Analysis and control for desiliconization process of low niobium hot metal by experimental approach

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Abstract: To clarify selective oxidation of silicon prior to the other elements such as niobium，the pre-desiliconization process of low niobium hot metal has been experimentally investigated. Desiliconization experiments were carried out in a medium frequency induction furnace with bottom-soft- blowing for promoting selective oxidation. The effect of initial slag addition was taken into account. It has been found that selective oxidization of silicon in preference to the other elements including niobium occurs under the good dynamical condition and with initial basic slag. In effective thermodynamic and dynamical conditions for selective oxidation, niobium may be oxidized prior to manganese. The initial basic slag addition was conducive to selective oxidation of elements in hot metal, which gave good conditions for improving silicon oxidation and suppressing of the oxidization of niobium and manganese. The bottom-soft-blowing might cause that the partial oxygen pressure in bath lowed down with the bath height rising, which could be a good dynamical condition for selective oxidation. The pretreatment process of low niobium hot metal could be divided into three stages: the desiliconization, extraction of niobium and manganese and dephosphorization.

Keywords: Hot metal treatment, desiliconization, niobium, selective oxidation, soft blowing

1. Introduction

Bayan Obo Ore is a poly-metallic ore predominantly containing iron, niobium, rare earth (RE) elements, etc. Because of chemical composition of raw mineral materials, niobium is an important element in the hot metal in Baotou Steel, with a content of 0.015~0.034%. But in the following BOF process, most of niobium is oxidized into BOF slag in which the content of niobium oxides is 0.2~0.3%, while niobium content in molten steel is only about 3~5 ppm[1]. Especially, niobium in BOF slag is hardly used. In order to efficiently utilize niobium resource in hot metal of Baotou Steel, the hot metal pretreatment is introduced to enrich niobium and to decrease the content of silicon in niobium-enriched slag. In order to have a better understanding of the selective oxidization of silicon in preference to the other elements such as niobium, desiliconization process of low niobium hot metal was studied firstly in this study.

Hot metal desiliconization, as a key process of hot metal treatment, has been interested in accompanied with dephosorization and desulphurization, especially in Japan [2-6]. Its main purpose is to decrease the amount of slag generated and to raise the productivity, consequently to reduce the total cost. Yukiyoshi Itoh et al [2] reported the development of slag minimum refining process by desiliconization of hot metal, and Hideki Ono-Nakazato et al[3] reported the oxidation behavior of silicon and carbon in molten iron-carbon-silicon alloys with carbon dioxide. Minoru Ishikawa [4] reported the analysis of hot metal desiliconization behavior in converter experiments by coupled reaction model. Shin-ya Kitamura et al [5] reported the analysis of dephosphorization reaction using a simulation model of hot metal dephosphorization by multiphase slag, and Farshid Pahlevani et al[6] reported the behavior of vanadium and niobium during hot metal dephosphorization by CaO – SiO_2 – Fe_tO slag. The selective oxidation of niobium and other related elements in liquid iron has been pointed out based on the thermodynamic calculations [7], experimental analysis[8,9] and mathematical model[10]. However, a little information is available concerning the effect of types of oxygen blowing and addition of initial slag which has an important role in selective oxidation of elements in hot metal.

2. Thermodynamic Analysis

It is found in Fig.1 that the relationship of the standard Gibbs energy [11,12] of the oxidation of elements in hot metal with temperature. The changes of standard Gibbs energy of the reactions for various elements be oxidized by 1 mole of dissolved oxygen become more negative in the order of silicon, niobium, manganese and phosphorus. So silicon can be oxidized prior to manganese, niobium and phosphorus under the standard state. Niobium in the bath is oxidized prior to manganese, but phosphorus is not oxidized under the standard state. Transition temperature of selective oxidization between silicon and carbon is 1507℃, while transition temperature between niobium and carbon is 1391℃. The lower reaction temperature is helpful to desiliconization. However, the composition of molten-slag and mass transfer in hot metal and slag are main factors to determine the quantity of an element oxidized

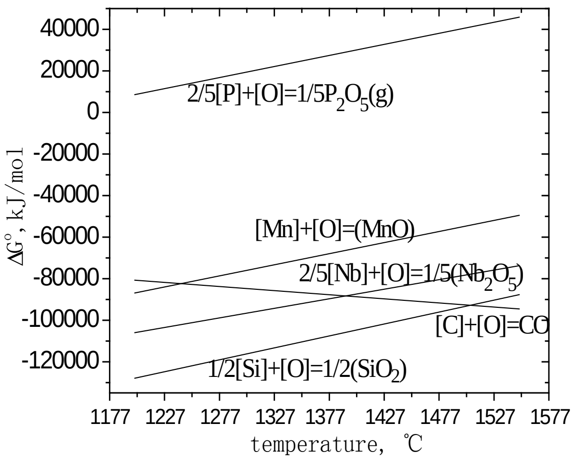

Fig.1 Relationship of the standard Gibbs energy of elements oxidizing reaction with temperature

