}} (1 - X_{\text{O}}) {}^0\Omega_{\text{Al-O}}
\end{aligned} \tag{7}$$

By substituting Eqs. [6] and [7] into Eq. [4], the fundamental equation for the thermodynamic analysis

of Al deoxidation in Fe-Ni alloy is obtained (Eq. [8])^[9]:

$$\begin{aligned}
0 = & 2RT \ln X_{\text{Al}} + 3RT \ln X_{\text{O}} - \Delta G_{\text{fAl}_2\text{O}_3}^\circ \\
& - 5X_{\text{Fe}}X_{\text{Ni}}^0\Omega_{\text{Fe-Ni}} - 10X_{\text{Fe}}X_{\text{Ni}}(X_{\text{Fe}} - X_{\text{Ni}})^1\Omega_{\text{Fe-Ni}} \\
& + X_{\text{Fe}}(2 - 5X_{\text{Al}})^0\Omega_{\text{Fe-Al}} + X_{\text{Fe}}(2X_{\text{Fe}} - 4X_{\text{Al}} - 10X_{\text{Fe}}X_{\text{Al}} + 10X_{\text{Al}}^2)^1\Omega_{\text{Fe-Al}} \\
& + X_{\text{Fe}}(3 - 5X_{\text{O}})^0\Omega_{\text{Fe-O}} + X_{\text{Fe}}(3X_{\text{Fe}} - 6X_{\text{O}} - 10X_{\text{Fe}}X_{\text{O}} + 10X_{\text{O}}^2)^1\Omega_{\text{Fe-O}} \\
& + X_{\text{Ni}}(2 - 5X_{\text{Al}})^0\Omega_{\text{Ni-Al}} + X_{\text{Ni}}(2X_{\text{Ni}} - 4X_{\text{Al}} - 10X_{\text{Ni}}X_{\text{Al}} + 10X_{\text{Al}}^2)^1\Omega_{\text{Ni-Al}} \\
& + X_{\text{Ni}}(3 - 5X_{\text{O}})^0\Omega_{\text{Ni-O}} + X_{\text{Ni}}(3X_{\text{Ni}} - 6X_{\text{O}} - 10X_{\text{Ni}}X_{\text{O}} - 10X_{\text{O}}^2)^1\Omega_{\text{Ni-O}} \\
& + (3X_{\text{Al}} + 2X_{\text{O}} - 5X_{\text{Al}}X_{\text{O}})^0\Omega_{\text{Al-O}} \quad [8]
\end{aligned}$$

All parameters in Eq. [8] have been proposed by Miki and Hino^[9]. To evaluate the validity of their parameters, the calculated correlation between Al and O is shown in **Fig. 3** (Fe) and **Fig. 4** (Ni).

Figure 3 shows the Al deoxidation equilibrium in Fe at 1873 K. The Al-O curve of the present study (see the discussion in section 3.3.2) is obtained by using the Miki and Hino's formula^[9], whereas JSPS^[23] and Itoh *et al.*^[24] applied Wagner's formulas and Paek *et al.*^[21, 22] used the Short Range Ordering Model (SRO model). In the high Al region (Al > 1.0mass%) all calculated curves except the one of Paek *et al.*^[21, 22] deviate from the experimental data. Pelton *et al.*^[25] and Paek *et al.*^[21, 22] explained that due to the strong affinity between Al and O, the regular solution model (random mixing of components), which has been assumed for both the Wagner's^[1] and Miki and Hino's^[9] formulas, does not apply there. Although applying the SRO model as done by Paek *et al.*^[21, 22] gives a good agreement between calculation and experimental data, it is difficult to apply this model in refining practice due to its limitation of available temperature (1873 K) and composition (Fe-Al-O system). On the other hand, despite the deviation in the high Al region, Miki and Hino's^[9] calculation is in a good agreement with that of other researchers except for the results of Hilty & Crafts^[12] and Schenck *et al.*^[14] in the low Al region (Al < 0.5 mass%). Itoh *et al.*^[24] considered that the deviations in these two studies^[12, 14] were generated from uncertainties of temperature and oxygen measurements.

