

Thermodynamic studies on selective oxidation of Nb, P and C in dephosphorization of low niobium hot metal

Yongli JIN^{1),2)}, Zengwu ZHAO²⁾, Jiayu Zhang¹⁾ and Baowei LI²⁾

1) School of Materials Science and Engineering, Shanghai University, Shanghai, 200072, China

2) Inner Mongolia Key Laboratory for Utilization of Bayan Obo Multi-Metallic Resources, Elected State Key Laboratory, Inner Mongolia University of Science and Technology, Baotou 014010, China

Abstract: The main problem with the efficient utilization of Nb resource in the Boyan Obo Ore lies in the selective oxidation of [Nb], [P] and [C]. In this work, thermodynamic studies have been conducted to determine the conditions of selective oxidation of [Nb], [P] and [C] in low niobium hot metal in the process of oxidizing dephosphorization. The thermodynamic condition for dephosphorization was determined as:

$$\lg a_{(P_2O_5)} \leq \frac{38754}{T} - 27.82 + 5 \lg a_{[O]} + 2 \lg a_{[P]}$$

The condition for retaining Nb from oxidation is:

$$\lg a_{(O-Nb)} \leq \frac{1}{5} \lg a_{(Nb_2O_5)} - \frac{2}{5} \lg f_{[Nb]} - \frac{2}{5} \lg [\% Nb] - \frac{70425}{T} + 28.14$$

The oxygen activity for oxidation of Nb, C and P is relevant to the initial [C] content in hot metal. The equilibrium oxygen activity of Nb-O reaction increases with an increase of the [C] content, whereas the equilibrium oxygen activity of C-O and P-O reactions varies oppositely with the [C] content. The reduction of $a_{P_2O_5}$ results in a decrease of the [C] content required for removing P and retaining Nb, as well as makes the process of dephosphorization more feasible. The increase of temperature decreases the [C] content of selective oxidation of Nb and P, but is unfavorable to dephosphorization.

Under the conditions of $T > 1650K$, $[C] = 4.0\%$, $[Nb] = 0.02\%$, $a_{P_2O_5} = 10^{-24}$, $a_{Nb_2O_5} = 10^{-10}$, [P] in hot metal can be removed to 0.01% while 0.02% of [Nb] can be retained in hot metal without oxidized.

Keywords: Dephosphorization, selective oxidation, niobium, phosphorus, thermodynamics

1. Introduction

The Bayan Obo Ore in Inner Mongolia is a polymetallic ore consisting predominately of iron, niobium and rear earth (RE) elements. Over the past half century, extensive works have been carried out in R&D on the resource of Bayan Obo Ore. A variety of technological and industrial achievements have been attained [1-3], such as magnetic-weak magnetic-flotation-reverse flotation process, techniques of RE metallurgy: decomposition of RE concentrate by sulfuric acid, and separation and purification by hydrochloric acid extraction system, niobium iron manufacturing process of blast furnace-convert-electric furnace-electric furnace, etc. However, due to the mineralogical complexity of the deposit

and limitation of the current techniques, there is still a great challenge to effective utilisation of valuable Fe, Nb and RE elements in the Bayan Obo Ore. Currently, hot metal contains about 0.02-0.04% of Nb through ironmaking of the Bayan Obo Nb iron ore, in which niobium pentoxide content is about 0.03-0.05%. Almost all of Nb in hot metal is oxidized into BOF slag in the following BOF steelmaking process instead of being retained in the steel product. This causes a significant waste of Nb resource. In order to efficiently utilize Nb resource in hot metal and achieve simultaneous extraction of Fe and Nb, it has been proposed to refine Nb-bearing hot metal into Nb-microalloyed steel on the basis of principles of elementary reaction and element selective oxidation. The previous studies^[4-5] have showed that the effective separation of Nb and P (i.e. selective oxidation of Nb, P and C in the process of oxidative dephosphorization of low niobium hot metal) is critical to the whole refinery process. Furthermore, as reported in literature, the major difficulty with making Nb-Fe alloys from Bayan Obo Nb iron ore is how to increase the ratio of Nb to P in the alloy product. In this regard, this manuscript will report a thermodynamic study on oxidative behaviours of Nb, P and C in the process of oxidative refining of low niobium hot metal, investigating the effects of initial [C], temperature, activity of (Nb₂O₅) and (P₂O₅) in slag on the oxidation of Nb, P and C, and determining the thermodynamic conditions for removing phosphorus but retaining Niobium.

