A Thermodynamic Study on the Inclusion Formation in Ferritic Stainless Steel Melt

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A type 430 stainless steel melt containing different Al levels was equilibrated with an AOD type slag saturated with Al2O3 or MgO to clarify the formation mechanism of slag-type inclusions containing MgO·Al2O3 spinel. The Al–O deoxidation equilibrium in the stainless steel melt was examined as a function of melt temperature to check the validity of available thermodynamic data, and to estimate the secondary deoxidation by Al picked up from the ladle slag. During the temperature drop from AOD to tundish, a small amount of entrapped AOD slag particles in molten steel can easily change their composition to a level where the MgO·Al2O3 spinel can crystallize. The refractory material, MgO or Al2O3 for a ladle, is one of critical factors to affect the Al level in the melt, and hence the formation of MgO·Al2O3 spinel inclusions in the final products.

KEY WORDS: stainless steel; inclusion; MgO·Al2O3 spinel; secondary deoxidation; AOD slag.

1. Introduction

Recently there has been an increased demand for low carbon ferritic stainless steels due to their high performance in various applications at low production cost. However, the surface quality of ferritic stainless steels is very susceptible to non-metallic inclusions such as high melting point MgO·Al2O3 spinel crystallized in a slag-type inclusion as shown in Fig. 1. These inclusions are the major causes for inclusion line defects on both hot and cold rolled stainless steel sheets.1)

For the production technology of clean ferritic stainless steels, it is important to know the origin and the formation mechanism of these non-metallic inclusions. In practice, the AOD stainless steelmaking process has a feature of tapping with slag, since there is no extra tapping hole in an AOD refining vessel. Therefore, some amount of slag particles can be entrapped in liquid steel, and they can provide the nucleation sites for the secondary deoxidation of Al with the decrease in molten steel temperature. This hypothesis can be confirmed by the close agreement between the compositions of AOD slag and inclusions in terms of CaO and SiO2 contents. Also, the Al2O3 content in inclusions found in the solidified steel product is high enough to form MgO·Al2O3 spinel phase despite the Al content in steel is very low.

In the present study, a small amount of AOD-type slag was reacted with a type 430 stainless steel melt containing different Al levels to see how the slag composition changes by the reaction with Al. The equilibrium relations between Al and O contents in the stainless steel melt were examined as a function of Al2O3 activity in slag contained in an alumina or MgO crucible at different melt temperatures. A model calculation was performed to clarify the formation

Fig. 1. SEM image and EDS analysis of a slag-type inclusion in stainless steel.
mechanism of slag-type inclusions containing MgO · Al₂O₃ spinel during the temperature drop along the stainless steel-making process. The effect of refractory materials on how they affect the Al level in the melt and the MgO · Al₂O₃ spinel formation was discussed.

2. Experimental Procedure

In order to check the composition change of entrapped slag by the reaction with Al in the melt, a small amount of AOD-type slag was equilibrated with a type 430 stainless steel melt containing different Al contents. One hundred and fifty grams of Fe–16% Cr–0.5% Mn–0.3% Si–0.04% C alloy, supplied from POSCO research center, was melted by a high frequency induction furnace shown in Fig. 2. The induction coil was specially designed to give a strong agitation of the melt. Strong agitation of melt would result in a faster attainment of reaction equilibrium and a good separation of nonmetallic inclusions from the steel melt. A detailed description of the furnace is given in the previous article. After melting the metallic charge, pure Al (0.03 to 0.75 g) was added and 1 g of AOD-type slag with a composition of 44%CaO–49%SiO₂–7%MgO was dropped onto the steel melt. In some experiments, stoichiometric MgO · Al₂O₃ spinel powder (0.5 g) was used as an equilibrium oxide phase for the Al–O deoxidation reaction of the melt in MgO crucible. The method of obtaining stoichiometric MgO · Al₂O₃ spinel powder is described elsewhere. The slag and metal were equilibrated for 1 h in MgO or Al₂O₃ crucible under a deoxidized Ar atmosphere at 1 873 and 1 923 K.