3. Experimental

The pig iron containing niobium from Baotou Steel, industrial pure oxygen (purity of more than 98%) and industrial pure argon (purity of more than 99%) with can packing were used as raw materials for experiments. The composition of the pig iron is shown in Table1. The experimental apparatus was a medium frequency melting furnace of 100kVA with a lining formed Mg-Al spinel, which was 220 mm in inner diameter. A bottom blowing system was equipped, which includes a porous brick (its apparent porosity was more than 12.5% and bulk density was lower than 3.75 $g.cm^{-3}$). The pig iron of about 50 kg was charged into the furnace and was heated up for melting while industrial pure argon was blown though the bottom blowing system. When the temperature of hot metal was heated to a specified temperature of 1350℃, industrial pure oxygen was blown through the porous brick instead of argon. In oxygen blowing course, the temperature of the hot metal was measured by a rapid high-temperature thermocouple and maintained at 1350±25℃ by adjusting the furnace power. Samples of molten metal were taken out with a sampling cup in 5 to 20 min intervals. The content of carbon and sulfur of all samples were analyzed by high-frequency combustion and infra-red absorption analysis meter, and other elements such as silicon, manganese, phosphorus, and niobium by ICP-AES.

In order to clarify the affection of initial slag addition on selective oxidization of elements in the hot metal, the slag addition with a weight ratio of 3% to the pig iron was dropped onto the metal surface at the beginning of oxygen blowing. The predetermined composition of initial slag agent, oxygen supply intensity and pig iron quantity are listed in Table 2.

Table 1 Composition of pig iron form Baotou Steel（mass%）

C	Si	Mn	P	S	Nb
4.2~4.5	0.30~0.45	0.3~0.7	0.07~0.095	0.058~0.75	0.015~0.028

Table 2 Experimental conditions

NO.	Pig iron weight(kg)	Composition of slag (mass %)	Oxygen blowing	
			Intensity ($Nm^3/t\cdot min$)	Time (min)
A	55.50	—	0.3	45
B	67.85	$60CaO-27SiO_2-13CaF_2$	0.9	240
C	48.60	$60CaO-25SiO_2-15CaF_2$	1.5	75

4. Results and Discussion

The experimental results are shown in Fig.2 to Fig.6 according to the experimental conditions shown in Table 2.

Fig.2 shows the variation of the bath temperature and the element content in the hot metal with oxygen blowing time in run A without initial slag. Just as shown in Fig.2, in early stage (about 15 minutes) during oxygen blowing, silicon was oxidized while carbon, manganese and niobium were not oxidized, and then carbon, manganese and niobium were oxidized simultaneously with silicon oxidation, but niobium oxidation was very slowly. At the end of oxygen blowing, [Si] of hot metal was decreased to 0.035% and desiliconization ratio was 82%. Oxidation rate of manganese was 57%, and carbon was 8.4%. But [Nb] in hot metal decreased from 0.015% to 0.010%, its ratio of oxidation is only 33%. For oxygen partial pressure in the bath was lower in the initial stage of oxygen blowing, the condition for selective oxidization of silicon was better. However, with oxygen partial pressure in the bath rising, selective oxidation of silicon prior to the other elements was not obvious, just as reported by Zongcai LIN [8].

Fig.3 and Fig.4 show the variation of the bath temperature and the element content in the hot metal with oxygen blowing course in run B and run C both with basic initial slag. The main differences between run B and run C were (1) that the initial niobium content of 0.028% in run C was higher than 0.015% in run B, and (2) that the oxygen supply intensity of $0.9Nm^3/t\cdot min$ in run B was lower than $1.5 Nm^3/t\cdot min$ in run C, and (3) oxygen blowing time. Just as shown in Fig.3 and Fig.4, silicon of the bath was oxidized rapidly in both runs. Carbon was oxidized from the beginning of oxygen blowing in run C shown in Fig.4, while the oxidation was very slowly in run B in Fig.3. The main reason was the difference of the oxygen supply intensity. While the oxidation of manganese and niobium was with the same rule In the early stage during oxygen blowing, manganese and niobium were not oxidized, until [Si] decreased to a certain extent, for example 0.089% in run B. But niobium was oxidized prior to manganese, more obvious in run C shown in Fig.4.