2. Reactions and basic parameters in oxidative dephosphorization of low niobium hot metal

Three basic reactions of P, Nb and C oxidation are involved in the process of oxidative dephosphorization of low niobium hot metal. The chemical reaction equations and their standard Gibbs free energy changes are^[6-7]:

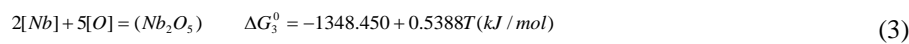
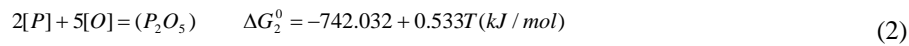
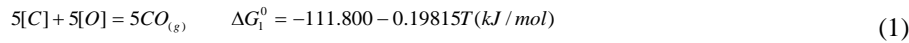


Table 1. Composition of hot metal and interaction coefficient of each component

Chemical composition	[C]	[Si]	[Mn]	[P]	[S]	[Nb]	[Ti]
[%]	4.00	0.10	0.40	0.10	0.004	0.02	0.05
$e_p^j(1873K)$	0.13	0.12	0	0.062	0.028	-0.017	-0.0026
$e_{Nb}^j(1873K)$	-0.49	0.15	0.0028	-0.06	-0.047	-0.22	0
$e_C^j(1873K)$	0.14	0.08	-0.012	0.051	0.046	-0.06	-0.0381

Low niobium hot metal of Baotou Steel was used for calculation of the equilibrium oxygen activity of Nb, P and C oxidation in the process of oxidative dephosphorization, analysis of effects of temperature, initial [C] content and activity of (Nb₂O₅) and (P₂O₅) on the equilibrium oxygen activity, as well as determination of thermodynamic conditions for removing P and retaining Nb and C. The composition of low niobium hot metal of Baotou Steel and the interaction coefficient of each component are listed in Table 1. $\lg P_{co}$ equates to 0 when the reaction occurs at the

atmospheric pressure. Table 2 shows the other parameters used for calculation including temperature, activity of (Nb_2O_5) and (P_2O_5) and initial [C] content.

Table 2. Other parameters used for calculation (temperature, activity of (Nb_2O_5) and (P_2O_5) and initial [C] content)

parameters	1	2	3	4	5	6
$a_{\text{Nb}_2\text{O}_5}$	1×10^{-10}	1×10^{-11}	1×10^{-12}	1×10^{-13}	1×10^{-14}	1×10^{-15}
$a_{\text{P}_2\text{O}_5}$	1×10^{-19}	1×10^{-20}	1×10^{-22}	1×10^{-24}	1×10^{-26}	1×10^{-28}
[%C]	0.1	1	2	3	4	5
T/K	1523	1573	1623	1673	1773	1873

From chemical reaction equations (1) - (3), the equilibrium activity for C-O, P-O and Nb-O reactions can be deduced as follows:

$$\lg a_{\text{[O-C]}} = \lg P_{\text{CO}} - \lg f_{\text{[C]}} - \lg [\% \text{C}] - \frac{1168.02}{T} - 2.07 \quad (4)$$

$$\lg a_{\text{[O-P]}} = \frac{1}{5} \lg a_{(\text{P}_2\text{O}_5)} - \frac{2}{5} \lg f_{\text{[P]}} - \frac{2}{5} \lg [\% \text{P}] - \frac{7751}{T} + 5.57 \quad (5)$$

$$\lg a_{\text{[O-Nb]}} = \frac{1}{5} \lg a_{(\text{Nb}_2\text{O}_5)} - \frac{2}{5} \lg f_{\text{[Nb]}} - \frac{2}{5} \lg [\% \text{Nb}] - \frac{14085}{T} + 5.63 \quad (6)$$

