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, CO_2 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 SiO_2 in slag. Both methods are dependent on the hotspot zone. The SiO amount generated from the former method is larger than the latter is.
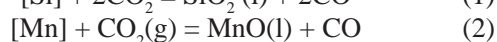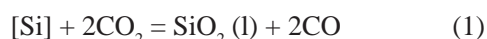
Key words: steel, BOF, thermodynamic analysis, gaseous desiliconization, limestone slagging;

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 CO_2 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 $CaCO_3$ 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 phenomeno-n 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 CO_2 gas that comes from limestone. The CO_2 can react with the elements in a hot metal:

$$[Si] + 2CO_2 = SiO_2 (l) + 2CO \qquad (1)$$
$$[Mn] + CO_2(g) = MnO(l) + CO \qquad (2)$$
$$[C] + CO_2(g) = 2CO \qquad (3)$$

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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

$$[Si] + CO_2 = SiO(g) + CO \qquad (4)$$
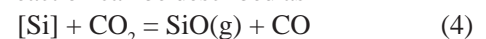
The following reaction can be achieved by reaction (1) and reaction (4)

$$SiO_2(l) + CO = SiO(g) + CO_2 \qquad (5)$$
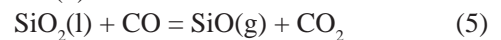
The Gibbs free energy for reaction

$$\Delta G = \Delta G^\theta + RTln\frac{P_{CO_2}P_{SiO}}{P_{CO}a_{SiO_2}}$$

where P_{SiO}, Pco, Pco_2 is the partial pressure of SiO, CO, CO_2. a_{SiO2} is the activity of SiO_2.

When the reaction reaches equilibrium, P_{SiO} can be obtained by

$$P_{SiO} = a_{SiO_2}\frac{P_{CO}}{P_{CO_2}}\exp(-\frac{\Delta G^\theta}{RT}),$$

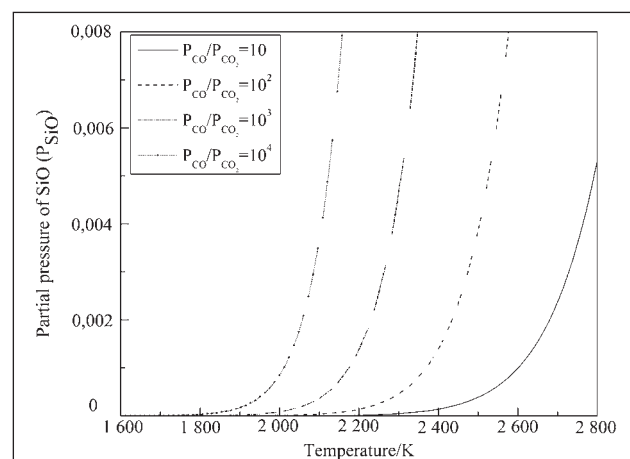assuming the activity of SiO_2 is 0,01, and P_{SiO} under different Pco/Pco_2 can be obtained.

Figure 1 Dependence of P_{SiO} and temperature and Pco/Pco_2

Figure 2 Dependence of SiO mass and (SiO_2) mass on temperature in $CaCO_3$-O_2-hot metal system
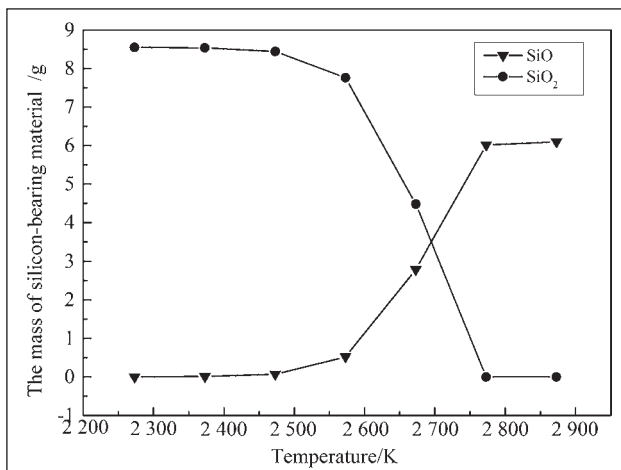

Figure 3 Dependence of SiO mass and (SiO_2) mass on temperature in CaO-O_2-hot metal system

As shown in Figure 1, P_{SiO} increases sharply along with the rise of temperature under the same *Pco/Pco₂*; the temperature needed to generate SiO decreases with increasing *Pco/Pco₂*. So two conditions are crucial to the generation of SiO: high temperature and high *Pco/Pco₂*. The zone that matches both conditions in all BOFs can only be the hotspot zone where temperatures could be as high as 2 773K [4, 5].

Figure 2 presents the influence of temperature on the mass of SiO and (SiO_2) in the $CaCO_3$-O_2 hot metal system calculated by Factsage software. The ratios between various materials were chosen according to industrial experimental data. The calculation conditions are a hot metal mass of 1 000 g with a component of [C %] = 4,2, [Si %] = 0,4, [Mn %] = 0,2, and an O_2 mass of 50 g, $CaCO_3$ 50 g. As seen in Figure, the mass of SiO increases slowly with a temperature below 2 450 K, and it grows faster when the temperature reaches 2 450 K, while the mass of (SiO_2) decreases with temperature. When the temperature reaches above 2 673 K, most silicon in the hot metal was oxidized into SiO.

