Technology for Production of Austenite Type Clean Stainless Steel

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We established the refining technology for cleanliness in regard to austenite type stainless steel. But immersion nozzle clogging in continuous casting occurred by formation of spinel (MgO–Al₂O₃) type inclusions in strong reduction refining for cleanliness. Therefore, we estimated the conditions for formation of spinel and it was possible to improve the castability while keeping cleanliness by controlling of inclusion compositions.

KEY WORDS: secondary refining; Si deoxidation; desulfurization; spinel inclusion; immersion nozzle clogging; magnesia inclusion; alumina inclusion.

1. Introduction

Austenitic clean stainless steel represented by SUS316L is used for semiconductor and automobile industry mainly, and high cleanliness and corrosion resistance are demanded.

However, the castability was prevented by build-up of MgO·Al₂O₃ (spinel) type inclusion on the inside wall of immersion nozzle, if high basicity slag was formed in refining for cleanliness.

The cause of formation of spinel type inclusion in spite of Si deoxidation was assumed that soluble Al and Mg in molten steel that supplied from ladle refractory and slag by strong reduction refining and alloy reduced conventional silicate type inclusions.

Generally, Ca treatment is carried out against immersion nozzle clogging. Most of enlarged inclusions, which made a low melting point by that, are removed by floating in tundish, but one part of them remains products, and it is unfavorable in a use of one.

Actually, when nozzle clogging occurred, most of inclusion compositions observed in billet were MgO·Al₂O₃ type, and MgO and Al₂O₃ partly.

Therefore, we estimated phase stability diagram about these oxides phases in order to confirm the conditions for formation of them in molten stainless steel and tried to improve nozzle clogging by avoiding formation of spinel type inclusions.

2. The Technology for Production of Clean Stainless Steel

2.1. Steelmaking Process

Figure 1 shows schematic of stainless steelmaking process in chita plant at Aichi Steel Co. Ltd. First, scrap and alloy are dissolved in 60t EAF, decarburization, desulfurization and denitrification are given in AOD furnace, subsequently. Next, slag refinement and adjustment of components and temperature of molten steel are given in ladle furnace, and ladle was transported to BT/CC process.

2.2. The Method of Secondary Refining for Cleanliness

Table 1 shows the factors for lowering [T.O] and [S] in secondary refining. Open and solid marks shows effective and more effective factors for them, respectively. Therefore, we investigated of the more effective factors shown as solid marks on deoxidation and desulfurization by exchanging the conditions for operation.

![Fig. 1. Schematic drawing of stainless steelmaking process.](image)

<table>
<thead>
<tr>
<th>Process</th>
<th>Operation factor</th>
<th>Low [T.O]</th>
<th>Low [S]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOD</td>
<td>Carbon reduction efficiency</td>
<td>![ ]</td>
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<tr>
<td></td>
<td>Slag composition</td>
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<tr>
<td></td>
<td>Flow rate of tuyere gas</td>
<td>![ ]</td>
<td>![ ]</td>
</tr>
<tr>
<td>LF</td>
<td>Treatment time</td>
<td>![ ]</td>
<td>![ ]</td>
</tr>
<tr>
<td></td>
<td>Flow rate of bottom blowing gas</td>
<td>![ ]</td>
<td>![ ]</td>
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<td></td>
<td>Slag composition</td>
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</tbody>
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2.2.1. Desulfurization

One of demand items is included high pitting corrosion resistance, so that low-sulfurization is required. Generally, the rate determining step for desulfurization reaction is considered as mass transfer to interface of slag/metal, and desulfurization reaction has been promoted by expansion of interface reaction area. In AOD, the refining with strong stirring is carried out by gas blowing of maximum 4000 Nm$^3$/h from tuyere. Therefore, desulfurization was promoted especially in AOD refining, and we investigated the influence of reduction slag on to the ratio of sulfur distribution ($[$%S$]/[$%S$]).

Figure 2 shows AOD operation pattern. There are two periods, and which are decarburization period and reduction one. In the former period decarburization and denitrrification were carried out, and in the latter period reduction of Cr oxide from slag and desulfurization. The molten steel, which was tapped from EAF, is charged into AOD furnace. Subsequently, decarburization and denitrification are carried out by blowing oxygen from top lance and oxygen and inert gas, which is N$_2$ or Ar, from tuyere while changing the ratio of them considering with carbon contents in molten steel. After carbon contents decreased to the target one, reduction refining was carried out by charging lime, fluorite and reducing agent.