where $a_{\text{[O-i]}}$ is the equilibrium oxygen activity of C-O, P-O and Nb-O reactions, $a_{\text{Nb}_2\text{O}_5}$ 和 $a_{\text{P}_2\text{O}_5}$ are activity of (Nb_2O_5) and (P_2O_5) in slag, [%i] is the mass percentage of component i in hot metal, f_i is activity coefficient of component i in hot metal (1% diluted solution as the standard state), The activity coefficient f_i is defined as^[6]:

$$\lg f_i = \left(\sum e_i^j [\% j] \right) \cdot \frac{1873}{T} \quad i = \text{C, P, Nb}; j = \text{C, Si, Mn, P, S, Nb, Ti}$$

where, e_i^j is the interaction coefficient of each component in hot metal at 1873K

3. Thermodynamic analysis of oxidative dephosphorization of hot metal

3.1 Effect of temperature on the equilibrium oxygen activity of C-O, P-O and Nb-O reactions

From formulas (4)-(6), the equilibrium oxygen activity of C-O, P-O and Nb-O reactions at 1523-1873K was obtained under various $a_{\text{Nb}_2\text{O}_5}$ and $a_{\text{P}_2\text{O}_5}$ while $\lg P_{\text{CO}}=0$, [%C]=4%. Figure 1 shows the equilibrium oxygen activity at different temperatures. It can be seen that the equilibrium oxygen activity for Nb-O, C-O and P-O ($\log a_{(\text{P}_2\text{O}_5)} = -24$) reactions increases as the temperature increases. The effect of temperature on the equilibrium oxygen activity is most significant for Nb-O reaction, less for P-O reaction, and least for C-O reaction, which indicates that a high temperature favors

retaining Nb while a lower temperature is advantageous to dephosphorization. When $\log a_{(P_{2O_5})} = -24$, $\log a_{(Nb_2O_5)} = -11$ and [P] content is reduced to 0.05%, the conversion temperature is 1589K. When temperature is higher than 1600K, the precedence order for Nb, P and C oxidation is C>P>Nb, Therefore, it is feasible to produce Nb-microalloyed steel using low niobium hot metal. Nb can be retained in hot metal both in the process of dephosphorization and decarbonization.

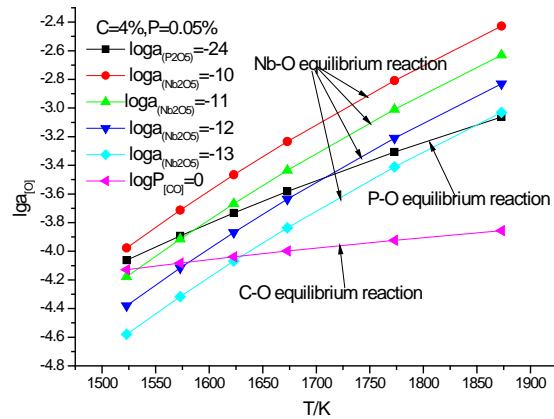


Figure 1. Equilibrium oxygen activity of P, Nb and C oxidation at various temperatures

As $a_{Nb_2O_5}$ decreases, the conversion temperatures of Nb-P and Nb-C increase and the window of oxygen potential required to reach equilibrium of Nb-O, C-O and P-O reaction becomes narrower, thus reducing the feasibility of the practice of removing phosphorus but retaining Nb. When $\log a_{(Nb_2O_5)} = -13$, oxidation of both C and Nb are preferred to that of P at temperatures of steelmaking. It is not possible to retain Nb in hot metal in the process of decarbonization until the temperature is above 1650K. Therefore, the rise of $a_{Nb_2O_5}$ is an effective way to achieve removing phosphorus but retaining Nb.