After each experiment, the melt was quenched rapidly by helium gas blowing in the chamber. The quenched metal sample was cross-sectioned and examined with an optical microscope for the presence of nonmetallic inclusions. The center part of metal sample was virtually clean without any noticeable inclusions, and was used for the chemical analyses. The Al content in metal was analyzed by inductively coupled plasma (ICP) spectroscopy. The metallic sample (0.5 g) was dissolved in 30 mL of HCl(l + 1) in a glass tube of 50 mL capacity heated in a block heater at 353 K for 12 h. Water and acids used were ultra pure grades. After dissolving the sample, the solution was transferred to the measuring flask (50 mL) using ultra pure water with filtration. Virtually no residue was remained in the filter paper, and it was confirmed by the fusion method using ultra pure Na₂CO₃ for the analysis of acid-insoluble Al.

Figure 3 shows the ICP intensities for Al in standard solutions containing 0 to 1 000 mass ppb of Al. The standard solution also contains 8 400 mass ppm of Fe and 1 600 mass ppm of Cr in order to have the same condition as the sample solution. At a wavelength of 396.152 nm, the ICP intensity shows a perfect correlation with Al content. The accuracy of Al analysis in stainless steel sample was 5 ± 0.5 mass ppm. The oxygen content was measured with an accuracy of ±1 mass ppm by the inert gas fusion-infrared absorptiometry, using the standard steel sample containing 10 ± 1 mass ppm oxygen.

3. Results and Discussion

3.1. Aluminum Deoxidation Equilibria in a Type 430 Stainless Steel

Experimental results of the Al–O deoxidation equilibria for a type 430 stainless steel melt are summarized in Table 1. Under the present experimental condition, the oxygen content in the stainless steel melt would be controlled by Al in the melt and Al₂O₃ in slag. The deoxidation equilibria of Al can be expressed by following equations:

\[ Al₂O₃(s) = 2Al + 3O \]
\[ \Delta G^\circ_T = 1225000 - 393.8 T \text{ (J/mol)} \]
\[ K_{Al} = \frac{a_{Al}^{2} a_{O}^{3}}{a_{Al₂O₃}} = \frac{(f_{Al} [%Al])^{2}(f_{O} [%O])^{3}}{a_{Al₂O₃}} \]

where \( a_{Al} \) and \( a_{O} \) are the activities \( a_{Al} \) of Al and O, respec-
tively, and their standard states are their infinitely dilute solution in pure liquid iron.

When the activity coefficients, $f_i$ in Eq. (2), are expressed by Wagner’s relation using the first-order interaction parameters, the following relation can be derived using the apparent equilibrium constant, $K_{Al}$.

$$
\log K_{Al} = 2 \log a_{Al} + 3 \log a_{O} - 2 \log a_{Al_{2}O_3} = 2 \log (f_{Al} [\% Al]) + 3 \log (f_{O} [\% O]) - \log a_{Al_{2}O_3}
$$

$$
= \log K_{Al} + 2(e^{i Al} [\% Al] + \sum e^{i j} [\% j]) - \log a_{Al_{2}O_3} - \sum e^{i j} [\% j] \quad (3)
$$

where $i$ and $j$ represent the elements other than O and Al, respectively, such as Cr, Mn, Si and C.

The values of $e^{i j}$ used in this study are given in Table 2. Therefore, the equilibrium relation between Al and O contents in a type 430 stainless steel melt can be calculated from Eq. (3) as a function of $Al_{2}O_{3}$ activity. The curves in Fig. 4 are the equilibrium Al–O relations calculated for $Al_{2}O_{3}$ saturation ($a_{Al_{2}O_3} = 1$) at 1873 and 1923 K. The measured Al–O relations for the melt deoxidized by Al in $Al_{2}O_{3}$ crucibles are also shown, and they are in good agreement with the calculated lines. This indicates that the thermodynamic parameters used in the calculation are relevant, and the Al–O deoxidation equilibrium has been attained under the present experimental condition.

Figure 5 shows the compositional change of an AOD-type slag with an initial composition of 44%CaO–49%SiO$_2$–7%MgO added to a type 430 stainless steel melt containing different Al contents in MgO crucible at 1873 K. The final slags contained 12–18 mass%MgO, and their compositions were plotted in CaO–$Al_{2}O_{3}$–SiO$_2$–(–15%MgO) pseudo-ternary system. As the Al content increased in the melt, the slag composition changed from a low $Al_{2}O_{3}$ content to a high range where the slag can precipitate MgO·$Al_{2}O_{3}$ spinel. In order to consider the Al–O equilibrium relation in the melt saturated with MgO·$Al_{2}O_{3}$ spinel, the activity of $Al_{2}O_{3}$ should be known under this condition.

