Optimization of the AOD Process at POSCO

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In order to meet the increased demand for stainless steel on the domestic market, POSCO produces 380 kt of stainless steel annually by the EAF-AOD-continuous casting process. A 90 t AOD converter with a top oxygen lance and five side tuyères was put into operation in April 1989 at Pohang Works. Some plant tests were carried out to find the optimum operational conditions for the production of type SUS304 steel. The first test was run to optimize the number of decarburization steps and the target carbon content corresponding to a given oxygen/inert gas ratio at each decarburization step. The second test was to establish the effect of slag composition on the efficiency of the chromium oxide reduction and desulphurization during the reduction period.

It was necessary to divide the decarburization period into 5 steps in order to maximize the decarburization rate without causing excessive oxidation of the chromium. The efficiencies of chromium oxide reduction and the desulphurization were improved as the slag basicity, the silicon content of the melt, and the temperature were increased. To optimize both the chromium oxide reduction and the desulphurization, the slag basicity should be >2.0. The silicon content of the melt should be >0.4 wt per cent and the temperature of the melt should be higher than 1670°C. Based on the test results, a modified process was adopted, and a substantial decrease in operating time and operating cost was achieved.

Introduction

In order to meet the rapidly increasing demand for stainless steel on the domestic market, as shown in Figure 1, POSCO decided to install a 90 t capacity AOD converter at Pohang Works. After a construction period of 24 months, the AOD converter was successfully put into operation in April 1989. It is designed to produce 380 kt of slabs and blooms annually by the route of EAF-AOD-continuous casting as shown in Figure 2. Table 1 shows the product mix of stainless steel at POSCO.

For an AOD process, three factors are of decided importance for the determination of production costs:
(1) cost of charging materials
(2) cost of the refractories of the vessel
(3) operation time (tap-to-tap time).

For example, the cost of alloys can be reduced by decreasing the oxidation loss of alloying elements. The oxygen blowing rate and the oxygen/inert gas mixing ratio influence the decarburization rate, the oxidation of metallics, and the operation time.
The lining life of the AOD vessel depends on the holding time of the melt in the vessel and the specific slag practice used during the reduction period. In order to decrease the holding time of the melt, the decarburization rate must be maximized. It is also necessary to develop an efficient slag-control technique during the reduction period.

This paper describes the experiences with, and some improvements made to, the AOD process at Pohang Works during the initial operation period, mainly as far as the blowing pattern for decarburization and the slag practice during the reduction period are concerned. Based on the initial operating results and experience, new operating methods were developed and applied to the AOD process from February 1990.

Plant Description

The construction of the stainless-steelmaking plant began in March 1987 and was completed in March 1989. The major equipment installed in the stainless-steelmaking shop is listed in Table II. This includes a 90 t EAF with a 70 MVA transformer, a 90 t capacity AOD converter, and a continuous-casting machine, which is a combi-caster for slab and bloom production.

The AOD vessel is 4 m in diameter and has a total height of 6.9 m. The inner volume after relining is 47 m$^3$ and the specific volume 0.52 m$^3$/t. The converter is equipped with a top lance and 5 side tuyères. The maximum flowrate of the top lance is 6000 Nm$^3$/h and that of the 5 side tuyères combined is 4800 Nm$^3$/h. The tuyères are spaced 27° apart, and they are located at the third lining step from the vessel bottom. Pure oxygen is supplied through the top lance, and an oxygen/inert gas mixture is injected through the side tuyères at a pressure of 16 bar. A sublance and an off-gas analysing system have been installed, and have been used for the automatic control of the AOD since May 1991.

Test Procedure

The three different blowing patterns investigated are summarized in Table III. Pattern A is the side-blown method without using the top lance and Pattern B is a combination of top and side blowing in the first decarburization step. Pattern C is the devised technique based on operational experience. For the reduction period, the variables slag basicity, melt silicon, and melt temperature were controlled by the addition of lime and ferrosilicon. Analyses of the base metal before it was charged into the AOD converter, as well as the end-point analyses, are listed in Table IV.