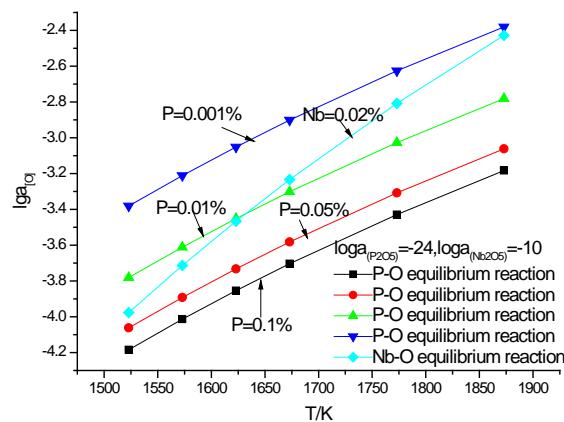


Figure 2. Variety of the equilibrium oxygen activity of P-O reaction with [P] content

Figure 2 shows the variety of the equilibrium oxygen activity of P-O reaction with [P] content. It can be seen that the lower the equilibrium [P] content is, the higher the equilibrium oxygen activity required for P-O reaction is. This makes the dephosphorization more difficult to proceed. When temperature is above 1650K, the carbon content in hot metal [C]=4.0%, and Nb content [Nb]=0.02%, the phosphorus content [P] can be reduced to 0.01% while 0.02% of [Nb] can be retained in hot metal. If the [P]<0.01%, the oxygen potential of Nb-O reaction is lower than that of P-O reaction, and it cannot be realized to remove phosphorus and retain niobium.

3.2 Effect of the initial [C] content on equilibrium oxygen activity of P-O, Nb-O and C-O reactions

The equilibrium oxygen activity of C-O, P-O and Nb-O reactions was calculated from formulae (4)-(6) under different temperatures, $a_{Nb_2O_5}$ and $a_{P_2O_5}$, when the initial [C] content [%C]=0.1-6% and $\lg P_{CO}=0$. The initial [C] content influences the equilibrium oxygen activity of three oxidation reactions. As the equilibrium oxygen activity of Nb-O reaction increases with the increase of [%C], whereas the equilibrium oxygen activity for P-O and C-O reaction decreases as [%C] increases. This indicates that an appropriate increase of [C] content favors the P-O and C-O reaction, but inhibits Nb oxidation. The equilibrium oxygen activity of C-O reaction is mostly affected by the initial [C] content. Figure 3 shows the effects of activity of (P_2O_5) on the selective oxidation of C, P and Nb when $\log a_{(Nb_2O_5)} = -11$.

With varied initial [C] content, the equilibrium oxygen activity for C-O, P-O and Nb-O reactions is different. The extend that the reaction is difficult to occur can be indicated by the equilibrium oxygen activity: the lower equilibrium oxygen activity is, the easier the reaction proceeds. In Figure 3, the cross point B is the turning point of selective oxidation of C and Nb, the [C] content of which is defined as the critical [C] content $[C]_B$. In a similar way, the [C] content at turning point A of selective oxidation of P and Nb is referred to as the critical [C] content $[C]_A$, and the critical [C] content $[C]_C$ means the [C] content at turning point C of selective oxidation of P and C. In order to retain Nb, the [C] content must be higher than $[C]_A$ in the process of dephosphorization of hot metal. When $\log a_{(P_2O_5)} \geq -24$, the precedence order for C, P and Nb oxidation is C>P>Nb, i.e. C and P oxidation reactions precede Nb oxidation. When $\log a_{(P_2O_5)} < -24$, the [C] content should be controlled within the range between $[C]_B$ and $[C]_C$. This is the optimum range of [C] for dephosphorization of low niobium hot metal, where C, P and Nb oxidation occurs in the precedence order of P> C>Nb thus realizing effective removal of P without oxidizing Nb and P. Since the optimum range of [C] content is clearly correspondent with the range of oxygen activity (i.e. given the optimum range of [C] extends, the range of oxygen activity will extend too), the optimum range of [C] can be used as an indicator of the oxygen activity range.