Figure 3 shows the influence of SiO$_2$ activities, which were estimated by regular solution model based on AOD reduction slag compositions, on the ratio of sulfur distribution, Si content, and activities of oxygen estimated by them before tapping (in AOD). With lower SiO$_2$ activities, in other words, with higher basicity, Si yields raised and activities of oxygen decreased, as a result the ratio of sulfur distribution increased drastically. Therefore, we determined the target basicity of reduction slag considering with specification of Si contents in products and viscosity of slag.

2.2.2. Deoxidation

Deoxidation was promoted especially in LF refining, therefore, the influence of the factors shown in Table 1 on deoxidation was investigated.

(1) Treatment Time

Figure 4 shows the relationship between treatment time in LF and total oxygen content in billet. Only the data under the nearly same conditions except for treatment time were plotted. As that was prolonged, total oxygen content tended to decrease, but one did not decrease after about 60 min and saturated. Therefore, we determined the suitable treatment time in consideration of matching between LF and CC.

(2) Flow Rate of Bottom Blowing Gas

Now Ar bottom blowing is carried out by single porous. So as to investigate the influence of gas flow rate of bottom blowing, in other words stirring power, on fining of inclusions, the double porous test, in which gas flow rate was double, was carried out, and inclusion distribution was compared with that of conventional treatment by extreme statistic method. The result is shown in Fig. 5 under the same refining conditions except for gas flow rate. As shown in Fig. 5, it was confirmed that the inclination was higher and estimated maximum inclusion size reduced by strong stirring, and it was assumed that floatation of inclusion were promoted. But, when the gas flow rate is extremely high, entrapment of top slag and non-stabilization of arc power rate could be occurred. Therefore, the suitable flow rate must be selected.

(3) Basicity of Slag

Figure 6 shows the results investigated the influence of the basicity of LF slag on total oxygen content, a difference of mark shows that gas flow rate and steel grade. With higher basicity, total oxygen content decreased, but over about 4.0 basicity total oxygen content tended to increase. That was deterioration of deoxidation ability of top slag itself, because the slag viscosity was increased by formation...
of high basicity slag. Therefore, it shows that there is most suitable slag basicity.

2.2.3. Changes of Total Oxygen Content and Sulfur Content in Improved Refining Process

Figure 7 shows the changes of total oxygen content and sulfur content in refining comparing improvement mentioned above with conventional in AOD and LF operation. In AOD, deoxidation and desulfurization with slag were promoted by rising Si yield and high basicity. In particular, sulfur content achieved less than 10 ppm. In LF, total oxygen content was decreased to 10 ppm by improved method for inclusion removal, especially adjusting the slag composition and rinsing gas flow rate most suitable.

3. Immersion Nozzle Clogging by Formation of Spinel Type Inclusion in Billet Casting

3.1. The Influence of LF Slag Composition on Inclusion Composition.

Inclusion compositions observed in conventional refining is SiO₂–Al₂O₃–MnO type mainly. Figure 8 shows that the relationship between inclusion compositions observed in billet and basicity of LF slag. With increase of basicity, the concentration of Al₂O₃ and MgO increased and the concentration of SiO₂ and MnO decreased. That is to say, soluble Al and Mg eluted from ladle refractory and high basicity slag reduced silicate type inclusions. If the target basicity is more than 3.0, as shown in Fig. 6, it is estimated that spinel type inclusions is formed naturally. As a result, immersion nozzle clogging and falling-off occurred. In a use of products, the castability must be improved surely.

