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OXIDATIONS BEHAVIOR OF C, Si, Mn, P, Nb IN Nb-BEARING HOT METAL BY BOTTOM BLOWING OXYGEN

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This paper focuses on oxidationS behavior of C, Si, Mn, P, Nb in Nb-bearing hot metal during bottom-blowing oxygen in a vacuum-induction furnace. This blowing process was carried out separately with and without slag at the flow rate of 0,4 m^3/min to 0,6 m^3/min. The results show that niobium is massively removed from the hot metal while silicon content in hot metal is decreased to lower than 0,01wt. % with adding slag , P content keeps unchanged, and sulfur content is decreased in hot metal at the beginning of blowing stage while it increased in hot metal with the extension of smelting time.

Key words: Nb - bearing, hot pig iron, oxidation C, Si, Mn, P, Nb, time, blowing to oxygen

INTRODUCTION

Baiyunebo Ore, containing Fe, rare earth, and Nb, is the largest polymetallic intergrowth ore in the world. Because Nb and other elements are intergrown complicatedly, it is difficult to recover them separately. 80 wt. % of the Nb in Baiyunebo iron ore was reduced into the hot metal in blast furnace process, the content of Nb in the hot metal is 0,015 - 0,035 wt. %. Nb in hot metal is almost completely oxidized into the slag in blast furnace oxygen and the content of Nb oxide in slag increase up to 0,20 – 0,3 wt. % while the content of Nb in hot metal decrease to 3 - 5ppm [1]. Thus, amounts of Nb is wasted for recycling Nb from the slag is unprofitable for it contains lots of lime, quartz, FeO and little Nb oxide. In order to recover effectively Nb resource, selective oxidation treatment is always used. It can reduce recycling Nb cast from hot metal for Si and Nb in hot metal are selectively oxidized and silica and Nb oxide are concentrated in various slag in various pretreatment stage. In this paper, selective oxidation in Nb-bearing hot metal was studied; the oxidation behavior of Si and Nb and other elements in hot metal was analyzed during bottom-blown oxygen.

Desiliconization and dephosphorization by means of selective oxidation and separation of elements in hot metal pretreatment can reduce subsequent cost and realize the production of clean steel. Carbon and silicon can be selectively oxidized and separated from molten iron by blowing CO_2, C is preferentially oxidized and Si can remain in molten iron and molten steel is obtained [2]. In the dephosphorization process by using of CaO-SiO_2- FetO slag, Nb was more stable than vanadium in hot metal [3], then it was possible to extract vanadium and retain Nb in molten iron. Contents of silicon and phosphorus in hot metal were reduced in the hot metal pretreatment process of dephosphorization [4] and desiliconization [5]. Hot metal smelting time and optimum smelting process of desiliconization were determined through the analysis of kinetics of hot metal desiliconization, and converter steelmaking was realized with less slag [6]. A large number of studies were focused on smelting process of desiliconization, extraction Nb or retain silicon [7 - 10]. However, because of the complexity of the smelting process, the technology of extraction and utilization of Nb was not so effective. Therefore, our study investigated the behavior of Nb and Si in hot metal with slag addition during bottom-blowng oxygen, which provides theoretical and experimental basis for further recycling Nb resources from the molten iron.

EXPERIMENTAL METHODS

In experiments, Nb-bearing pig iron from BaoTou Steel, whose composition is shown in Table 1, is melted by bottom-blowing industrially pure oxygen (the purity is greater than 98 wt. %) and industrial argon (the purity higher than 99 wt. %) separately in mid-frequency (MF) induction furnace rammed with alumina-magnesia spinel brick. The porosity of the brick is greater than 12,5 %, and its density is 3,75 g / cm^3. The inner diameter of the MF induction furnace is 200 mm where 50 - 70 kg pig iron is melted, which leads to a 220 - 250 mm-height of the hot metal. High-temperature rapid respond thermocouple is used to measure the temperature. The molten iron temperature is kept at 1 350 ± 25 °C. In the beginning of the melting, argon is blown at the bottom, and then oxygen is blown when the temperature meets the requirements.