Figure 4 shows the Al-O correlation of the Al deoxidation equilibrium in Ni at 1823 to 1973 K in which the calculated curve by using Miki and Hino's parameters^[9] is compared to the experimental

data by Ishii & Banya^[26]. It is clear that the calculated curve doesn't agree with the experimental data^[26]. This indicates that the parameters proposed by Miki and Hino^[9] need to be modified to satisfy the experimental results in the full composition range of Fe-Ni alloys. To identify which parameters need modification, the reliability of the applied interaction parameters by Miki and Hino was checked; $\Delta G_{f, Al_2O_3}^\circ$ was taken from NIST-JANAF Thermochemical Tables^[27]. The Fe-Ni interaction parameters (${}^0\Omega_{Fe-Ni}$ and ${}^1\Omega_{Fe-Ni}$) were taken from the Fe-Ni binary phase diagram^[28]. The Fe-O interaction parameters (${}^0\Omega_{Fe-O}$ and ${}^1\Omega_{Fe-O}$) were obtained from the Gibbs free energy change of oxygen dissolution into molten Fe^[23]. The Ni-O interaction parameters (${}^0\Omega_{Ni-O}$ and ${}^1\Omega_{Ni-O}$) were estimated from Si deoxidation equilibrium in Fe, Ni and Fe-Ni alloys^[2]. These 6 interaction parameters of the three binary systems (i.e. Fe-Ni, Fe-O and Ni-O) were also used in the study of Si deoxidation in Fe-Cr, Fe-Cr-Ni, Ni-Cu and Ni-Co alloys^[29] and their validity for the calculations was confirmed. On the other hand, the interaction parameters around Al (i.e. Fe-Al, Ni-Al and Al-O interactions) were obtained only from the Fe and Fe-Ni alloy. Since the calculation in Ni doesn't fit well with the experimental data (**Fig. 4**), interaction parameters around Al should be less reliable than the other interaction parameters. And there are also mathematical difficulties in the parameter determination in Miki and Hino^[9]. For example of ${}^0\Omega_{Ni-Al}$ and ${}^1\Omega_{Ni-Al}$ determination; Eq. [8] was converted into Eq. [9],

$$\begin{aligned}
& -\{-5X_{Fe}X_{Ni}{}^0\Omega_{Fe-Ni} - 10X_{Fe}X_{Ni}(X_{Fe} - X_{Ni}){}^1\Omega_{Fe-Ni} \\
& + X_{Fe}(2 - 5X_{Al}){}^0\Omega_{Fe-Al} + X_{Fe}(2X_{Fe} - 4X_{Al} - 10X_{Fe}X_{Al} + 10X_{Al}^2){}^1\Omega_{Fe-Al} \\
& + X_{Fe}(3 - 5X_O){}^0\Omega_{Fe-O} + X_{Fe}(3X_{Fe} - 6X_O - 10X_{Fe}X_O + 10X_O^2){}^1\Omega_{Fe-O} \\
& + X_{Ni}(3 - 5X_O){}^0\Omega_{Ni-O} + X_{Ni}(3X_{Ni} - 6X_O - 10X_{Ni}X_O - 10X_O^2){}^1\Omega_{Ni-O} \\
& + (3X_{Al} + 2X_O - 5X_{Al}X_O){}^0\Omega_{Al-O} \\
& + 2RT \ln X_{Al} + 3RT \ln X_O - \Delta G_{Al_2O_3}^\circ\} / X_{Ni}(2 - 5X_{Al}) \\
& = {}^0\Omega_{Ni-Al} + \frac{(2X_{Ni} - 4X_{Al} - 10X_{Ni}X_{Al} + 10X_{Al}^2){}^1\Omega_{Ni-Al}}{(2 - 5X_{Al})} \quad [9]
\end{aligned}$$

By defining the left side of Eq. [9] as Y_{Ni-Al} and the coefficient term of ${}^1\Omega_{Ni-Al}$ as X_{Ni-Al} , Eq. [9] can

be simplified to Eq. [10].