<table>
<thead>
<tr>
<th>Pattern</th>
<th>Step</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
</tr>
<tr>
<td>Aim [%C]</td>
<td>0.45</td>
<td>0.15</td>
<td>0.06</td>
<td>0.035</td>
</tr>
<tr>
<td>Oxygen gas flowrate (Nm$^3$/min)</td>
<td>Top lance</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Side tuyère</td>
<td>80</td>
<td>60</td>
<td>20</td>
<td>12</td>
</tr>
<tr>
<td>Inert gas (Nm$^3$/min)</td>
<td>Side tuyère</td>
<td>20</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>Ratio of flowrate of oxygen to inert gas</td>
<td>4:1</td>
<td>2:1</td>
<td>1:2</td>
<td>1:4</td>
</tr>
</tbody>
</table>
Refining process

Results and Discussion

Decarburization Period

Figure 3 shows the typical progress during AOD refining of the melt. As the carbon content decreases, the chromium content also decreases and the amount of chromium oxidized is between 2 and 3 per cent towards the end of the decarburization period. The melt temperature increases sharply in the first decarburization step but levels off in the range 1700 to 1720°C because of coolant additions such as lime or ferrous materials, which are added inter alia to protect the vessel refractory.

When oxygen is supplied to the chromium-containing melts, the chromium is oxidized preferentially, followed by the reduction of chromium oxide by the carbon in the melt. Therefore, the decarburization of chromium-containing melts can be expressed as follows:

\[ \frac{3}{2} \, \text{O}_2(g) + 2 \, [\text{Cr}] = \text{Cr}_2\text{O}_3(s) \]  
\[ \text{Cr}_2\text{O}_3(s) + 3 \, [\text{C}] = 2 \, [\text{Cr}] + 3 \, \text{CO}(g) \]

\([\text{Cr}] = \) chromium dissolved in the metal phase.

It is of great importance for the optimization of the stainless-steel refining technique to establish the mechanism by which carbon is oxidized preferentially over chromium. The preferential oxidation is dependent on the activities of chromium and carbon in the melt, the melt temperature, and the rate of oxygen supply. Theoretically, decarburization can proceed without the oxidation of chromium at high temperature and under a low partial pressure of CO. However, the contribution of oxygen to decarburization is decreased as the carbon content of the melt decreases. As a consequence, the decarburization rate decreases linearly with the carbon content, and the rate of chromium oxidation increases significantly after reaching a 'critical carbon content'. This critical carbon content depends on the operating parameters, such as the oxygen-blowing rate and the mixing ratio of oxygen and inert gas.

Fruehan and other investigators\(^5,3\) have shown that the mechanism of decarburization in the AOD process is different in two carbon ranges and that the transition occurs at a carbon content of 0.15 per cent. In Fruehan's proposed reaction model of the decarburization of stainless steel\(^2\), he suggested that the rate of decarburization is determined by the oxygen-blowing rate in the high carbon range and that liquid-phase mass transfer of the carbon from the bulk metal to the melt/bubble interface is the rate-controlling step in the low carbon range. The following rate equations were suggested for the decarburization reaction in the two different carbon concentration ranges:

\[ \frac{d[\%\text{C}]}{dt} = -k_3 \, : [\%\text{C}] > 0.15 \]  
\[ \ln \left( \frac{[\%\text{C}]}{[\%\text{C}]_0} \right) = -k_4 \cdot t \, : [\%\text{C}] < 0.15, \]

where \([\%\text{C}] = \) carbon content in the melt  
\([\%\text{C}]_0 = \) initial carbon content in the melt  
\(k_3 = \) rate constant for equation [3] (min\(^{-1}\))  
\(k_4 = \) rate constant for equation [4] (min\(^{-1}\)).

In order to verify this model, the operational results obtained in this study were compared with calculations based on equations [3] and [4].

Figure 4 compares the extent of decarburization calculated by equations [3] and [4] with practically observed values. There is evidently good agreement, implying that Fruehan's model can be used for the analysis of the decarburization rate in the present study.