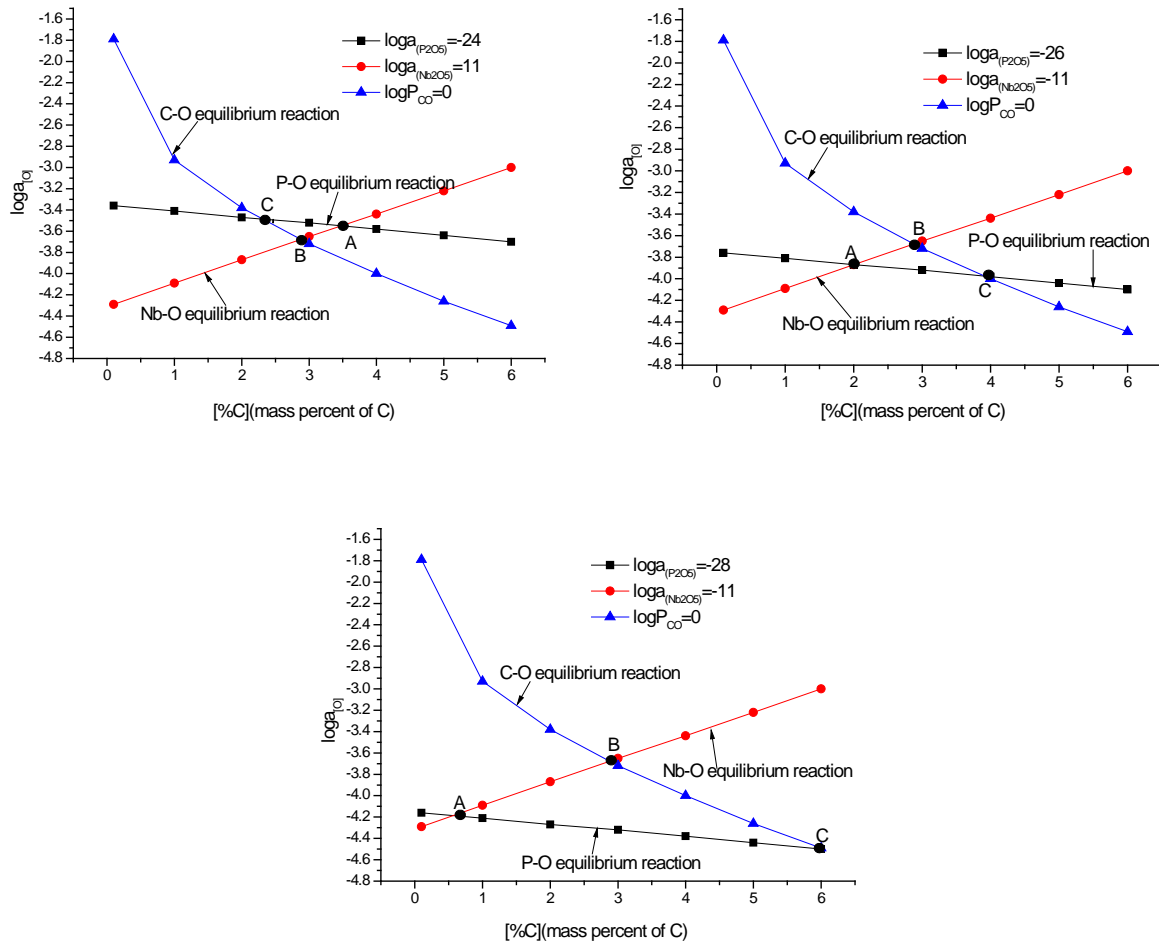


Figure 3. The effects of activity of (P_2O_5) on the selective oxidation of C, P and Nb

As activity of (P_2O_5) in slag decreases, the equilibrium oxygen activity for P-O reaction will decrease, turning point A for selective oxidation of P and Nb will be shifted to the left, and turning point B for selective oxidation of P and C will be shifted to the right. However, the decrease of $a_{P_2O_5}$ does not cause a significant effect on turning point B. The variety of $[C]$ content ($[C]_A - [C]_C$) between tuning point A and C demonstrate the feasibility of the process of dephosphorization. A higher value of $[C]_A - [C]_C$ shows a larger extend of practice in process. A low temperature, high $[C]$ content and adopting a highly basic oxidizing slag with higher phosphate capacity favour the reduction of $a_{P_2O_5}$ so as to increase the control range of $[C]_A - [C]_C$ and $[C]_B - [C]_C$.

