Improvement of steel cleanliness by controlling slag composition

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Abstract

The properties of slag are very important to improve steel cleanliness. Most of all, the value of \((\%\text{CaO})/(\%\text{Al}_2\text{O}_3)\), slag basicity, fluidity and Oxygen activity in the slag is considered to affect the steel cleanliness directly. To control these values effectively, the way of deoxidation and slag composition control by additives was changed. And the effect of oxygen content before tapping was investigated. Through the optimizing these factors, the total oxygen content of bearing steel was improved from 12ppm to 8ppm.
1. Introduction
Bearing unit applied to the junction of axis and so on is such a part that it causes the trouble of machinery after a certain lifetime because it received repeated stress. Therefore, it is needed to improve the quality of bearing steel so that it can be used during all the life of machinery. Generally the bearing steel used in most products is mainly composed of high Cr-C system and the bearing steel produced by POSCO is also composed of high Cr-C system as shown in table 1.

The factors affecting the life of bearing steel can be classified as nonmetallic inclusions, segregation etc. and among these factors, the effect of nonmetallic inclusions on bearing steel has been studied especially in the various methods. So from those studies it has been known that the nonmetallic inclusions are acting as the stress concentration point and finally cause the creation and grow up of fatigue crack.

The representative nonmetallic inclusions causing the crack are Al$_2$O$_3$, SiO$_2$, TiO$_2$ etc. Fig. 1-(a)[1] shows that the life of bearing steel decreases with the increase of the sum of Al$_2$O$_3$ and SiO$_2$ in the steel.

But as shown in fig. 1-(b), the sulfide, which exists as the form of MnS in the neighborhood of inclusion, decreases the tensile stress due to inclusions with the compressive stress acting itself, so gives the positive effects to the fatigue failure. However, considering general harmful effects caused by the sulfur, its contents should be limited under a proper range.[2]

2. Theoretical background

2-1. The effect of slag composition on the removal of Al$_2$O$_3$ inclusion
The main inclusion existing at the bearing steel is Al$_2$O$_3$ type, so it is needed to control the slag composition for the removal of Al$_2$O$_3$ type inclusion. The absorption ability of slag for Al$_2$O$_3$ can be improved by lowering Al$_2$O$_3$ activity or the melting temperature of slag to promote mass transport of Al$_2$O$_3$.

The range of slag composition satisfying these conditions should be near the binary system of Al$_2$O$_3$ and CaO considering the slag composition of bearing steel and reoxidation of molten steel by the SiO$_2$. If the former is considered to be more important, the proper composition range should be near the CaO saturation region marked as the region A in the figure 2. However, if the latter is considered to be more important the composition should be placed in the region B.

2-2. Reoxidation of molten steel by the low-grade oxide in the slag
As shown in equation (1), the low-grade oxides in the slag like FeO and MnO react with oxidant in the molten steel and create the nonmetallic inclusion.

\[
\begin{align*}
3(\text{FeO}) + 2\text{Al} &= (\text{Al}_2\text{O}_3) + 3\text{Fe} \quad (1-a) \\
3(\text{MnO}) + 2\text{Al} &= (\text{Al}_2\text{O}_3) + 3\text{Mn} \quad (1-b) \\
3(\text{SiO}_2) + 4\text{Al} &= 2(\text{Al}_2\text{O}_3) + 3\text{Si} \quad (1-c)
\end{align*}
\]

From the equation (1-a) and (1-b) when the contents of FeO and MnO in slag are high, the nonmetallic inclusions are created, therefore it is essential to decrease the FeO and MnO contents in slag. But as shown in fig. 3, the reoxidation behavior of SiO$_2$ is different from that of FeO and MnO because Si is stronger oxidant than Fe and Mn and
if the basicity of molten slag is controlled over a certain degree, the reoxidation of molten steel by the \( \text{SiO}_2 \) in slag doesn’t happen. Therefore if the slag basicity is controlled over a certain degree, we can prevent the reoxidation of molten steel by the \( \text{SiO}_2 \).