$$Y_{\text{Ni-Al}} = {}^0\Omega_{\text{Ni-Al}} + X_{\text{Ni-Al}} {}^1\Omega_{\text{Ni-Al}} \quad [10]$$

Then, using experimental data and known parameters and taking $Y_{\text{Ni-Al}}$ as a vertical axis and $X_{\text{Ni-Al}}$ as a horizontal axis, ${}^0\Omega_{\text{Ni-Al}}$ and ${}^1\Omega_{\text{Ni-Al}}$ can be determined, respectively as the intercept and the slope of the regression line. Since $X_{\text{Ni-Al}}$ is approximately equal to X_{Ni} in the low Al content range, ${}^0\Omega_{\text{Ni-Al}}$ means a value of $Y_{\text{Ni-Al}}$ at Fe ($X_{\text{Ni}}=0$). Since $Y_{\text{Ni-Al}}$ contains a term with the inverse of X_{Ni} (see Eq. [9]), a small error in experimental data will result in a large deviation in $Y_{\text{Ni-Al}}$ at low X_{Ni} region ($X_{\text{Ni}} \rightarrow 0$). Therefore, it is difficult to mathematically obtain reliable parameters in this way. In addition, this linear regression method can't be applied for the determination of higher order interaction parameters. This is because with higher order interaction parameters it can't be expressed by linear line anymore. Therefore, modified interaction parameters of Fe-Al, Ni-Al and Al-O for a correct description of the Al deoxidation of Fe-Ni alloy during solidification for large ingots are proposed in the next section.

3.3.2. Determination of Fe-Al, Ni-Al and Al-O interaction parameters

In the present study, the interaction parameters of the Al deoxidation equilibrium have been determined from the apparent equilibrium constant ($\log K'$) in Fe-Ni alloys. It is well known that the deoxidation reaction product of the Al deoxidation equilibrium is a constant value at low Al content range (Al < 0.5 mass%) , where there is a linear relation between Al and O contents and the apparent deoxidation constant is function of temperature and alloy composition.

Figure 5 shows the apparent equilibrium constant ($\log K'$) of the Al deoxidation equilibrium in Fe-Ni alloy, where the apparent equilibrium constant in Fe ($\log K'_{\text{Fe}}$) and that in Ni ($\log K'_{\text{Ni}}$) are adopted from the work of Seo *et al.*^[19] and Ishii *et al.*^[26].

$$\log K'_{\text{Fe}} = 12.32 - 47400 / T \quad [19] \quad [11]$$

$$\log K'_{\text{Ni}} = 1.67 - 28770 / T \quad [26] \quad [12]$$

By fitting the apparent equilibrium constants for Fe and Ni, respectively through Eqs. [11] and [12],

with the ones calculated from experimental data for Fe-Ni alloys, the $\log K'$ in the full range of Fe-Ni alloy from 1773 to 1973 K is estimated as the dot lines in **Fig. 5**. There is a maximum $\log K'$ value around 50 to 60 mass%Ni at each of the equilibrium temperatures. Although deoxidation products are gradually increasing with Ni content in the lower Ni region, it drops around 80 mass% Ni.

Since X_{Al} and X_O are small enough in the region where the Al and O content have a linear relation, the standard equation of the Al deoxidation equilibrium in the Fe-Ni-Al-O system (Eq. [8]) can be simplified to Eq. [13] by eliminating X_{Al} and X_O and by replacing X_{Fe} by $(1-X_{Ni})$.

$$\begin{aligned} & RT \ln X_{Al}^2 \cdot X_O^3 - \Delta G_{FeAl_2O_3}^\circ \\ & - 5(1 - X_{Ni})X_{Ni}^0 \Omega_{Fe-Ni} - 10X_{Ni}(1 - X_{Ni})^1 \Omega_{Fe-Ni} \\ & = -2(1 - X_{Ni})^0 \Omega_{Fe-Al} - 2(1 - X_{Ni})^2 \Omega_{Fe-Al} - 3(1 - X_{Ni})^0 \Omega_{Fe-O} - 3(1 - X_{Ni})^2 \Omega_{Fe-O} \\ & - 2X_{Ni}^0 \Omega_{Ni-Al} - 2X_{Ni}^2 \Omega_{Ni-Al} - 3X_{Ni}^0 \Omega_{Ni-O} - 3X_{Ni}^2 \Omega_{Ni-O} \end{aligned} \quad [13]$$