The model also indicated that the oxidation behaviour of chromium could influence the decarburization rate. The extent of chromium oxidation can be calculated from the following equation:

\[ \Delta\%\text{Cr} = 4M_{\text{Cr}}\gamma_3\text{W}^{-3}2/[\text{O}_2]e^{-W^{-1}0.32/2M_{\text{O}}([\%\text{C}]_0 - [\%\text{C}])}. \]  

\[ \text{FIGURE 3. Changes of various components and melt temperature during refining} \]

\[ \text{FIGURE 4. Comparison of the calculated extent of decarburization and practically observed values} \]
where $\Delta Cr$ = the amount of oxidized chromium (%)

$M_{Cr}$ = atomic weight of chromium

$f$ = relative amounts of chromium and iron oxidized during the process

$N_{O_2}$ = oxygen supply rate (Nm$^3$/min)

$t$ = time (min)

$W$ = melt mass (t)

$M_c$ = atomic mass of carbon.

Figure 5 compares the values calculated by equation [5] with observed results and there is a relatively good relationship. Therefore, equation [5] was also used for the quantitative evaluation of chromium oxidation in the present study.

Figure 6 shows the variation of the decarburization rate for three types of blowing patterns as a function of the carbon content in the melt. The decarburization rate at high carbon concentration was constant, but the constant depended on the oxygen-blowing rate (O$_2$/Ar ratio) at each step. At carbon concentrations lower than 0.2 per cent, the decarburization rate is a function of the carbon content of the melt. In the case of pattern A, where the oxygen blowing was carried out using only 5 side tuyères, the decarburization rate in the first step was higher than those of patterns B and C. This result indicated that the decarburization efficiency of side-blown oxygen was higher than that of top-blown oxygen. Pattern B, which consists of 5 decarburization steps, see Table III, did not show a steep decrease in decarburization rate as pattern C did. This implies that pattern B can decarburize more smoothly without a sudden decrease in decarburization rate. On the other hand, pattern C maintains a high decarburization rate up to lower carbon concentrations than pattern B.

Figure 7 shows the chromium-oxidation rate as a function of the carbon content of the melt. The oxidation rate of chromium displays a similar trend to that of the decarburization rate. Generally, the chromium-oxidation rate should increase as the carbon content in the melt decreases. However, the chromium-oxidation rate decreases at low carbon concentrations because of a reduced oxygen-blowing rate. The actual amount of chromium oxidized at low carbon contents is large because the decarburization rate is very low. As indicated in Figure 7, pattern A showed more chromium oxidation for all steps, compared with patterns B and C. As shown in Figures 6 and 7, pattern A resulted in higher rates of decarburization and chromium oxidation than pattern B or C, in spite of the lower oxygen supply rate used. This observation implies that side-blown oxygen reacts more efficiently with the melt than oxygen blown from the top.

Figure 8 shows the relationship between the rate of the rise in temperature of the melt and the rate of chromium oxidation during the decarburization period. The rate of temperature rise had a linear relationship with the chromium-oxidation rate for all three blowing patterns. However, top blowing (patterns B and C) gave a higher rate of temperature rise in the first step than side blowing only.
The initial higher rate of temperature rise observed with the top-blowing patterns, in spite of the lower efficiencies of chromium oxidation and decarburization, indicates that a significant amount of oxygen from the top lance is used for the post-combustion of CO gas in the vessel:

\[ \text{CO(g)} + \frac{1}{2} \text{O}_2(g) = \text{CO}_2(g) \]  

Therefore, the heat generated from post-combustion can be utilized to increase the temperature of the melt. These results led to a new, revised blowing pattern using a top lance and side tuyères (Table V) to optimize the decarburization process. The target decarburization path of this new blowing pattern is shown as arrows in Figure 6.