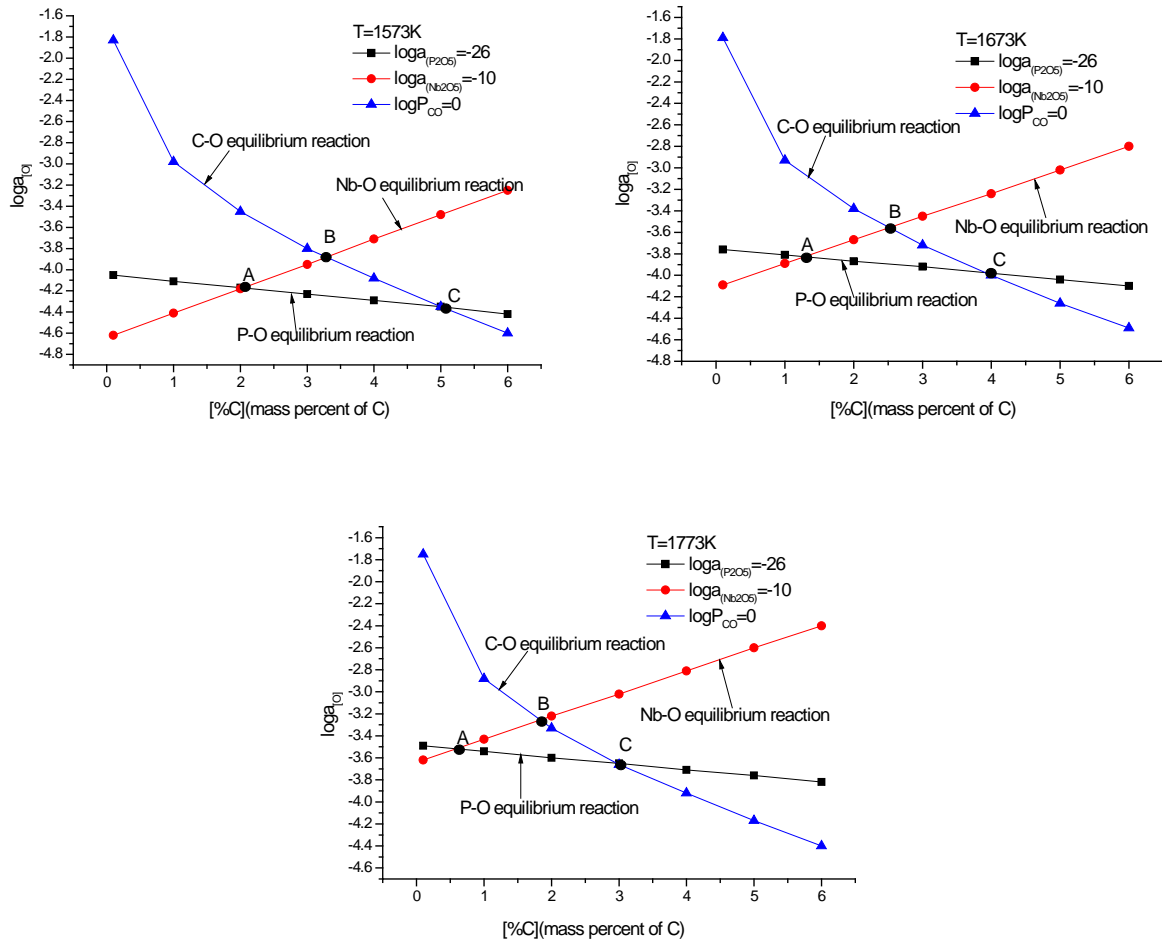


Figure 4. Variety of equilibrium oxygen activity of Nb-O, C-O and P-O reactions with [%C] at various temperatures

Figure 4 shows the variety of equilibrium oxygen activity of Nb-O, C-O and P-O reaction with [%C] at various temperatures. At a given activity of (Nb_2O_5) and (P_2O_5) in slag, turning points A, B and C shift to the left as the temperature increases, resulting in a decrease of $[C]_A - [C]_C$ and $[C]_B - [C]_C$. This exhibits that as the temperature increases, the equilibrium oxygen potential increases and the [C] content in molten metal required for selective oxidation of Nb, P and C is reduced. However, as the equilibrium oxygen potential of P-O reaction increases quickly with the increase of temperature, the high temperature is unfavorable to dephosphorization. The control window of the optimum [C] content for removing P and retaining Nb becomes narrower, thus making the process of removing P and retaining Nb less feasible to operate in practice.