2-3. Effect of the oxygen content at the blow end of BOF on steel cleanliness
Since the oxygen content in the molten steel at the blow end of BOF is the origin of nonmetallic inclusion, it affects the cleanliness of steel. Therefore, the effect of oxygen content on the steel cleanliness should be considered.

3. Experimental procedure
Table 2 shows the steelmaking process in production of bearing steel at POSCO. As shown in this figure, the process consists of BOF-LF-RH-CC and the operation patterns at the unit process greatly affect the cleanliness of bearing steel. In this study three tests were carried out to remove the nonmetallic inclusion in molten steel. Those are change of deoxidation method, control of slag composition and decrease of oxygen content at the tapping.

3-1. Change of \( \text{CaO}/\text{Al}_2\text{O}_3 \) value
\( \text{Al}_2\text{O}_3 \) absorption ability of slag is different according to the slag composition. If the slag composition is in the \( \text{CaO} \) saturation region, the activity of \( \text{Al}_2\text{O}_3 \) inclusion becomes low and then better thermodynamic condition can be acquired. However, the absorption of the inclusion could be worse due to the higher melting temperature. When the slag composition is in the low melting temperature area, the absorption ability is increased but the thermodynamic equilibrium state is deteriorated. The slag composition was in the region of \( \text{CaO} \) saturation at the conventional method but the composition was change to the low melting temperature area at the improved method as shown at table 2. \( \text{CaO} \) was added and small amount of \( \text{CaF}_2 \) was also added to improve slagging rate before arc heating at the ladle furnace in the case of the conventional method. However, in spite of \( \text{CaF}_2 \) addition the slag didn’t melt completely and most of slag is solidified after arc heating. In this study to resolve this problem \( \text{CaO}/\text{Al}_2\text{O}_3 \) ratio was controlled from 1.7 to 1.8 by the addition of \( \text{Al}_2\text{O}_3 \) and decrease of \( \text{CaO} \).

3-2. Change of deoxidation method at the tapping
As can be seen in the table 3, \( \text{FeSi} \), \( \text{FeMn} \) and \( \text{Al} \) were added successively at the tapping by the conventional method. In this case, the oxides created during the deoxidation have the composition of \( \text{SiO}_2 \) and \( \text{MnO} \) and then when \( \text{Al} \) is added the oxides are changed to \( \text{Al}_2\text{O}_3 \) due to the difference of the affinity for oxygen. However, the composition of the oxides does not reach the thermodynamic equilibrium state. Therefore, the content of \( \text{SiO}_2 \) and \( \text{MnO} \) is higher than that of the thermodynamic equilibrium state and the slag basicity is low and the oxidation degree of slag is high.
As the method to improve the basicity and oxidation degree, \( \text{Al} \) was added first and then \( \text{FeMn} \) and \( \text{FeSi} \) was added. By this method the \( \text{Al}_2\text{O}_3 \) oxides are created first and then only a small part of the oxides are changed to \( \text{SiO}_2 \) and \( \text{MnO} \). Consequently the main composition of the oxides should be \( \text{Al}_2\text{O}_3 \). As a result, the basicity is higher and oxidation degree of slag is lower than the conventional method.
3-3. Decrease of oxygen content at the tapping
As previously mentioned, it is beneficial for the improvement of steel cleanliness to decrease the oxygen content at the tapping because the oxygen at the tapping can be the origin of inclusions. However, when the oxygen content of BOF is decreased, dephosphorization is disturbed. Therefore, hot metal dephosphorization is required. In this study to decrease the oxygen content at the tapping, hot metal dephosphorization was carried out at HMPS (Hot Metal Pretreatment Station).

4. Result and discussion

4-1. The effect of \(\%\text{CaO}/(\%\text{Al}_2\text{O}_3)\)
The change of slag composition after RH is shown at fig. 4. By the conventional method the value of \(\%\text{CaO}/(\%\text{SiO}_2)\) (C/A) was widely spread from 2.0 to 4.4 but the C/A value was 1.2~2.0 by the improved method. The value of T.O was minimum at 1.7 regardless of the method. Therefore, in the case of bearing steel the C/A value at 1.7 gives best result to improve the steel cleanliness. The reason is that decrease of slag melting temperature is more efficient than control of slag composition to CaO saturation region.