The deoxidation product in mole fraction ($\ln X_{Al}^2 X_O^3$) can be expressed by Eq. [14] using $\log K'$ in the low Al and O content region:

$$\ln X_{Al}^2 \cdot X_O^3 = 2.303 \log K' - \ln M_{Al}^2 \cdot M_O^3 + 5 \ln \left(\frac{100 - [\%Ni]}{M_{Fe}} + \frac{[\%Ni]}{M_{Ni}} \right) \quad [14]$$

As defining the left side of Eq. [13] as F , F consists then of $\log K'$, Ni content, temperature and known parameters ($\Delta G_{FeAl_2O_3}^\circ$, $^0 \Omega_{Fe-Ni}$ and $^1 \Omega_{Fe-Ni}$). **Fig 6** shows a plot of the left side of Eq. [13] (i.e. F) against X_{Ni} , using the estimated values of $\log K'$ for Fe-Ni alloy at 1773 to 1973 K from **Fig. 5**. The asymmetry in the F curves resembles the asymmetry in the $\log K'$ curves. However, the right side of Eq. [13] which consists of X_{Ni} and first and second order interaction parameters (Fe-Al, Fe-O, Ni-Al and Ni-O) is a quadratic function with X_{Ni} as a variable. As asymmetric curves for F can't be expressed by a quadric function of X_{Ni} , the higher order interactions should be considered in this system.

As mentioned in section 3.3.1, the interaction parameters of Fe-O and Ni-O have been confirmed to be reliable to describe the Si deoxidation in many systems^[29]. Due to the fact that the F - X_{Ni} relation (see **Fig.6**) greatly changes in the high Ni region, where the Ni-Al interaction is stronger than the Fe-Al interaction, the third order Ni-Al interaction is considered in the present study. By introducing the

third order Ni-Al interaction parameter (${}^2\Omega_{\text{Ni-Al}}$), Eqs. [8] and [13] are changed into Eqs. [15] and [16] respectively.

$$\begin{aligned}
& -5X_{\text{Fe}}X_{\text{Ni}}{}^0\Omega_{\text{Fe-Ni}} - 10X_{\text{Fe}}X_{\text{Ni}}(X_{\text{Fe}} - X_{\text{Ni}}){}^1\Omega_{\text{Fe-Ni}} \\
& + X_{\text{Fe}}(2 - 5X_{\text{Al}}){}^0\Omega_{\text{Fe-Al}} + X_{\text{Fe}}(2X_{\text{Fe}} - 4X_{\text{Al}} - 10X_{\text{Fe}}X_{\text{Al}} + 10X_{\text{Al}}^2){}^1\Omega_{\text{Fe-Al}} \\
& + X_{\text{Fe}}(3 - 5X_{\text{O}}){}^0\Omega_{\text{Fe-O}} + X_{\text{Fe}}(3X_{\text{Fe}} - 6X_{\text{O}} - 10X_{\text{Fe}}X_{\text{O}} + 10X_{\text{O}}^2){}^1\Omega_{\text{Fe-O}} \\
& + X_{\text{Ni}}(2 - 5X_{\text{Al}}){}^0\Omega_{\text{Ni-Al}} + X_{\text{Ni}}(2X_{\text{Ni}} - 4X_{\text{Al}} - 10X_{\text{Ni}}X_{\text{Al}} + 10X_{\text{Al}}^2){}^1\Omega_{\text{Ni-Al}} \\
& + X_{\text{Ni}}(X_{\text{Ni}} - X_{\text{Al}})(2X_{\text{Ni}} - 6X_{\text{Al}} - 15X_{\text{Ni}}X_{\text{Al}} + 15X_{\text{Al}}^2){}^2\Omega_{\text{Ni-Al}} \\
& + X_{\text{Ni}}(3 - 5X_{\text{O}}){}^0\Omega_{\text{Ni-O}} + X_{\text{Ni}}(3X_{\text{Ni}} - 6X_{\text{O}} - 10X_{\text{Ni}}X_{\text{O}} - 10X_{\text{O}}^2){}^1\Omega_{\text{Ni-O}} \\
& + (3X_{\text{Al}} + 2X_{\text{O}} - 5X_{\text{Al}}X_{\text{O}}){}^0\Omega_{\text{Al-O}} \\
& + 2RT \ln X_{\text{Al}} + 3RT \ln X_{\text{O}} - \Delta G_{\text{fAl}_2\text{O}_3}^\circ = 0
\end{aligned} \tag{15}$$