For the hot metal containing 0.02-0.04% of Nb, when the temperature is at 1623-1773K, activity of (Nb_2O_5) in slag is controlled within 10^{-10} - 10^{-12} , and activity of (P_2O_5) is less than 10^{-24} , removing P and retaining Nb can be realized during the process of dephosphorization.

3.3 Thermodynamic conditions for removing phosphorus and retaining niobium

$$\Delta G_3 = \Delta G_3^0 + RT \ln \frac{a_{Nb_2O_5}}{a_{[O]}^5 a_{[Nb]}^2}$$

From chemical reaction equation (3):

When $\Delta G_3 > 0$, Nb cannot be oxidized^[6-7]. Herein, the oxygen activity at the interface of slag and metal must be controlled to be:

$$\lg a_{[O-Nb]} < \frac{1}{5} \lg a_{(Nb_2O_5)} - \frac{2}{5} \lg f_{[Nb]} - \frac{2}{5} \lg [\% Nb] - \frac{14085}{T} + 5.63 \quad (7)$$

The oxygen activity at the interface of slag and metal is considered as the critical oxygen activity deciding whether the Nb-O reaction can occur. The oxygen activity is dependent on the activity of (Nb_2O_5) , $[Nb]$ content in hot metal and reaction temperature. When $T=1673K$ and $[Nb]=0.02\%$, the critical oxygen activity ($a_{[O]}$) and the equilibrium partial pressure of oxygen (P_{O_2}) at varied activity of (Nb_2O_5) ($a_{Nb_2O_5}$) can be calculated, and listed in Table 3.

Table 3 equilibrium oxygen activity of Nb-O reaction and equilibrium partial pressure of oxygen

$a_{Nb_2O_5}$	1×10^{-10}	1×10^{-11}	1×10^{-12}	1×10^{-13}	1×10^{-14}
$a_{[O]}$	5.84×10^{-4}	3.67×10^{-4}	2.31×10^{-4}	1.46×10^{-4}	1×10^{-4}
P_{O_2}	8.18×10^{-15}	3.23×10^{-15}	1.28×10^{-15}	5.11×10^{-16}	2.40×10^{-16}

In the process of dephosphorization of low niobium hot metal, Nb cannot be oxidized as long as the partial pressure of oxygen at the interface of slag and metal is controlled be below the critical partial pressure of oxygen. The lower the activity of (Nb_2O_5) is, the more difficult the critical oxygen potential at the interface between slag and metal is to be realized during dephosphorization.. Under the temperatures of pre-treatment of hot metal, the activity of oxygen required for dephosphorization of low niobium hot metal $a_{[O]}=10^{-3}$ - 10^{-4} and $P_{O_2}=10^{-13}$ - 10^{-16}

From chemical reaction equation (2), $\Delta G_2 < 0$ if P is oxidized under the equilibrium oxygen potential of Nb-O. That is the activity of (P_2O_5) in slag should be:

$$\lg a_{(P_2O_5)} \leq \frac{38754}{T} - 27.82 + 5 \lg a_{[O]} + 2 \lg a_{[P]} \quad (13)$$

At 1673K, in order to reduce $[P]$ to below 0.05%, the relationship of $a_{(P_2O_5)}$ with the equilibrium oxygen activity is:

$$\lg a_{(P_2O_5)} \leq 5 \lg a_{[O]} - 6.06 \quad (14)$$

Thus, if Nb is not oxidized and P is oxidized to 0.05%, $a_{(P_2O_5)}$ required for dephosphorization under the oxygen

potential of retaining Nb can be obtained from formula (14) using data in Table 4.