Fig. 5 shows the comparison of slagmaking between the conventional and the improved methods after arc heating at the ladle furnace facility. As shown in this figure in the case of the conventional method much part of the slag is solidified but in the case of improved method the uniformly melted slag is spread on the top of ladle. Therefore, it can be confirmed that the slag melting temperature was lowered and inclusion absorption ability was increased by the improved method. The T.O could be reduced to 8ppm from 12ppm by the improved method.

4-2. Change of slag composition by the new deoxidation method
The slag compositions of the conventional and the improved method were compared at fig. 6. By the conventional deoxidation method slag basicity was in the range of 3.5~4.5 due to the oxidation of Si and Mn, but the basicity was 4.5~7.0 because Al was oxidized prior to Si and Mn by the improved method.

Fig. 7 shows the relation between slag basicity and T.O in bloom. Though the T.O was slightly decreased following the increase of basicity, slag basicity hardly affected T.O in comparison with other factor such as CaO/Al\(_2\)O\(_3\) ratio. To investigate these phenomena the SiO\(_2\) stable zone was calculated using the bearing steel composition with equation (2). The composition of bearing steel used at the calculation was 0.99wt% C-1.3wt% Cr-0.3wt%Mn and the activity coefficient was calculated from these values.

\[
3(\text{SiO}_2) + 4\text{Al} = 2(\text{Al}_2\text{O}_3) + 3\text{Si}, \quad \log K = -6.947 + 47,645/T \quad (2)
\]

Fig. 8 shows the result of equation (2). Sol. Al and Si contents of POSCO bearing steel, which are in the square of fig. 8, is 0.02~0.03wt% and 0.02% respectively. In this area if the basicity is more than 4, SiO\(_2\) doesn’t act as an oxygen source. Therefore, the basicity doesn’t affect the steel cleanliness.

4-3. Decrease of oxygen potential at the tapping
As previously mentioned, hot metal dephosphorization was carried out at HMPS facility.
before BOF operation to minimize the oxygen content at the tapping. This operation was adapted to both the conventional and the improved methods. Fig. 9 shows the relation between CD (carbon determinant) carbon and T.O in slab because the oxygen content at the end point of BOF couldn’t be measured easily and the CD carbon shows very good relation with oxygen content. In the case of the conventional method T.O in slab showed similar value regardless of CD carbon. However, in the case of the improved method the T.O was decreased as the oxygen content was decreased. The relation between T.O in slab and CD carbon is present in equation (3).

\[ T.O(\text{ppm}) = 11.2 - 0.0606(CD\ [C]\times10^{-2}\text{wt\%}) \]  

(3)

Based on these results the difference between the conventional and the improved method is caused by the slag composition. The slag has a tendency to decrease inclusions in molten steel to a certain level and the time needed to reach at the level depends on the difference between current T.O and equilibrium T.O as shown at equations (4) and (5).

\[ \frac{dO}{dt} = -k(O - O_e) \]  

(4)

\[ O = (O_i - O_e)(O-O_e)^{kt} + O_e \]  

(5)

From the equation (5), the time needed to reach at equilibrium T.O (equilibrium time) decreases when the initial T.O is low or equilibrium T.O is high. In the case of the conventional operation the equilibrium time is shorter than the steelmaking time regardless of initial T.O because the equilibrium T.O is high. However, in the case of the improved method the equilibrium time is longer than the steelmaking time because the equilibrium T.O is low. Therefore, when the CD carbon is low, the initial T.O becomes low and as a result effectiveness by the CD carbon is achieved.

In this study the \(O_e\) and \(k\) of the slag composition couldn’t be calculated because the steelmaking process consists of some unit operation.