$$\begin{aligned}
F = & -2(1 - X_{\text{Ni}}){}^0\Omega_{\text{Fe-Al}} - 2(1 - X_{\text{Ni}}){}^2{}^1\Omega_{\text{Fe-Al}} \\
& - 3(1 - X_{\text{Ni}}){}^0\Omega_{\text{Fe-O}} - 3(1 - X_{\text{Ni}}){}^2{}^1\Omega_{\text{Fe-O}} \\
& - 2X_{\text{Ni}}{}^0\Omega_{\text{Ni-Al}} - 2X_{\text{Ni}}{}^2{}^1\Omega_{\text{Ni-Al}} - 2X_{\text{Ni}}{}^3{}^2\Omega_{\text{Ni-Al}} \\
& - 3X_{\text{Ni}}{}^0\Omega_{\text{Ni-O}} - 3X_{\text{Ni}}{}^2{}^1\Omega_{\text{Ni-O}}
\end{aligned} \tag{16}$$

Equation [15] is the fundamental equation for the numerical analysis of Al deoxidation in Fe-Ni alloy with taking into account the third order interaction parameter of Ni-Al. From Eq. [16], at $X_{\text{Ni}}=0$, where the Ni-Al interaction terms are equal to zero, the Fe-Al interaction parameters can be obtained as:

$${}^0\Omega_{\text{Fe-Al}} = -291670 + 117.4T \tag{17}$$

$${}^1\Omega_{\text{Fe-Al}} = 85260 - 39.36T \tag{18}$$

By fitting the curves in **Fig.6** with a cubic function, F can be expressed as Eq. [19]

$$F = aX_{\text{Ni}}^3 + bX_{\text{Ni}}^2 + cX_{\text{Ni}} + d \tag{19}$$

Where, a, b, c and d are obtained respectively as Eqs. [20] to [23]

$$a = -2^2\Omega_{\text{Ni-Al}} \tag{20}$$

$$b = -2^1\Omega_{\text{Fe-Al}} - 3^1\Omega_{\text{Fe-O}} - 2^1\Omega_{\text{Ni-Al}} - 3^1\Omega_{\text{Ni-O}} \tag{21}$$

$$c = 2^0\Omega_{\text{Fe-Al}} + 4^1\Omega_{\text{Fe-Al}} + 3^0\Omega_{\text{Fe-O}} + 6^1\Omega_{\text{Fe-O}} - 2^1\Omega_{\text{Ni-Al}} - 3^1\Omega_{\text{Ni-O}} \tag{22}$$

$$d = -2(^0\Omega_{\text{Fe-Al}} + ^1\Omega_{\text{Fe-Al}}) - 3(^0\Omega_{\text{Fe-O}} + ^1\Omega_{\text{Fe-O}}) \quad [23]$$