The underlying principles for the new blowing pattern can be formulated as follows:

1. A high decarburization rate in the high-carbon region (>0.6 per cent carbon) by combined oxygen blowing with a top lance and side tuyères
2. A high rate of temperature increase by post-combustion in the first step

<table>
<thead>
<tr>
<th>Step</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aim [%C]</td>
<td>0.60</td>
<td>0.40</td>
<td>0.20</td>
<td>0.06</td>
<td>0.035</td>
</tr>
<tr>
<td>Oxygen gas flowrate (Nm³/min)</td>
<td>Top lance</td>
<td>100</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Side tuyère</td>
<td>20</td>
<td>60</td>
<td>45</td>
<td>20</td>
</tr>
<tr>
<td>Inert gas flowrate (Nm³/min)</td>
<td>Side tuyère</td>
<td>N₂</td>
<td>25</td>
<td>30</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>60</td>
</tr>
<tr>
<td>Ratio of flowrate of oxygen to inert gas</td>
<td>5:1</td>
<td>2:1</td>
<td>1:1</td>
<td>1:3</td>
<td>–</td>
</tr>
<tr>
<td>Lining life</td>
<td>120 – 140 heats</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar consumption</td>
<td>12 – 15 Nm³/t</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tap-to-tap time</td>
<td>65 – 70 min</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Figure 9 shows the effect of slag basicity on the total chromium oxide content of the slag. The chromium oxide content of the slag was decreased as the slag basicity increased, but the effect was not significant at basicities higher than 2. As the slag basicity increases, the activity of SiO₂ in the slag decreases and the reduction reaction is favoured as shown in equation [8]. However, when the slag basicity is higher than 2, additional lime added to the bath cannot dissolve and the fluidity of slag is decreased. Consequently, an increase in the basicity above a value of 2 has little effect on the reduction of chromium oxide from the slag.

Figure 10 shows the chromium oxide content of the slag as a function of the temperature of the melt. Reduction of chromium oxide becomes more effective at high temperature. For example, the final chromium oxide content of slag can be maintained below 0.5 per cent at temperatures greater than 1,600°C.
above 1670°C. The beneficial effect of high temperature seems to be due to increased slag fluidity.

Figure 11 shows the effect of the silicon content of the melt on the chromium oxide content of the slag. As the silicon content increases, the efficiency of the chromium oxide reduction increases, equation [8]. The increased Si content of the melt also contributes to a decrease in the oxygen potential at the slag/metal interface.

From a linear regression analysis on the total chromium oxide content of the slag as a function of the slag basicity, the melt temperature, and the silicon content, the following equation was obtained:

\[
\log (T\%\text{Cr}) = -4.72 + 10602/T(\text{K}) + 0.27 \log [\%\text{Si}] - 4.31 \log \left(\frac{[\%\text{CaO}]}{([\%\text{SiO}_2])}\right). \tag{9}
\]

Figure 12 compares the calculated total chromium oxide content of the slag with that observed in practice.

**Desulphurization during the Reduction Period**

It is generally accepted that the reduction period of the AOD process is favourable for desulphurization because of the low pertaining oxygen potential and the high stirring energy of the melt. The desulphurization reaction can be expressed as follows:

\[
(CaO) + [S] = (CaS) + [O] \tag{10}
\]

\[
K_{10} = \frac{a_{(CaS)}}{a_{[O]}} \frac{a_{[S]}}{a_{(CaO)}} \tag{11}
\]

Generally, high slag basicity, a low oxygen potential, and high temperatures favour desulphurization. Figure 13 shows the effect of slag basicity on the desulphurization efficiency. At basicities higher than 2, about 90 per cent desulphurization efficiency was obtained. Figure 14 shows the effect of the silicon content of the melt on the sulphur distribution ratio at high slag basicities \( (B>2) \). The sulphur distribution ratio increases significantly as the silicon content increases because of the decreased oxygen potential.

In summary: to optimize the reduction of chromium oxide and desulphurization, the slag basicity should be >2, the silicon content of the melt should be >0.4 per cent, and the temperature of the melt should be kept higher than 1670°C.
New Operational Conditions and Results

Based on the results of the present study, the new operational conditions were established as shown in Table V. Furthermore, a practice of adding 1.5 t of dolomite per heat was adopted to improve the life of the vessel lining. The new method has been applied to the AOD process since February 1990, and the results of this new method of operation are summarized in Table V and Figure 15.

The main advantages obtained with the new process are as follows:

1. Improvement of the decarburization rate with a concomitant decrease in the extent of chromium oxidation
2. Decrease of tap-to-tap time from 83 to 68 minutes
3. Increase of vessel lining life from 70 to 130 heats per campaign.

References