POSSIBILITY OF GASEOUS DESI-LICONIZATION IN LIME SLAGGING MODE

Figure 3 shows the relationship between the mass of SiO and (SiO_2) and temperature when the system reaches balance. The calculation condition is the same as Figure 2. $CaCO_3$ (50 g) was replaced with CaO (28 g). As seen in Figure, the mass of SiO increases along with temperature, while (SiO_2) remains 0 in the process. This fact indicates that the oxidation atmosphere is not strong. In the case shown in Figure 2, silicon can only be oxidized into SiO. And the mass of SiO is only 1,4 g compared with that in Figure 2 (5,1 g).

As discussed above, in the $CaCO_3$-O_2-hot metal system, [Si] can be oxidized into SiO by CO_2 from $CaCO_3$. However, no CO_2 was obtained from CaO, so the formation mechanism of SiO in the CaO-O_2-hot metal system must be different than in the $CaCO_3$-O_2-hot metal system. The possible reactions can be
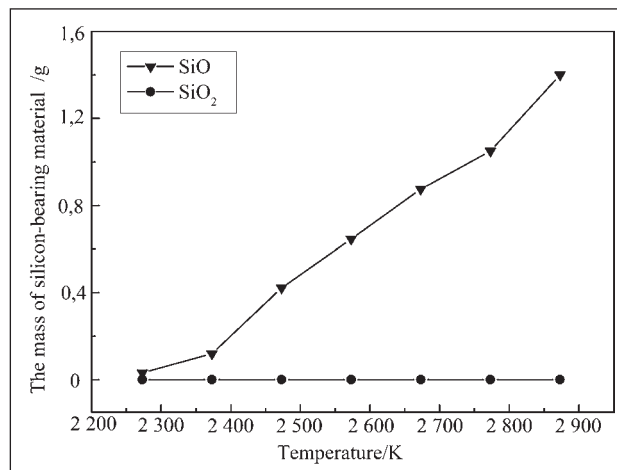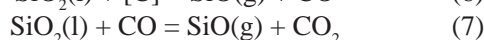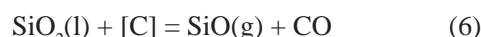
$$SiO_2(l) + [C] = SiO(g) + CO \qquad (6)$$
$$SiO_2(l) + CO = SiO(g) + CO_2 \qquad (7)$$

In other words, SiO_2 in slag may be reduced to SiO in a CaO-O_2-hot metal system.

While the reduction of (SiO_2) has been studied in a blast furnace [6, 7], and silicon elements are reduced in the hot metal, (SiO_2)→SiO→[Si]. (SiO_2) reduction by H_2 and CO in the CaO-SiO_2 and CaO-SiO_2-Al_2O_3 slag systems were studied by B. Ozturk [8]. However, the reduction of (SiO_2) in the BOF slag has been hardly studied at all. As for (FeO) and (MnO), whose oxidability is stronger than (SiO_2), 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 SiO_2 would always be

$$SiO_2(l) + [Mn] = SiO(g) + (MnO) \qquad (8)$$

According to the coexistence theory of slag, the activity of SiO_2, MnO could be calculated according to the literature [9].

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

$$P_{SiO} = \frac{a_{Mn} \cdot a_{SiO_2}}{a_{MnO}} \cdot \exp\left(16.64 - \frac{58\ 548,35}{T}\right), \qquad (8)$$

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

As seen in Figure 4, the reduction temperature of (SiO_2) in the MnO-CaO-FeO-SiO_2 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 (SiO_2) is very active, the trend in the reduction of (SiO_2) increases. As shown in the figure, although the impact is not large, the smaller the MnO % is, the easier (SiO_2) is reduced. Therefore, at the initial blowing stage, the reduction of (SiO_2) would be pro-
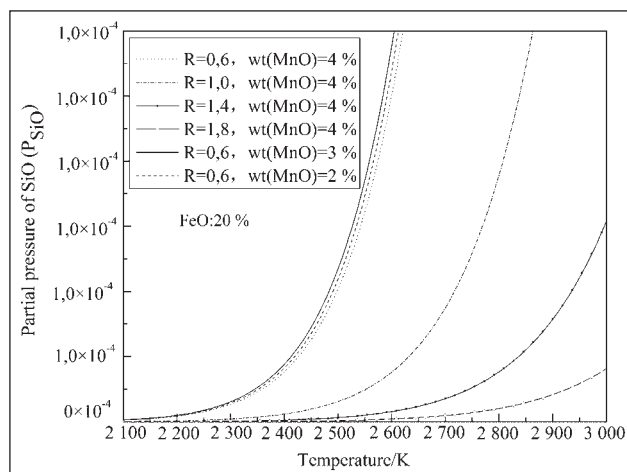
Figure 4 Relationship between P_{SiO} and temperature in different basicity in MnO-CaO-FeO-SiO$_2$ slag system

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 CO_2 from limestone, while in lime slagging mode, SiO can be reduced from (SiO_2). 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.

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