From Eqs. [20] to [23], the Ni-Al interaction parameters have been determined to be:

$$^0\Omega_{\text{Ni-Al}} = 11790 - 30.0T \quad [24]$$

$$^1\Omega_{\text{Ni-Al}} = -526800 + 163.8T \quad [25]$$

$$^2\Omega_{\text{Ni-Al}} = 101730 + 15.2T \quad [26]$$

Moreover, by rearranging Eq. [15], the first order interaction parameter of Al-O can be determined through Eq. [27]:

$$\begin{aligned} Y_{\text{Al-O}} &= 2RT \ln X_{\text{Al}} + 3RT \ln X_{\text{O}} - \Delta G_{\text{fAl}_2\text{O}_3}^{\circ} \\ &- 5X_{\text{Fe}}X_{\text{Ni}}^0\Omega_{\text{Fe-Ni}} - 10X_{\text{Fe}}X_{\text{Ni}}(X_{\text{Fe}} - X_{\text{Ni}})^1\Omega_{\text{Fe-Ni}} \\ &+ X_{\text{Fe}}(2 - 5X_{\text{Al}})^0\Omega_{\text{Fe-Al}} + X_{\text{Fe}}(2X_{\text{Fe}} - 4X_{\text{Al}} - 10X_{\text{Fe}}X_{\text{Al}} + 10X_{\text{Al}}^2)^1\Omega_{\text{Fe-Al}} \\ &+ X_{\text{Fe}}(3 - 5X_{\text{O}})^0\Omega_{\text{Fe-O}} + X_{\text{Fe}}(3X_{\text{Fe}} - 6X_{\text{O}} - 10X_{\text{Fe}}X_{\text{O}} + 10X_{\text{O}}^2)^1\Omega_{\text{Fe-O}} \\ &+ X_{\text{Ni}}(2 - 5X_{\text{Al}})^0\Omega_{\text{Ni-Al}} + X_{\text{Ni}}(2X_{\text{Ni}} - 4X_{\text{Al}} - 10X_{\text{Ni}}X_{\text{Al}} + 10X_{\text{Al}}^2)^1\Omega_{\text{Ni-Al}} \\ &+ X_{\text{Ni}}(X_{\text{Ni}} - X_{\text{Al}})(2X_{\text{Ni}} - 6X_{\text{Al}} - 15X_{\text{Ni}}X_{\text{Al}} + 15X_{\text{Al}}^2)^2\Omega_{\text{Ni-Al}} \\ &+ X_{\text{Ni}}(3 - 5X_{\text{O}})^0\Omega_{\text{Ni-O}} + X_{\text{Ni}}(3X_{\text{Ni}} - 6X_{\text{O}} - 10X_{\text{Ni}}X_{\text{O}} - 10X_{\text{O}}^2)^1\Omega_{\text{Ni-O}} \\ &= -(3X_{\text{Al}} + 2X_{\text{O}} - 5X_{\text{Al}}X_{\text{O}})^0\Omega_{\text{Al-O}} \quad [27] \end{aligned}$$

Taking $Y_{\text{Al-O}}$ on the vertical axis and $-(3X_{\text{Al}} + 2X_{\text{O}} - 5X_{\text{Al}}X_{\text{O}})$ on the horizontal axis, $^0\Omega_{\text{Al-O}}$ was obtained as the slope of the regression line through multiple $Y_{\text{Al-O}} - (3X_{\text{Al}} + 2X_{\text{O}} - 5X_{\text{Al}}X_{\text{O}})$ data points in **Fig. 7**. Comparison with the previous Al-O interaction parameter^[9] determined only from the data of Fe, the newly determined Al-O interaction in this study is believed to be more reliable as the parameter ($^0\Omega_{\text{Al-O}}$) was determined from a comprehensive experimental data of Fe, Ni and Fe-Ni alloy.

3.3.3 Al-O correlation

By using the newly determined interaction parameters of Fe-Al, Ni-Al and Al-O in this work, the Al-O correlation of the Al deoxidation equilibrium in Fe-Ni alloy can be thermodynamically predicted by Miki and Hino's formula considering the third order interaction parameters of Ni-Al (i.e. Eq. [15]). The interaction parameters and Gibbs free energy of Al_2O_3 formation ($\Delta G_{\text{f,Al}_2\text{O}_3}^{\circ}$) employed for the Al-

