

INVESTIGATION ON REMOVAL OF Nb FROM Nb-BEARING HOT METAL WITH CO₂

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This paper focuses on removal niobium from Nb-bearing hot metal by bottom blown-CO₂ gas at flow rate of 1,0×10³Nm³/h, 1,5×10³ Nm³/h at 1 350 °C and 1 450 °C in a medium induction furnace. The results show that Nb and P are oxidized and the ratio of Nb to P in Nb-bearing slag at blowing termination reaches to 46,66 at 1 350 °C and CO₂ flow rate of 1,5m³/h, which is more than that in the other condition; it improves to remove more Nb from hot metal with bottom-blown CO₂ at 1 350 °C than at 1 450 °C; Nb starts to oxidize by CO₂ to form slag when Si content in molten iron decreases to low 0,1 wt. %.

Key words: hot metal, removal of Nb, bottom-CO₂, time, temperature

INTRODUCTION

Niobium is a strategical metal for micro-alloyed steel used in steelmaking technology such as electrical superconducting alloy and heat-resisting alloy. It is rich in Bayan - obo Iron Ore in Baotou Steel in China. However, there is no way to separate Nb from the ore for Nb-mineral is intimately paragenetic with other minerals in the Iron Ore. So, Nb, reduced from the Iron Ore in blast furnace, amounted to about 0,02 to 0,1 wt. % of the molten iron, is not reused in subsequent process in Baotou Steel. Several literatures [1 - 4] have been made for recovery of niobium from Nb-bearing hot metal. Chen et al. [5] reported the removal of Nb by oxidation process with bottom-blowing oxygen. Zhang et al.[6] also reported to recover Nb with ferric oxide. However, no information is available concerning the effect of CO₂ which has an important role in a recovery of Nb operation.

In the study, bottom - blown CO₂ process was used to remove Nb from the hot metal in a 100 kg-graded medium induction furnace. By the process, it is able to analyze the oxidized behavior of Nb and Si and the ratio of niobium to phosphorus in Nb-containing slag in order to improve removal of Nb from the hot metal. On the other hand, it becomes important to solve 'CO₂ problem' relevant to global warming and the control of CO₂ emission[7,8] is also an important problem. This paper focused on the effect of sinter behavior with biomass as additive. By sintering cup experiment

EXPERIMENTAL METHOD

Removal of Nb experiment was done in a 100 kg-grade medium induction furnace with bottom-blowing facilities. Nb-bearing pig iron with chemical shown in Table 1 was put in the furnace and heated to molten iron. When the hot iron was heated to 1 350 °C or 1 450 °C, CO₂ was injected into the molten iron through the bottom blowing lance of the furnace. Experimental conditions are shown in Table 2. The first metal sample was taken just before the start of bottom CO₂ blowing, but the last slag sample was taken after the termination of CO₂ blowing. Other metal samples were taken at 10 minutes or 15 minutes intervals, and hot metal temperature was measured with platinum - rhodium thermocouple. After metal sample was taken out from the furnace, the composition (except for C) was analyzed by Thermo iCAP – MS6300, while the carbon content was analyzed by LECO - CS844. At the blowing end, slag was sampled by Fe wire and analyzed by chemical methods combined with the TG - DTG system, investigated the changes of the relevant performance indexes of this sinter behavior, explored the emission laws of harmful gases in flue gas emissions and analyzed the mechanism of emission reduction.

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

No.	C	Si	Mn	P	Nb
A	3,6	0,10	0,23	0,089	0,035
B	3,5	0,11	0,14	0,097	0,037
C	3,7	0,13	0,20	0,089	0,033
D	3,7	0,17	0,24	0,088	0,030

Table 2 **Experimental condition**

Blowing method	A	B	C	D
CO ₂ Blowing flow /×10 ³ Nm ³ /h	1,5	1,0	1,0	1,5
Temperature/°C	1 350	1 450	1 350	1 450
Blowing time /min	130	130	240	150

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Experimental results

Figure 1 shows the relation between the ratio of MnO to the sum of SiO₂ and P₂O₅, i. e. $(\text{MnO})/((\text{SiO}_2)+(\text{P}_2\text{O}_5))$, and the ratio of Nb to P $(\text{Nb})/(\text{P})$, in the slag, in which $(\text{Nb})/(\text{P})$ increase linearly with $(\text{MnO})/((\text{SiO}_2)+(\text{P}_2\text{O}_5))$. The ratio of Nb to P increases with the MnO content increased in the slag and with SiO₂ and P₂O₅ content in the slag decreased. So, from the result, the ratio of Nb to P is not more than 20 unless $(\text{MnO})/((\text{SiO}_2)+(\text{P}_2\text{O}_5))$ is more 0,635 in the slag.