Table 4 Relationship of $a_{(P_2O_5)}$ with $a_{[O]}$ and $a_{(Nb_2O_5)}$

$a_{Nb_2O_5}$	1×10^{-10}	1×10^{-11}	1×10^{-12}	1×10^{-13}	1×10^{-14}
$a_{[O]}$	5.84×10^{-4}	3.67×10^{-4}	2.31×10^{-4}	1.46×10^{-4}	1×10^{-4}
P_{O_2}	8.18×10^{-15}	3.23×10^{-15}	1.28×10^{-15}	5.11×10^{-16}	2.40×10^{-16}
$a_{(P_2O_5)}$	5.89×10^{-23}	5.75×10^{-24}	5.75×10^{-25}	5.75×10^{-26}	8.71×10^{-27}

In order to prevent Nb from oxidizing in low niobium hot metal, as well as dephosphorize to 0.05%, $a_{(P_2O_5)}$ must be kept below 5.75×10^{-24} when $a_{[O]} \leq 3.67 \times 10^{-4}$ ($a_{(Nb_2O_5)} = 10^{-11}$), whereas $a_{(P_2O_5)}$ must be kept below 5.75×10^{-26} when $a_{[O]} \leq 1.46 \times 10^{-4}$ ($a_{(Nb_2O_5)} = 10^{-13}$).

Table 5 Relationship of $a_{(P_2O_5)}$ and [%P]

[%P]	0.06	0.05	0.04	0.02	0.01
$a_{(P_2O_5)}$	8.13×10^{-24}	5.75×10^{-24}	3.63×10^{-24}	9.12×10^{-25}	2.24×10^{-25}

It can be seen that the lower $a_{(Nb_2O_5)}$ is, the lower the allowed oxygen potential and the lower $a_{(P_2O_5)}$ to reach removing P and retaining Nb. At a given partial pressure of oxygen at interface of slag and metal, the extent to which dephosphorization can be achieved relies on $a_{(P_2O_5)}$. At 1673K, when $a_{[O]} = 3.67 \times 10^{-4}$ ($a_{(Nb_2O_5)} = 10^{-11}$), the [%P] contents that is obtained in dephosphorization and their corresponding $a_{(P_2O_5)}$ are calculated from formula (13), and shown in Table 5. It is obvious that the lower $a_{(P_2O_5)}$ is, the lower the [%P] in hot metal can be achieved after dephosphorization.

4. Results

1) The equilibrium oxygen activity of Nb, P and C oxidation is relevant to the initial [%C] content in hot metal. The equilibrium oxygen activity of Nb-O increases with an increase of the [%C] content, whereas the equilibrium oxygen activity of P-O and C-O varied oppositely with the [%C] content. As the temperature is increased, the lowest [%C] in hot metal required for dephosphorization is decreased. When $\lg a_{P_2O_5} < -24$, it is feasible to realize removing P and retaining Nb in hot metal.

2) Under the conditions of $T > 1650K$, [%C]=4.0%, [%Nb]=0.02%, $a_{P_2O_5} = 10^{-24}$, $a_{Nb_2O_5} = 10^{-10}$, [%P] in hot metal can be removed to 0.01% while 0.02% of [%Nb] can be retained in hot metal without oxidized.

The thermodynamic condition for removing P:

$$\lg a_{(P_2O_5)} \leq \frac{38754}{T} - 27.82 + 5 \lg a_{[O]} + 2 \lg a_{[P]}$$

The thermodynamic condition for retaining Nb:

$$\lg a_{[O-Nb]} \leq \frac{1}{5} \lg a_{(Nb_2O_5)} - \frac{2}{5} \lg f_{[Nb]} - \frac{2}{5} \lg [\% Nb] - \frac{14085}{T} + 5.63$$

3) Oxidation dephosphorization of low niobium hot metal requires very low oxygen potential at atmosphere $P_{O_2} \leq 10^{-13}$, which becomes the major difficulty in controlling the process of dephosphorization.

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