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At the same time, the slag with a mass fraction of 3 wt. % is added to the surface of the molten iron. The slag composition and oxygen blowing intensity as well as blowing time are listed in Table 2. The temperature was measured and hot metal was sampled every 5 minutes or 10 minutes during the blowing process. Carbon and sulfur in samples were analyzed by high-frequency infrared carbon and sulfur analyzer CS - 800, and other elements in hot metal were analyzed by Leco - ICP6 000.

Table 1 **Chemical composition/wt. %**

C	Si	Mn	P	S	Nb
4,0-4,5	0,3-0,4	0,3-0,4	0,09-0,1	0,05-0,05	0,01 -0,032

Table 2 **Experimental condition**

Blowing method	A	B	C
O$_2$ Blowing flow /×10^{3}Nm^3/h	0,3	0,2	0,3
Composition of slag / wt.%	-	60 %CaO-27 %SiO$_2$-13 %CaF$_2$	60 %CaO-25 %SiO$_2$-15 %CaF$_2$
Blowing time /min	45	240	75
Pig iron weight /kg	55,50	67,85	48,60

RESULTS AND DISCUSSION

Figures 1 (exp. A, B and C) show the variations of C, Si, Mn, Nb in hot metal with time in blowing melting process. It is found that silicon and manganese are oxidized slowly, while Nb and carbon are not oxidized when the blowing melting time is less than 25 min as shown on the left side of line While all elements in hot metal are oxidized, and Nb is slowly oxidized when the blowing melting time is more than 25min as can be seen on the right of line a in the Figure 1 (A). At the end of melting, silicon content is decreased to 0,035 %, desilication rate is 4,8 %/min, demanganization rate is 2,7 %/min, decarburization rate is 0,34 %/min, Nb content in hot metal is decreased from 0,015 % to 0,01 %, and the oxidation rate of Nb is 0,09 %/min. In the early stage of oxygen soft blowing smelting, oxygen partial pressure in hot metal is low, the oxidation rate of silicon in molten iron is higher than the rate of manganese. With the increase of oxygen partial pressure in hot metal, the elements in hot metal are oxidized, and the oxidation rate of Nb in hot metal is lower than that of other elements. The result shows that silicon is preferentially oxidized to other elements in hot metal in the oxygen bottom blowing process, which is in agreement with the research work by Lin, et al. [11].

In experiment B, Nb content is 0,015 %, the intensity of blowing oxygen is 0,5 Nm^3/t·min, whereas Nb content is 0,032 % and the intensity of blowing oxygen is 0,6 Nm^3/t·min in experiment C. The oxidization rates of silicon and carbon are higher in both of the experiments B and C. While in experiment B, the oxidization rate of manganese is lower when smelting time is shorter than 120 min, which is shown as line b in Figure 1 (B), and it is higher when smelting time is longer than 120 min, the oxidization rates of manganese is 0,497 %/min on the right side of line b. While in experiment C, the oxidization rate of Nb and manganese is higher when smelting time is longer than 30 min as shown in line c in Figure 1 (C), where the oxidization rate of manganese is 0,5 %/min on the right side of line c. It is found that the oxidization rates of manganese are same in experiments B and C, while the oxidization rates of silicon is 2,04 %/min and 11,74 %/

