INVESTIGATION OF GASEOUS DESILICONIZATION IN BASIC OXYGEN FURNACE (BOF)

In this paper, the gaseous desiliconization during slagging by limestone and lime in a Basic Oxygen Furnace (BOF) were studied by thermodynamic analysis. The results showed that part of the silicon in molten iron could volatilize into SiO in both slagging modes, but by using different methods. In the limestone slagging mode, CO2 from limestone could massively oxidize the silicon in molten iron into gaseous SiO in the hotspot zone. In the lime slagging mode, SiO can be reduced from SiO2 in slag. Both methods are dependent on the hotspot zone. The SiO amount generated from the former method is larger than the latter is.

Key words: steel, BOF, thermodynamic analysis, gaseous desiliconization, limestone slagging;

INTRODUCTION

On the basis of long-term laboratory studies, a process of using limestone as a substitute for lime to slag in all Basic Oxygen Furnaces (BOFs) has been proposed [1]. Due to its significant economic benefits and CO2 emission reduction [2], the limestone slagging mode has been adopted by an increasing number of iron and steel enterprises. Industrial production reveals that, if the amount of limestone charged into a BOF to substitute for lime for slagging was based on the CaCO3 and CaO molecular mass ratio (100:56), the final slag basicity of limestone mode would be much larger than that of lime slagging mode with nearly same silicon content. About 30 % of limestone amount can be reduced, and the dephosphorization rate is still as good as the lime mode. This phenomenon reveals that not all silicon in hot metal becomes part of the slag. A considerable portion becomes part of the furnace gas. This discovery provides a new way to consider the desiliconization process in all BOFs. In order to explore the gaseous desiliconization phenomenon in all BOFs, thermal analysis and Factsage software were used.

THE GASEOUS DESILICONIZATION MECHANISM IN LIMESTONE SLAGGING MODE

A big difference between limestone mode and lime mode is the large amount of CO2 gas that comes from limestone. The CO2 can react with the elements in a hot metal:

\[
\begin{align*}
[\text{Si}] + 2\text{CO}_2 &= \text{SiO}_2 (l) + 2\text{CO} \quad (1) \\
[\text{Mn}] + \text{CO}_2(g) &= \text{MnO}(l) + \text{CO} \quad (2) \\
[\text{C}] + \text{CO}_2(g) &= 2\text{CO} \quad (3)
\end{align*}
\]

Wu Nian et al. [3] believed that the gaseous desiliconization phenomenon after charging limestone is caused by a large portion of silicon in hot metal that is oxidized into a low valence state compound, SiO, and goes into the furnace gas. The reaction can be described as

\[
[\text{Si}] + \text{CO}_2 = \text{SiO}(g) + \text{CO} \quad (4)
\]

The following reaction can be achieved by reaction (1) and reaction (4)

\[
\text{SiO}_2(l) + \text{CO} = \text{SiO}(g) + \text{CO}_2 \quad (5)
\]

The Gibbs free energy for the reaction

\[
\Delta G = \Delta G^\circ + RT \ln \frac{P_{\text{CO}}P_{\text{SiO}}}{P_{\text{CO}}^2P_{\text{SiO}}}
\]

where \(P_{\text{SiO}}, P_{\text{CO}}, P_{\text{CO}_2}\) is the partial pressure of SiO, CO, CO2, \(a_{\text{SiO}}\) is the activity of SiO.

When the reaction reaches equilibrium, \(P_{\text{SiO}}\) can be obtained by

\[
P_{\text{SiO}} = a_{\text{SiO}}P_{\text{CO}}e^{-\frac{\Delta G^\circ}{RT}}
\]

assuming the activity of SiO is 0.01, and \(P_{\text{SiO}}\) under different \(P_{\text{CO}}/P_{\text{CO}_2}\) can be obtained.

Figure 1 Dependence of \(P_{\text{SiO}}\) and temperature and \(P_{\text{CO}}/P_{\text{CO}_2}\)
SiO₂(l) + [C] = SiO(g) + CO  (6)
SiO₂(l) + CO = SiO(g) + CO₂  (7)

In other words, SiO₂ in slag may be reduced to SiO in a CaO-O₂-hot metal system. While the reduction of (SiO₂) has been studied in a blast furnace [6, 7], and silicon elements are reduced in the hot metal, (SiO₂) → SiO → [Si]. (SiO₂) reduction by H₂ and CO in the CaO-SiO₂ and CaO-SiO₂-Al₂O₃ slag systems were studied by B. Ozturk [8]. However, the reduction of (SiO₂) in the BOF slag has been hardly studied at all. As for (FeO) and (MnO), whose oxidability is stronger than (SiO₂), they exist in the BOF slag. Thus, the selective reduction issue should be considered. Besides, as the oxidability of (MnO) is stronger than (FeO), the selective reduction between (FeO) and (MnO) is what needs to be considered.

Whether the reducing agent is [C] or CO, the selective reduction reactions between MnO and SiO₂ would always be

SiO₂(l) + [Mn] = SiO(g) + (MnO)  (8)

According to the coexistence theory of slag, the activity of SiO₂, MnO could be calculated according to the literature [9].

When reaction (8) reaches equilibrium, the partial pressure of SiO can be obtained:

\[ P_{SiO} = \frac{a_{MnO} \cdot a_{Mn} \cdot \exp(\frac{58 548.35}{T})}{a_{SiO}} \]  (8)

where \( a_{MnO} \) and \( a_{Mn} \) are the activity of MnO and Mn. The result is plotted in Figure 4.

As shown in Figure 4, the reduction temperature of (SiO₂) in the MnO-CaO-FeO-SiO₂ slag system is very high, the possible reaction area in BOF could only be the hotspot zone. \( P_{SiO} \) increases with temperature. Meanwhile, basicity has a remarkable influence on Psio. This fact indicates that at the initial blowing stage of the BOF, when (SiO₂) is very active, the trend in the reduction of (SiO₂) increases. As shown in the figure, although the impact is not large, the smaller the MnO % is, the easier (SiO₂) is reduced. Therefore, at the initial blowing stage, the reduction of (SiO₂) would be pro-
moted through lowering the oxygen lance’s position, which will lead to lower MnO % and a high hotspot temperature.

CONCLUSIONS

The paper researched the phenomenon of gaseous desiliconization in BOF slagging by limestone and discussed the possibility in the lime slagging mode. Thermodynamic analysis showed the gaseous desiliconization phenomenon could happen in both slagging modes. In limestone slagging mode, gaseous desiliconization is caused by CO₂ from limestone, while in lime slagging mode, SiO can be reduced from (SiO₂). Both mechanisms occur in the hotspot zone and is profitable at the initial stage of blowing. Besides, lower basicity and MnO content is favorable for gaseous desiliconization in lime mode.

Acknowledgements

The authors acknowledge that this research is financially supported by the National Natural Foundation of China. (Project No. 51334001).

REFERENCES


Note: The responsible translator for English language is ACCDON LLC, Waltham, Massachusetts.