4-4. Key factors affecting the inclusion removal
Considering all the data, the C/A value affected steel cleanliness at every test. And the oxygen content affected the cleanliness selectively when the C/A value is lowered. Therefore, the C/A value should be controlled first to the proper range and then the initial T.O should be lowered.
5. Conclusions
1) The basicity of top slag does not affect the steel cleanliness on the removal of the inclusion in the bearing steel of which composition is 0.99wt%-1.3wt%Cr-0.3wt%Mn when the basicity is over 4 because SiO$_2$ is stable and does not react as an oxygen source.
2) The control of C/A is the most efficient method to remove the inclusions in bearing steel and the C/A value was most effective at 1.7~1.8. From this method the T.O could be reduced to 5~8ppm from 1~12ppm.
3) As the oxygen content at the tapping is decreased, the T.O of the bearing steel is decreased. However, when the C/A value is over 2.0 there is no substantial effect of oxygen content at the tapping since the equilibrium T.O is too high to reach equilibrium state within the steelmaking time.
6. References

1) Johnson, R. F. and Sewel, J. JISI, December, 1960, p.414
2) Brooksbank, D. and Andrews, K. W. JISI, December, 1972, p.246
3) Y. Fukuzaki et al, Steelmaking conference proceedings, 1992, p.397
Fig. 1. Relationship between average life and inclusion content:
counts based on total inclusions observed (×750) in 516
fields representing a total area of $9 \times 10^6$. 
Fig. 2. Control of slag composition at bearing steel.
Fig. 3. Effect of slag basicity on the total oxygen contents in steel.
Fig. 4 Comparison T.[O] between the improved and the conventional method at Bloom.
a) Nonfluid ladle slags: conventional method.

b) Fluid ladle slags: improved method.

Fig. 5. Comparison of slag state after LF treatment.
Fig. 6. Change of slag basicity by improving deoxidation method and slag control.
Fig. 7. Relationship between slag basicity and T.[O] of bloom.
Fig. 8. Stable condition of $a_{SiO_2}$ in ladle slag at bearing steel production.
Fig. 9. Relationship between blow end CD [C] and T.[O] of bloom.
Table 1. The composition of bearing steel

<table>
<thead>
<tr>
<th>Standard</th>
<th>Grade</th>
<th>Composition (wt%)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>J</td>
<td>SUJ1</td>
<td>0.95</td>
</tr>
<tr>
<td>I</td>
<td>SUJ2</td>
<td>0.95</td>
</tr>
<tr>
<td>S</td>
<td>SUJ3</td>
<td>0.95</td>
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</table>
Table 2. Change of characteristic temperatures

<table>
<thead>
<tr>
<th></th>
<th>Softening temp.</th>
<th>Melting temp.</th>
<th>Fluidizing temp.</th>
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<tbody>
<tr>
<td>Conventional</td>
<td>1468</td>
<td>1505</td>
<td>&gt;1510</td>
</tr>
<tr>
<td>Improved</td>
<td>1347</td>
<td>1349</td>
<td>1368</td>
</tr>
<tr>
<td>Difference</td>
<td>121</td>
<td>156</td>
<td>142</td>
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</table>
Table 3. Comparison between the conventional and the Improved method

<table>
<thead>
<tr>
<th>Conventional</th>
<th>Process</th>
<th>Improved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deoxidation order: FeSi, FeMn, Al</td>
<td>Tapping 1. Deoxidation</td>
<td>Deoxidation order: Al, FeMn, FeSi</td>
</tr>
<tr>
<td></td>
<td>2. Slagmaking</td>
<td></td>
</tr>
<tr>
<td>Arc heating</td>
<td>LF 1. Temperature adjustment</td>
<td>Arc heating CaO, Al₂O₃ addition</td>
</tr>
<tr>
<td>CaO, CaF₂ addition</td>
<td>2. Slagmaking 3. Inclusion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>removal</td>
<td></td>
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<tr>
<td>Circulation: 25min</td>
<td>RH 1. Inclusion removal</td>
<td>Circulation: 25min</td>
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<tr>
<td>Bloom Casting</td>
<td>Continuous casting</td>
<td>Bloom Casting</td>
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</tbody>
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