3.2. Control of Inclusion Composition Based on Phase Stability Diagram

Most of inclusion compositions observed in billet, which was refined for cleanliness, were MgO·Al₂O₃ type, and MgO and Al₂O₃ were observed partly. Therefore, we estimated phase stability diagram about these oxide phases in order to confirm the conditions for formation of them in SUS304 type molten steel with the use of the following equations,

\[
\log K_1 = \log \left( \frac{a_{MgO} \cdot a_{AlO_3}}{a_{Mg} \cdot a_{O}} \right) = 980/T - 0.336
\]

\[
\log K_2 = \log \left( \frac{a_{MgO}}{a_{Mg} \cdot a_{O}} \right) = 38060/T - 12.457
\]

\[
\log K_3 = \log \left( \frac{a_{AlO_3}}{a_{Al}^2 \cdot a_{O}} \right) = 62790/T - 20.187
\]

\[
\text{MgO (s)} + \text{Al}_2\text{O}_3 (s) = \text{MgO} \cdot \text{Al}_2\text{O}_3 (s) \quad \text{........... (1)}
\]

\[
\text{Mg} + \text{O} = \text{MgO (s)} \quad \text{........... (2)}
\]

\[
2\text{Al} + 3\text{O} = \text{Al}_2\text{O}_3 (s) \quad \text{........... (3)}
\]
Where are \( a_{\text{Mg}} \), \( a_{\text{Al}} \) and \( a_{\text{O}} \) are the activities of magnesium, aluminium, and oxygen in molten steel, and their standard states are their infinitude dilute solution. The activities of spinel oxide, \( a_{\text{MgO}} \cdot \text{Al}_2\text{O}_3 \) at MgO and Al\(_2\)O\(_3\) saturated states were used at 1 873 K as 0.80\(^5\) and 0.47\(^5\) respectively. The thermodynamic interaction parameters between Al, Mg and O in molten steel\(^{7,9}\) used for calculation were shown in Table 2, and that between another elements were refered to the other references\(^{7,10–13}\) and the boundary lines of each phase were calculated with the use [mass\%O] as a parameter. The result calculated and observed inclusion in billet were shown with other’s result\(^{14}\) studied in the nearly same system in Fig. 9. In the region of below 10 mass ppm Al, which is conventional refining states, there are SiO\(_2\)-MnO oxides inclusions only\(^{14}\) which was not observed in refining for cleanliness. As shown in Fig. 9, it was found that spinel type inclusion was formed easely under the condition of a very small amount of Al and Mg content, as reported in other studies\(^{3,15,16}\). In addition, the spinel inclusion can be changed into MgO, which is non-spinel, by controlling of soluble Al content and Mg content in molten steel.

### 3.3. The Control Method of Soluble Al Content in Molten Steel

As shown in Fig. 9, in order to form MgO, inhibiting elution of Al and promoting elution of Mg were carried out. The ladle refractory, LF slag and alloy are considered as a source of supply of Al. Therefore, we tried to inhibit for eluting of Al from them in refining process by removing a source of Al as much as possible. Table 3 shows comparison between conventional and improved refining. As for the ladle refractory, Dolomite, which is Al free and elutes much amount of Mg\(^{15}\) was adopted. Fe-Si alloy with low Al content, which is used as reducing agent in AOD mainly and is used for adjustment of components of molten steel in LF, was adopted. As a result, Al\(_2\)O\(_3\) content in LF slag was less than 2 mass%.

### 4. Result

#### 4.1. Castability

Refining for cleanliness, which was the controlling soluble

![Fig. 10. Inclusion shapes in polishing section and immersion nozzle after use.](image-url)
Al content and Mg content in molten steel were carried out. Figure 10 shows inclusion shapes in polished section of billet and immersion nozzle after use. The most of inclusions were produced as pure MgO as a result of promoting to elute of Mg and to supply Mg to inclusion and it was possible that there were not deposits at all by improvement refining. As a result, nozzle clogging and falling-off did not occurred.

4.2. Cleanliness

Figures 11, 12 show total oxygen content, degree of cleanliness (JIS) and the result of evaluated maximum inclusion size by extreme statistic as comparison between conventional and improved refining. It was possible that cleanliness was improved considerably, while inhibiting nozzle clogging, and inclusion was also fined in comparison with conventional by promotion of removing inclusions and change SiO₂ type into MgO.

5. Conclusion

The method of secondary refining for cleanliness was examined in austenite type molten stainless steel, and the effect for cleanliness was confirmed in improved refining, as explained above. In addition, the conditions of forming spinel type inclusion were examined to improve castability, and it was found that the control of soluble Al content and Mg content in molten steel was important for inhibiting nozzle clogging. As a result, we established the technology for producing clean stainless steel stably.

REFERENCES

13) Q. Han: Proc. 6th Int. Iron and Steel Cong., Vol. 1, ISIJ, Tokyo, (1990), 166.