O equilibrium calculation in this study is summarized in **Table 3**. The calculated results of the Al-O correlation in the Al deoxidation equilibrium are shown in **Fig. 3** (Fe at 1873 K), **Fig. 8** (Fe-36 to 46 mass%Ni alloy at 1773 and 1873 K) and **Fig. 9** (Ni at 1773 to 1973 K), respectively. In case of Fe (**Fig. 3**), the present calculation on Al-O equilibrium correlation is similar to that of Miki & Hino^[9] and it is in a good agreement with experimental data in the low Al region ($Al < 0.5$ mass%), where the liquid metal can be considered as a regular solution. As shown in **Fig 8**, for the Al deoxidation equilibrium in Fe-36 to 46 mass%Ni the present calculation agrees well with the measured result even in the low oxygen region. This confirms that the dissolved oxygen determination (in this work) by combination of the total oxygen measurement and inclusion analysis is not only precise but also reliable. It is clear that in **Fig. 9**, the Al deoxidation equilibrium in Ni is precisely calculated by using the parameters determined in this study. As compared to **Fig. 4**, it is notable that the newly determined parameters in this study greatly improved the calculation validity in the high Ni region (see **Fig. 9**). **Fig. 10** shows as an example the Al-O correlation of the deoxidation equilibrium in the complete composition range of Fe-Ni alloys at 1873 K. By using the parameters in **Table 3** and Eq. [15], the Al-O correlation in the temperature range of 1773 to 1973K can be predicted. This meets the need to describe the Al deoxidation reactions during solidification of large ingots, thereby enabling the quality control of the casted ingots.

4. Conclusion

The Al deoxidation equilibrium in molten Fe-Ni alloy was experimentally determined at 1773 and 1873 K. The dissolved oxygen in the metal samples was determined from the total oxygen content (LECO) and the undissolved oxygen content determined from SEM-EDS inclusion analysis. The Al deoxidation equilibrium was expressed by using the Redlich-Kister type polynomial with up to the third order interaction parameters of Ni-Al. The interaction parameters were determined by the measured deoxidation product in the complete composition range of Fe-Ni alloys from 1773 to 1973 K.

$$\begin{aligned}
& {}^0\Omega_{\text{Fe-Al}} = -291670 + 117.4T \\
& {}^1\Omega_{\text{Fe-Al}} = 85260 - 39.36T \\
& {}^0\Omega_{\text{Ni-Al}} = 11790 - 30.0T \\
& {}^1\Omega_{\text{Ni-Al}} = -526800 + 163.8T \\
& {}^2\Omega_{\text{Ni-Al}} = 101730 + 15.2T \\
& {}^0\Omega_{\text{Al-O}} = -6739250 + 2250T \\
& (1773K \leq T \leq 1973K, 0 \leq X_{\text{Al}} \leq 0.02)
\end{aligned}$$

By using the interaction parameters obtained in this work, the Al deoxidation equilibrium can be described with high accuracy in the complete composition range of Fe-Ni alloys at temperatures from 1773 to 1973 K.