Compared with the literatures [8,9], behavior of manganese oxidation was obviously different. In our study, especially in run B and run C with basic initial slag, manganese oxidation began still silicon was oxidized to a great degree, while manganese was oxidized easily at the beginning of oxygen blowing in literatures [8,9]. There are two main reasons, one is the oxygen blowing type, the other is the basic initial slag addition. In experiments, the bottom blowing system with a porous brick was equipped and the oxygen supply intensity was small, so the partial oxygen pressure in bath falls as the height of bath rising, the high partial oxygen pressure zone was at the bath bottom rather than near the oxygen jet flow. This is helpful to selective oxidation of element in hot metal and avoiding the formation of high FeO slag. Basic initial slag was used to selective oxidation of elements in hot metal, which provided good conditions for improving silicon oxidation and suppressing oxidization of niobium and manganese. Consequently, pretreatment process for selective oxidation of low niobium hot metal may be divided into three stages, which were respectively desiliconization, exatracing niobium and manganese, and dephosphorization. In niobium exatracing process, manganese was recovered at the meantime.

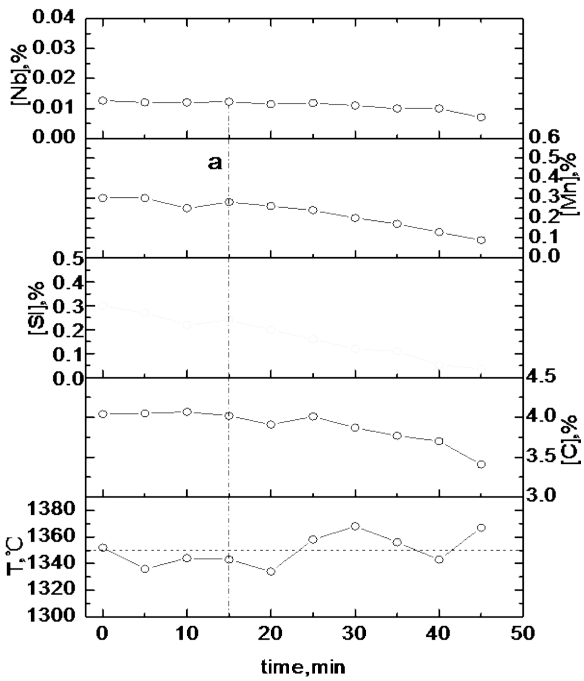

Fig.2 Variation of hot metal temperature and [C], [Si], [Mn], [Nb] with time in Run A

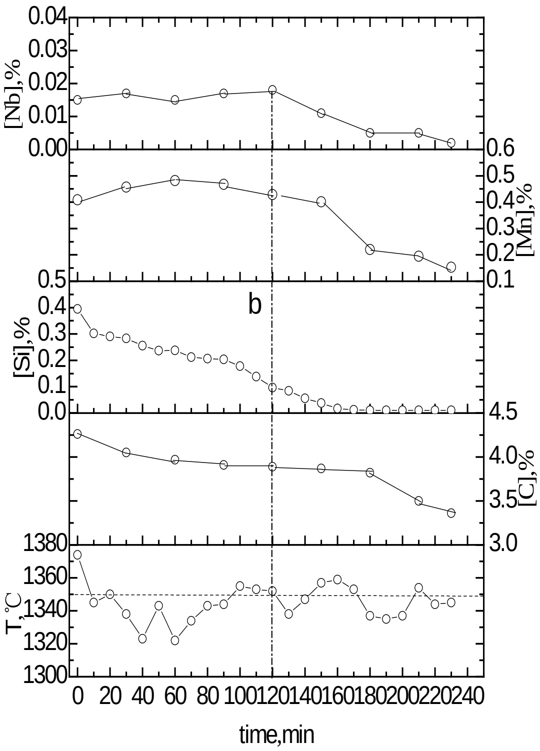

Fig.3 Variation of hot metal temperature and [C], [Si], [Mn], [Nb] with time in Run B