Fujii et al. determined the free energy of formation of MgO·$Al_{2}O_{3}$ spinel as Eq. (4), and they estimated the $Al_{2}O_{3}$

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### Table 1. Experimental results of Al deoxidation for a type 430 stainless steel melt.

| Test No. | Temp. K | Crucible | Metal | Slag |
|----------|---------|----------|-------|------|
|          |         |          | [Al]  | [Si] | [Mn] | [O]  | (CaO) | SiO$_2$ | Al$_2$O$_3$ | MgO |
| 1        | 1873    | Al$_2$O$_3$ | 0.0040 | 0.341 | 0.496 | 0.00470 | Al$_2$O$_3$ |
| 2        | 0.0069  | 0.335 | 0.501 | 0.00308 | Al$_2$O$_3$ |
| 3        | 0.0228  | 0.329 | 0.510 | 0.00150 | Al$_2$O$_3$ |
| 4        | 0.0832  | 0.332 | 0.509 | 0.00105 | Al$_2$O$_3$ |
| 5        | 0.0026  | 0.321 | 0.486 | 0.00173 | 42.2 | 43.3 | 2.1 | 12.4 |
| 6        | 0.0032  | 0.351 | 0.496 | 0.00166 | 41.2 | 40.2 | 3.1 | 15.5 |
| 7        | 0.0038  | 0.372 | 0.501 | 0.00092 | 41.7 | 37.5 | 8.3 | 12.5 |
| 8        | 0.0045  | 0.391 | 0.506 | 0.00135 | 39.2 | 29.9 | 18.5 | 12.4 |
| 9        | 0.0433  | 0.449 | 0.508 | 0.00035 | 35.7 | 4.1  | 41.8 | 18.4 |
| 10       | 0.0060  | 0.325 | 0.503 | 0.00651 | Al$_2$O$_3$ |
| 11       | 0.0200  | 0.318 | 0.498 | 0.00273 | Al$_2$O$_3$ |
| 12       | 0.0049  | 0.431 | 0.498 | 0.00212 | 37.1 | 25.8 | 20.6 | 16.5 |
| 13       | 0.0070  | 0.516 | 0.508 | 0.00163 | 36.1 | 17.5 | 28.9 | 17.5 |
| 14       | 0.0894  | 0.551 | 0.503 | 0.00035 | 36.1 | 3.1  | 46.4 | 14.4 |
| 15*      | 0.0185  | 0.327 | 0.493 | 0.00104 | MgO·Al$_2$O$_3$ |
| 16*      | 0.1221  | 0.331 | 0.507 | 0.00032 | MgO·Al$_2$O$_3$ |

* MgO·Al$_2$O$_3$, Added
** Average value of 5 measurements

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### Table 2. Interaction parameters of Al and O in liquid iron at 1873 K.

| $i$ | $j$ | $\epsilon^{i j}$ | Temperature Dependence |
|-----|-----|-------------------|------------------------|
| Al  | O   | -1.98             |                        |
| Al  | Mn  | 0.043             | 80.35/T                |
| Cr  | -   | 0.0123            |                        |
| Si  | 0.056 |                  |                        |
| C   | 0.091 |                  |                        |
| O   | Al  | -1.17             |                        |
| O   | Mn  | -0.174            | -1750/T+0.76           |
| Cr  | -0.052 |                | -3800/T+0.151         |
| Mn  | -0.021 |                  |                        |
| Si  | -0.066 |                |                        |
| C   | -0.421 |                |                        |
activity as 0.034 at the phase boundary of spinel with MgO at 1 873K as shown in Fig. 6.\(^6,7\)

\[
\text{MgO(s)} + \text{Al}_2\text{O}_3(s) = \text{MgO} \cdot \text{Al}_2\text{O}_3(s) \quad \cdots \cdots \quad (4)
\]

\[
\Delta G^\circ = -20 790 - 15.7 T \quad (J/mol)^6
\]

Figure 7 shows the equilibrium Al–O relations calculated for a type 430 stainless steel melt saturated with both MgO and MgO·Al₂O₃ spinel at 1 873 and 1 923 K. The measured Al–O relations by equilibrating the melt with a small amount of AOD-type slag in MgO crucibles are also shown. In some experiments at 1 923 K, MgO·Al₂O₃ spinel was added instead of AOD-type slag to insure its saturation of the melt. The measured Al–O relations in a type 430 stainless steel melt using an AOD-type slag or MgO·Al₂O₃ spinel show an excellent agreement with the calculated lines.
3.2. Mechanism of Inclusion Formation