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References

1. C. Wagner: Thermodynamics of Alloys, Addison-Wesley Press, Cambridge, MA, 1952.
2. T. Miki and M. Hino: *ISIJ Int.*, **44**(2004), 1800.
3. L. S. Darken: *Trans. Met. Soc. AIME*, **239**(1967), 80.
4. L. S. Darken: *Trans. Met. Soc. AIME*, **239**(1967), 90.
5. M. Hillert and L. -I. Staffanson; *Acta Chem. Scand.*, **24**(1970), 3618.
6. N. Saunders and A. P. Miodownik: Calphad(Calculation of Phase Diagrams), A Comprehensive Guide, Pergamon, Oxford, 1988.
7. S. B. Lee, S. M. Jung, H. G. Lee and C. H. Rhee: *ISIJ Int.*, **42**(2002), 679.
8. R.T. DeHoff and F. N. Rhines: Quantitative Microscopy, McGraw-Hill Publishing Co. Ltd., New York, (1968)
9. A. Hayashi, T. Uenishi, H. Kandori. T. Miki and M. Hino: *ISIJ Int.*, **48**(2008), 1533.
10. H. Ohta and H. Suito: *ISIJ Int.*, **43**(2003), 1301.
11. H. Fujiwara, A. Hattori and E. Ichise: *Tetsu-to-Hagané*, **85**(1999), 201.
12. D. C. Hilty and W. Crafts: *J. Met.*, **2**(1950), 414.
13. R. J. Fruehan: *Metall. Trans.*, **1**(1970), 34031
14. H. Schenck, E. Steinmetz and K. K. Mehta: *Arch. Eisenhüttenwes.*, **41**(1970), 131.
15. L. E. Rohde, A. Choudhury and M. Wahlster: *Arch. Eisenhüttenwes.*, **42**(1971), 165.
16. D. Janke and W. A. Fischer: *Arch. Eisenhüttenwes.*, **46**(1975), 297.
17. H. Suito, H. Inoue and R. Inoue: *ISIJ Int.*, **31**(1991), 1381
18. S. Dimirov, A. Weyl and D. Janke: *Steel Res.*, **66**(1995), 3.
19. J. D. Seo, S. H. Kim and K. R. Lee: *Steel Res.*, **69**(1998), 49.
20. Y. Kang, M. Thunman, D. Sichen, T. Morohoshi, K. Mizukami and K. Morita: *ISIJ Int.*, **49**(2009),
21. M. K. Paek, J. M. Jang, Y. B. Kang and J. J. Pak: *Metall.Mater.Trans.B.*, **46B**(2015), 1826.
22. M. K. Paek, J. J. Pak and Y. B. Kang: *Metall.Mater.Trans.B.*, **46B**(2015), 2224.
23. The Japan Society for Promotion of Science The 19th Committee in Steelmaking: Steelmaking

- 1 Data Sourcebook, Gordon and Breach Science Publishers, New York, (1988).
- 2 24. H. Itoh, M. Hino and S. Ban-ya: *Tetsu-to-Hagane*, 83(1997), 773.
- 3 25. I. H. Jung, S. A. Decterov and A. D. Pelton: *Metall.Mater.Trans.B*, **35B**(2004), 493.
- 4 26. F. Ishii, S. Ban-ya and M. Hino: *ISIJ Int.*, **36**(1996), 25.
- 5 27. NIST-JANAF Thermochemical Tables, 4th ed., ed. by M. W. Chase, Jr., J. Phys. Chem. Ref. Data,
- 6 (1998).
- 7 28. B. -J. Lee: *Calphad*, 17(1993), 251.
- 8 29. T. Miki and M. Hino: *ISIJ Int.*, **45**(2005), 1848.
- 9 30. S.W.Cho and H.Suito: *Steel Res.*, **66**(1995)6, 237
- 10 31. K. Kobayashi, Y. Omori and K. Sanbongi: *Tetsu-to-Hagané*, **53**(1967), 141.

1 **Tables**

2 **Table 1.** Average composition of the detected inclusions by Auto SEM-EDS analysis.

3 **Table 2.** Experimental results.

4 **Table 3.** Lists of thermodynamic data from literature and those determined in this study.

5

6 **Figures**

7 **Figure 1.** Schematic diagram of experimental apparatus and quenched sample: (a) experimental
8 apparatus, (b) vertical section of quenched sample, (c) horizontal section at 5mm from the bottom of
9 the sample.

10 **Figure 2.** Experimental results and Al deoxidation equilibrium in Fe-36 to 46%Ni.

11 **Figure 3.** Al deoxidation equilibrium in Fe at 1873 K.

12 **Figure 4.** Al deoxidation equilibrium in Ni at 1823 to 1973 K.

13 **Figure 5.** Apparent equilibrium constant ($\log K'$) of Al deoxidation in Fe-Ni alloy.

14 **Figure 6.** F curves against X_{Ni} at 1773 to 1973 K.

15 **Figure 7.** Determination of Al-O interaction parameter.

16 **Figure 8.** Calculation of Al deoxidation equilibrium in Fe-36 to 46%Ni.

17 **Figure 9.** Calculation of Al deoxidation equilibrium in Ni at 1823 to 1973 K.

18 **Figure 10.** Calculation of Al deoxidation equilibrium in Fe-Ni alloy at 1873 K.