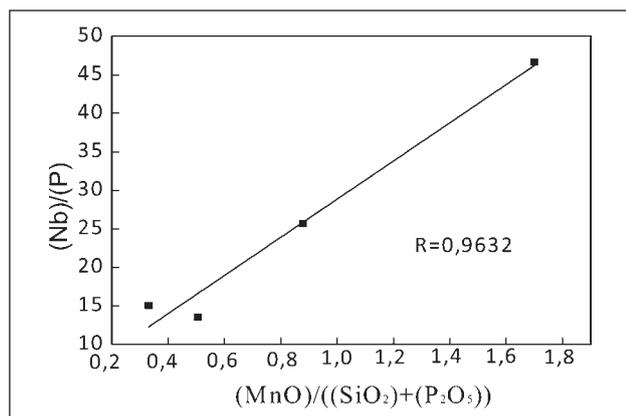


Figure 1 Relation between the ratio of $(\text{MnO})/((\text{SiO}_2)+(\text{P}_2\text{O}_5))$ and $(\text{Nb})/(\text{P})$

Figure 2 shows the variation of concentrations of Si, Mn, P, C and Nb in hot metal and temperature of hot metal with time. The Nb content decreased significantly when Si, Mn and Nb were oxidized by bottom blowing CO₂ for 70 minutes at 1 350 °C in Test A, shown in line a, while it decrease at 1 450 °C in Test B, shown in line b, at the same blowing intensity. However, it decreased markedly when contents of Si, Mn, and Nb of hot metal decreased greatly after CO₂-blowing for 30 minutes at 1 350 °C in Test C at CO₂-blowing flow up to $1,5 \times 10^{-3}$ Nm³/h, shown in line c, while it decreased for 140 minutes at 1 450 °C at the same CO₂-blowing intensity in Test D, shown in line d. In all tests, the content of P decreased from 5 percent to 10 percent of initial P content. On the other hand, niobium was significantly removed to form slag with other oxide such silica and manganese oxide while Si content in the molten metal decreased to low 0,1 % in the molten iron. Temperature of hot metal was not significantly different with time in all tests.

In the termination of bottom-blown CO₂, the content of oxides of Si, Mn, P, Fe and Nb in the slag are shown in Table 3, in which the ratio of Nb to P in the slag in Test A is 46,66, more than other tests for its lower blowing temperature and larger blowing intensity.

Table 3 Composition of Nb-bearing slag in experiments

No.	TFe	MnO	SiO ₂	P ₂ O ₅	Nb ₂ O ₅	(Nb)/(P)
A	8,1	14,8	29,4	0,16	4,92	46,66
B	5,3	6,5	19,5	0,11	1,09	15,04
C	19,9	36,2	21,1	0,13	2,2	25,67
D	32,2	7,2	14,1	0,15	1,34	13,54