Based on the above thermodynamic study on Al deoxidation equilibrium in a type 430 stainless steel melt, a model can be derived for predicting the composition change of AOD slag particles entrapped in the melt along the manufacturing route. The following assumptions can be made for the calculation:

1. Thermodynamic equilibrium exists between slag and molten steel.
2. Entrapped slag in molten steel provides the nucleation site for the secondary deoxidation of Al on cooling.
3. Deoxidation products are mixed completely with entrapped slag particles.
4. Entrapped slag particles are not removed during the steelmaking process.

For a model calculation, it is necessary to have information such as composition and weight of entrapped AOD slag and those of deoxidation products. In this calculation, the composition of entrapped slag is 55%CaO–30%SiO2–5%Al2O3–10%MgO, which is the average composition of AOD tapping slag. The weight of entrapped AOD slag in stainless steelmaking process is regarded as 65 to 100 g/ton-steel.1,8,9) In the present study, 80 g/ton-steel of entrapped slag was assumed.

Figure 8 shows the equilibrium relations of Al–O in a type 430 stainless steel melt for two different temperatures of 1 923 and 1 773 K at AOD tapping and tundish (T/D), respectively. If the ladle is lined with alumina, the top slag after AOD tapping would be readily saturated with Al2O310) and hence the steel melt would pick up a significant amount of Al from the slag. The oxygen content in stainless steel melt at AOD tapping is controlled by Si, and the level is about 65 ppm at 1 923 K.11) The equilibrium Al content at Al2O3 saturation is then about 53 ppm as shown in the figure. During the temperature drop of 150 K from AOD to tundish, Al would react with available O in the melt to form Al2O3 by the secondary deoxidation reaction. Using the mass balance and thermodynamics between Al and O, new equilibrium contents of Al and O can be calculated at 1 773 K as 12 ppm and 29 ppm, respectively as shown in Fig. 8.

If all of formed Al2O3 (77 ppm) is mixed with entrapped slag particles, the Al2O3 content in slag particles would increase significantly. When the amount of entrapped slag is regarded as 80 g/ton-steel, the calculation shows that the Al2O3 content increases from 5% up to 45% where the MgO·Al2O3 spinel can primarily crystallize in CaO–Al2O3–SiO2(–10%MgO) pseudo-ternary system as shown in Fig. 9. In general, the Al content in the melt would not readily reach the equilibrium level after the slag is saturated with alumina due to the kinetic factors. However, the calculated result assuming the equilibrium Al content of 53 ppm falls within the range of inclusion compositions observed in a type 430 stainless steel product treated in alumina ladle as shown in Fig. 9.

If the ladle is lined with MgO refractory, the activity of
Al₂O₃ in top slag would be low. For the composition of AOD tapping slag, the activity of Al₂O₃ is reported to be less than 0.01 at 1873 K. Assuming the Al₂O₃ activity as 0.01 at 1923 K, the equilibrium Al content is about 5.5 ppm at 65 ppm of O in the melt. The amount of Al₂O₃ formed by the secondary deoxidation would be well below the level where the formation of MgO·Al₂O₃ spinel can be considered as shown in Fig. 9. Therefore, the use of MgO refractory for ladle lining or at least at the slag line would help to keep Al level in the melt low during the secondary refining process.

In the present study, the effect of refractory, alumina or MgO, for ladle on the Al level in the stainless steel melt and hence the formation of MgO·Al₂O₃ spinel inclusions was studied. In actual processes, to avoid the formation of this high melting point spinel phase, it is also recommended to use Al-free ferro-alloys and to reduce MgO content in AOD slag.¹³

4. Conclusions

In the present study, the equilibrium relations between Al and O contents in a type 430 stainless steel melt were examined as functions of Al₂O₃ activity in slag and melt temperature. A model calculation was performed to clarify the composition change of entrapped slag particles during the temperature drop along the process. Aluminum pick up from the refractory or any other sources can increase the Al₂O₃ content in slag particles significantly to a level where MgO·Al₂O₃ spinel inclusion can form. The use of MgO refractory for ladle lining would help to keep Al level in the melt low during the process.

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