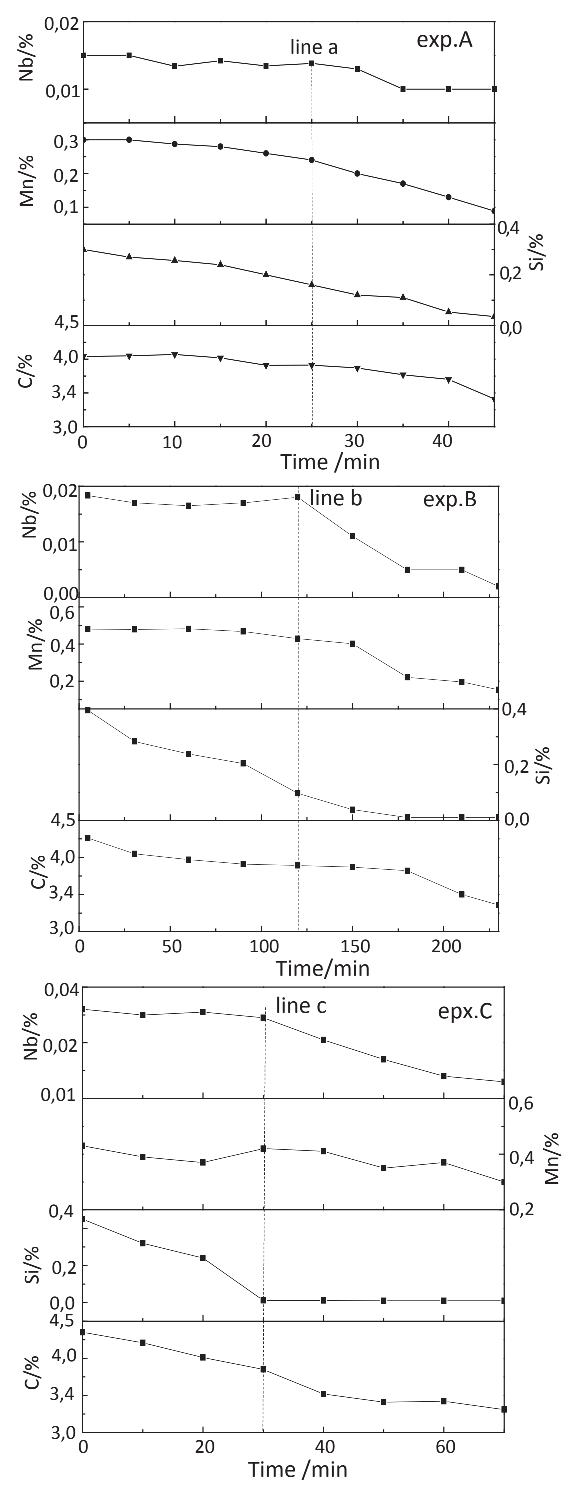

Figure 1 Change of concentrations of C, Si, Mn and Nb with time

min, respectively, and the oxidization rate of Nb is respectively 0,96 %/min and 2,4 %/min. Besides, the oxidization rates of silicon and Nb in experiment C are higher than that in experiment B, and Nb begins to be oxidized massively when the content of silicon is decreased to 0,01 %.

As shown in Figure 1, manganese in the molten iron is hardly to be oxidized in the initial stage of smelting process in the experiments A and B, while Nb and manganese in the hot metal begin to be oxidized massively when silicon is oxidized to be 0,01 %. And then, silicon and manganese in molten iron are oxidized simultaneously. It is also found that the manganese oxidation rate in molten iron is decreased and the silicon oxidation rate is increased with the increase of slag basicity as reported in references [12-13]. What found also in experiment C is that the oxidation rate of silicon in molten iron is increased with both of the increase of the oxygen blowing intensity and slag basicity. Especially, oxygen potential decreases gradually from bottom to top of molten iron during the oxygen bottom blowing process, which can avoid formation of massive FeO in slag and promote the selective oxidation of elements in molten iron. When silicon content in molten iron is decreased to 0,01 %, Nb in hot metal begins to be oxidized. In general, selective recycling of Nb in hot metal should be divided into three steps: firstly, silicon in the hot metal is oxidized to 0,01 %; secondly, Nb in the hot metal begins to be oxidized, and Nb oxide gets into slag, then Nb is extracted from the Nb oxide containing slag; finally, dephosphorization and manganese extraction in molten iron are carried out in the smelting process, which means that manganese can also be recycled as Nb so as to avoid massive oxidation and getting into slag of manganese.