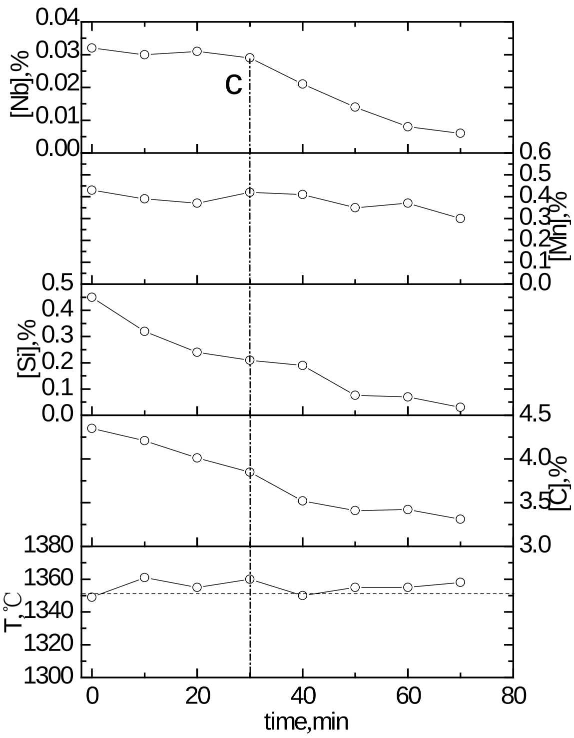

Fig.4 Variation of hot metal temperature and [C], [Si], [Mn], [Nb] with time in Run C

For all the three experimental runs, [P] in hot metal hardly decreased with oxygen blowing, as shown in Fig.5. This is in agreement with the thermodynamic result shown in Fig.1, which phosphorus gasification reported in the literature [5] did not happen in our experiment, which could be caused by the mode of oxygen blowing.

Fig.6 gives the variations of sulphur content with time for all the three experimental runs. Initial basic slag addition removed sulphur of hot metal at the beginning of oxygen blowing in run B and run C, but with the slag basicity lower, resulfurization occured as shown in Fig.6.

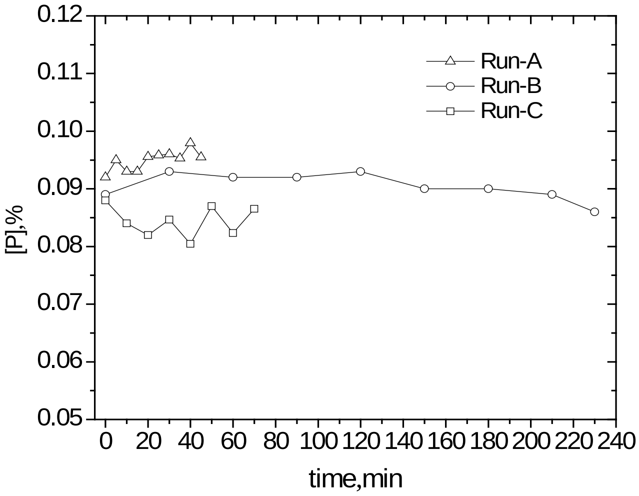

Fig.5 Variation of [P] with time in Run A, B and C

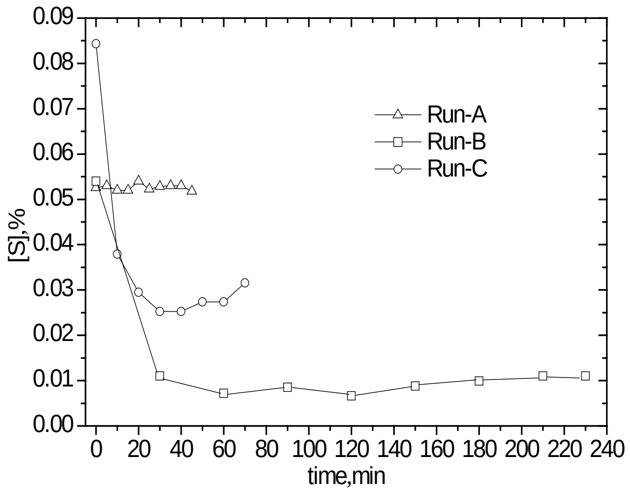

Fig.6 Variation of [S] with time in Run A, B and C

5. Conclusion

The selective oxidation of silicon prior to the other elements such as niobium was investigated. The bottom-soft-blowing and the addition of initial basic slag affect obviously the oxidizing behavior of elements in low niobium hot metal.

1) The pretreatment process for selective oxidation of low niobium hot metal may be divided into three stages: the desiliconization, extraction of niobium and manganese, as well as dephosphorization. In

effective thermodynamic and dynamical conditions for selective oxidation, niobium may be oxidized prior to manganese.

2) The bottom- soft- blowing made that the partial oxygen pressure in bath falls as the height of bath rising. This could be helpful to selective oxidation of element in hot metal and avoiding the formation of high FeO slag.

3) Initial basic slag was used to selective oxidation of elements in hot metal, which could provide good conditions for improving silicon oxidation and suppressing oxidization of niobium and manganese.

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