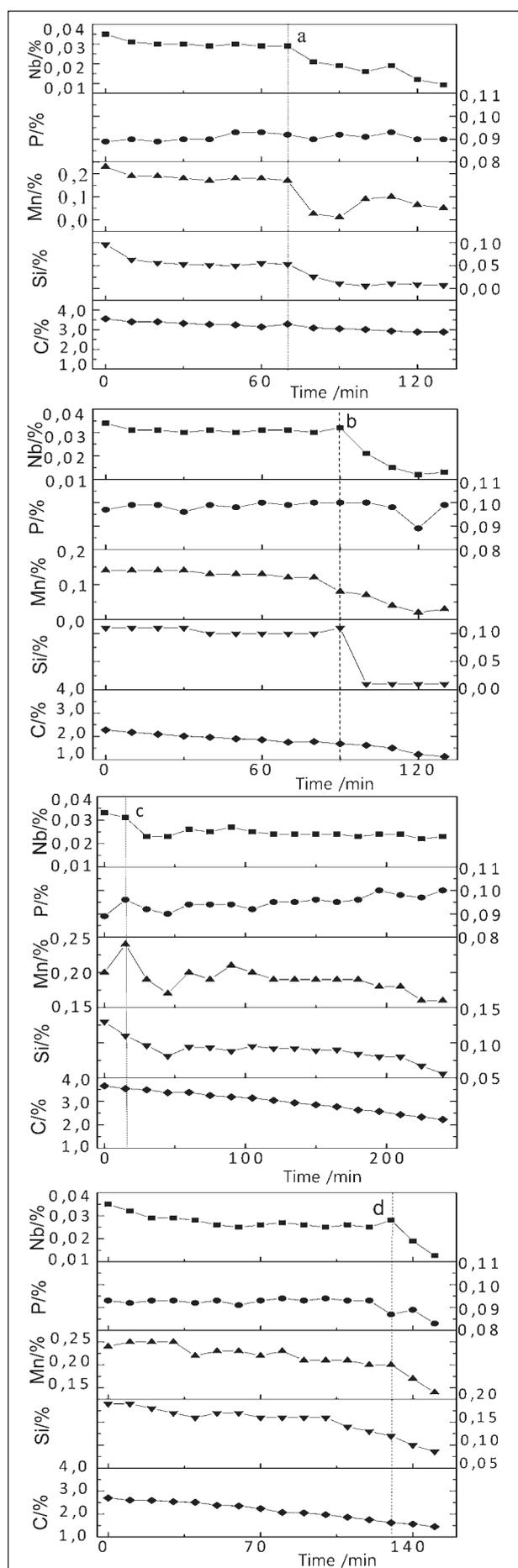
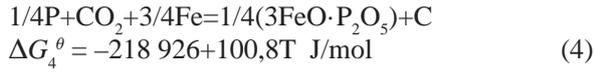
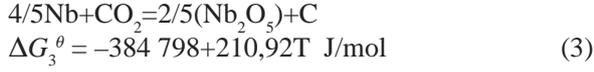
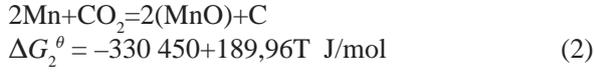


Figure 2 Change of concentrations of Si, Mn, P, C and Nb with time

Experimental analysis

Reactions for removal of Nb and other elements oxidized in the hot metal with CO₂ are represented by Eqs.(1) through (4)[9], respectively:



The standard Gibbs energies for Eqs.(1) though (4) are represented by Eqs.(5) though (7):

$$\Delta G_1 = -436\,103 + 225,02T + RT \ln \frac{a_{(\text{SiO}_2)} a_C^2}{p_{\text{CO}_2} a_{\text{Si}}} \quad (5)$$

$$\Delta G_2 = -330\,450 + 189,96T + RT \ln \frac{a_{(\text{MnO})}^2 a_C^2}{p_{\text{CO}_2} a_{\text{Mn}}^2} \quad (6)$$

$$\Delta G_3 = -961\,995 + 527,3T + RT \ln \frac{a_{(\text{Nb}_2\text{O}_5)} a_C^{5/2}}{p_{\text{CO}_2} a_{\text{Nb}}^2} \quad (7)$$

$$\Delta G_4 = -292\,433 + 420,44T + RT \ln \frac{a_{(\text{P}_2\text{O}_5)} a_C^{5/2}}{p_{\text{CO}_2} a_{\text{P}}^2} \quad (8)$$

Where T denotes as reaction temperature $a_{(\text{SiO}_2)}$, a_C and $a_{(\text{Nb}_2\text{O}_5)}$ denote activity of SiO₂, carbon, Nb₂O₅ relative to pure solids, and a_{Si} and a_{Nb} activity of silicon and niobium. a_{Si} , a_{Nb} and a_C are represented by Eqs.(7) through (8) based on Wagner’s model:

$$a_i = f_i^i \quad (i = \text{C, Si, Mn, P, Nb})$$

$$\log f_i^j = \sum_{j=\text{C, Nb}}^{i, \text{Mn}} e_i^j j \quad (9)$$

Where f denotes activity coefficient of Nb, Si or C in Nb-containing hot iron. e_i^j is the interaction coefficient of element j on the element i . e_i^j is represents by Table 3[10].