In the experiments, the phosphorus content in molten iron keeps unchanged in the oxygen bottom blowing smelting process as shown in Figure 2, and the gasification dephosphorization is also inapplicable in the process[14]. To be pointed out, in hot metal pretreatment processing, dephosphorization is usually carried out under condition that basic slag is added and silicon is oxidized and its content is decreased to a certain value. It is also found in experiment B and C that desulphurization can occur in hot metal by adding basic slag, while desulphurization in hot metal cannot be realized without using basic slag in experiment A. With lasting of the smelting, sulfur in the slag will gradually get into the molten iron, which results in the increase of the sulfur content in molten iron as shown in Figure 3.

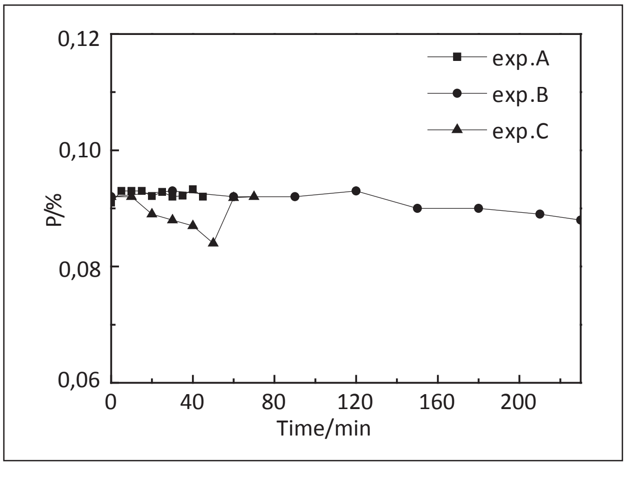

Figure 2 Variation of P with time in experiments A, B and C

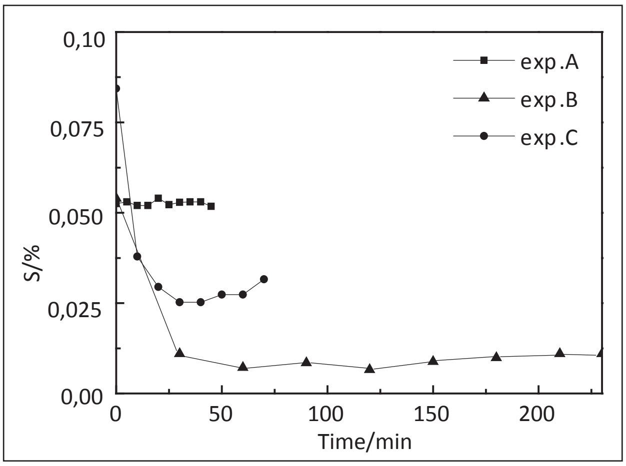

Figure 3 Variation of S with time in experiments A,B and C

CONCLUSIONS

In the work, the behaviors of selective oxidation of Nb, silicon and other elements in molten iron were investigated in the smelting process which was carried out separately with and without adding slag. The results reveals that silicon is preferentially oxidized than other elements in hot metal both with and without adding slag in oxygen blowing smelting process. In the process with adding slag, Nb is not oxidized until silicon content is decreased to be below 0,01 %. With increasing both the oxygen blowing intensity and slag basicity, silicon and Nb oxidation rates are increased, and manganese is extracted partially. Besides, bottom blowing oxygen provides suitable oxidation kinetics condition for elements in hot metal in the smelting process, and preferential oxidation of elements are realized. Without adding slag in the blowing smelting process, silicon and manganese are more preferentially oxidized than Nb in hot metal, while with adding slag, carbon and silicon are more preferentially oxidized than Nb and manganese. Moreover, in the blowing smelting process, adding basic slag is profitable to silicon oxidation and decrease of sulfur content in hot metal. On the contrary, phosphorus is not oxidized and its content in molten iron is unchanged both with and without adding slag in the oxygen blowing smelting process.

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Note: The responsible translator for English language is Z.Y. Xu - Inner Mongolia University of Technology, China