Table 3 Interaction parameter of i and j

$i \backslash e_i^j$	Si	Nb	C	P	Mn
Si	0,11	0,04	0,18	0,11	0,002
Nb	0,13	-0,22	-0,49	-0,11	0,0028
C	0,08	-0,06	0,14	0,051	-0,012
P	0,12	-0,017	0,13	0,029	0
Mn	0,022	0,0035	-0,07	-0,0035	0

Oxidation equilibrium for removal of Nb reaction of Nb-bearing hot metal with CO₂ based on Eqs.(1) through (4) at temperatures calculated using the above equations is shown in Figure 2 under the condition of $a_{(\text{Nb}_2\text{O}_5)} = 8,8e^{-3}$ [11], $a_{(3\text{FeO} \cdot \text{Nb}_2\text{O}_5)} = 1e^{-3}$ [11] and Eqs.(9), (10), and Table 2 and Table 3.

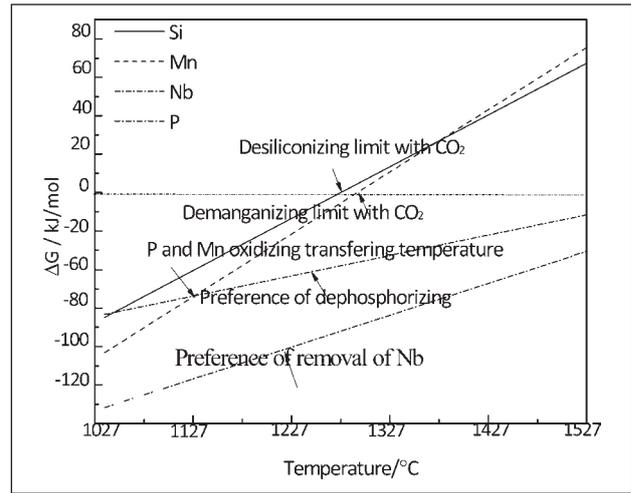


Figure 3 Change of ΔG of [C],[Si],[Mn] and [P] oxidized with CO₂ at temperatures

$$a_{(\text{SiO}_2)} = 0,5854 \times \exp((0,3392 \times T + 979,1)/T) \quad (10)$$

$$a_{(\text{SiO}_2)} = 0,2899 \times \exp((6,19 \times T - 13744,0)/T) \quad (11)$$

It is found from Figure 3 that the temperature of desiliconization limit with CO₂ is 1 277 °C, and that of removal of Mn limit is 1 295 °C. However, under the condition of bottom-blowing CO₂, removal of Nb and dephosphorization is performed in preference to silicon and Manganese at every blowing temperature. Moreover, it can be concluded impossible to remove Phosphorus from Nb-bearing hot metal while niobium is removed from the metal at low phosphorus and manganese oxidizing transferring temperature, which is 1 129 °C, for below 1 129 °C, manganese is oxidized by CO₂ in preference to phosphorus in hot metal [12]; Nb and P can suppress silicon and manganese from oxidation with CO₂ at higher temperature than 1 129 °C. In addition, the Nb - P ratio can decrease at higher temperature for oxidizing ΔG of Nb is close to and that of P at higher temperature.

CONCLUSIONS

Removal of Nb and oxidized behavior of the elements in the low-Si and Nb-containing hot iron was researched by bottom-blown CO₂ in the medium.

- (1) It is necessary to remove niobium from Nb-bearing hot metal with CO₂, because niobium was oxidized in preference to other elements in the hot metal by thermodynamic calculation. The conclusions are as follows:
- (2) It is subject to carry out for Nb to extract form Nb-containing hot iron at low temperature and large blowing intensity in all experiments, in which the ratio of Nb to P in the slag is 46,66 at 1 350 °C and 1,5×10⁻³Nm³/h CO₂- blowing flow.
- (3) Si, Mn, Pand C are oxidized in the hotmolten in case of removal of Nb, and Nb of the molten iron is oxidized significantly while Si content of the molten metal to be low 0,1 %.

Acknowledgments

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