Selective Recovery of Silicon, Niobium, or Manganese from Pig Iron with Fe$_3$O$_5$-based Fluxes by Flux Extraction Method*  

By Akira SATO,** Goro ARAGANE,** Akira KASAHARA,** Muneyuki KORI,** and Shiro YOSHIMATSU**

Synopsis  
The oxidation rates of the elements in pig iron contained in a graphite crucible were measured by adding Fe$_2$O$_3$, CaO, Na$_2$CO$_3$, and B$_2$O$_3$ onto the bath. The effects of temperature, oxygen feeding rate (Fe$_2$O$_3$ g/5 min), and weight of flux added on the oxidation rates were discussed.  

Niobium was selectively recovered from pig iron produced from the iron ore are found in China. By means of a multi-stage continuous treatment, silicon in the pig iron was first removed by adding an optimum amount of Fe$_2$O$_3$ as an oxidizer at high temperatures, followed by the selective removal of niobium in excess of manganese by the addition of Fe$_2$O$_3$ containing CaO or Na$_2$CO$_3$ as a basic flux and by the selective removal of manganese in excess of niobium by the addition of Fe$_2$O$_3$ containing B$_2$O$_3$ as an acidic flux.

I. Introduction  
The iron ore found in Baotou Baiyunebo, Inner Mongolia of China contains rare earth elements and niobium.$^{1,2}$ Table 1 shows the compositions of pig irons produced from the iron ore of Baotou.$^{1-3}$ The pig irons produced from the iron ore of Baotou contain not only niobium but also manganese and phosphorus in high concentration. Joint research between the National Research Institute for Metals (NRIM) and The Beijing University of Iron and Steel Technology (BUIST) was started in 1981. The purposes of the current research are:

i) to recover such valuable elements as niobium and manganese as the mineral resources

ii) to remove such a harmful elements as phosphorus as the fertilizer

iii) to produce iron and steel of high quality from the pig iron.

Batch processes for the recovery of niobium were studied in China.$^{2,4-11}$ According to the reports, the bottom-blown process is the best one among the open hearth, top-, side- and bottom-blown processes because of the lowest phosphorus content in the slag recovered.$^{3,5}$ The content of Nb$_2$O$_5$ in the slag obtained is 2.7 wt%.$^{4,5}$ In the spray continuous steel-melting process, the content of Nb$_2$O$_5$ in the slag did not increase.$^{5}$

The selective removal and the sequence of the removal of a desired element have been investigated in NRIM by the use of a multi-stage continuous steel-melting process similar to the one studied before.$^{12}$ By this process, the slag can easily be discharged at an arbitrary stage of treatment, the elements can be removed one by one, and the content of a desired element can be increased in the slag recovered. The content of Nb$_2$O$_5$ in the slag recovered in the 2nd stage furnace after desiliconization was in the range of 5.5~6.5 wt%.$^{13}$

This report describes the conditions adopted for the selective removal of silicon in excess of niobium, niobium in excess of manganese and phosphorus, and manganese in excess of niobium and phosphorus by means of a multi-stage continuous treatment of pig iron.

II. Selective Removal  
The composition of the slag obtained by the complete oxidation of Baotou-I pig iron shown in Table 1 except for iron is 22.4%SiO$_2$--33.7%MnO--39.9%P$_2$O$_5$--3.99%Nb$_2$O$_5$. In order to obtain the slag with highly concentrated valuable elements, it is necessary to selectively remove one element by one element.

The selective removal has to be discussed on the basis of both the statics and the kinetics. Zhang et al.$^{14}$ expressed the oxidation of an element in molten pig iron by the following equations:

$$M + \frac{x}{2}O_2 = MO_x$$  

$$R = k \cdot A \cdot F \cdot V$$  

$$\frac{1}{k} = \frac{1}{k_w} + \frac{1}{k_f \cdot L}$$

where, $M$: an element in pig iron  
$x$: the moles of oxygen required to oxidize $M$  
$R$: the reaction rate  
$k$: the rate constant  
$F$: the motive force of reaction

Table 1. Chemical compositions of various pig iron. (wt%)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baotou 1</td>
<td>4</td>
<td>0.6</td>
<td>1.5</td>
<td>0.5</td>
<td>0.03</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4</td>
<td>0.9</td>
<td>1.3</td>
<td>0.7</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4</td>
<td>0.7</td>
<td>1.0</td>
<td>2.9</td>
<td>0.03</td>
</tr>
<tr>
<td>Ordinary</td>
<td>4</td>
<td>0.5</td>
<td>0.6</td>
<td>0.1</td>
<td>0.03</td>
<td>—</td>
</tr>
<tr>
<td>JIS 1</td>
<td>&gt;3.5</td>
<td>&lt;1.20</td>
<td>&gt;0.40</td>
<td>&lt;0.300</td>
<td>&lt;0.050</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>&gt;3.5</td>
<td>&lt;1.40</td>
<td>&gt;0.40</td>
<td>&lt;0.500</td>
<td>&lt;0.070</td>
</tr>
</tbody>
</table>

Baotou 1: Pig iron received by NRIM from China.  
Baotou 2: Pig iron smelted from the concentrate of ore.  
Baotou 3: Pig iron smelted from the ore without ore-dressing.
$A$: the area of reaction interface  
$V$: the volume of pig iron  
$k_m, k_s$: the mass transfer coefficients in metal and slag phases, respectively  
$L$: the distribution ratio.

If it is assumed that the reaction proceeds rapidly, the rate determining step of the reaction is the mass transfer process, and that the slag-metal interface is in the equilibrium state, the two-film theory can be applied to the reaction. The distribution ratio, $L$, is expressed as follows:

$$
\log L = \left( \frac{\% M_{slag}}{\% M_{metal}} \right) = -\frac{\Delta G^o}{4.575T} \cdot \frac{V}{A} + \frac{\log (P_{O_2})}{2} - \log \gamma_{MO_x} \frac{f_M}{f_{slag}}
$$

where, $\Delta G^o$: the standard free energy of the reaction shown in Eq. (1),  
$(P_{O_2})$: the oxygen potential at the slag-metal interface  
$\gamma_{MO_x}, f_M$: the activity coefficients of MO$_x$ in slag and metal, respectively.

The selective removal of element A in excess of element B can be realized when L of A is greater than L of B, and, at the same time, the coefficient of mass transfer of element A is higher than that of element B.

Figure 1 shows the standard free energy of the formation of oxide ($\Delta G^o$) and temperature. A solid circle shows transformation of reactant or product. In the range of 1300-1500 °C, the value of $\Delta G^o$ for silicon is much smaller than those of manganese, niobium and iron. The values of $\Delta G^o$ for silicon, manganese, and niobium are lower than that of carbon below 1330 °C, and therefore, these elements are hardly recovered from slag. The value of $\Delta G^o$ for niobium is nearly equal to that of manganese.

The activity coefficient of MO$_x$ in slag, $\gamma_{MO_x}$, decreases when MO$_x$ in slag is fixed by a flux. Cation-oxygen anion attraction, $I$, is used as an index of the basicity of oxides. The value of $I$ for oxides are calculated from the valences and ionic radii of cations and oxygen anion. Table 2 shows the values of $I$ and the melting points. The lower value of $I$ indicates the higher basicity. It can be seen from Table 2 that $\gamma_{MO_x}$ and $\gamma_{MO_y}$ decrease as the flux becomes basic while $\gamma_{MO_z}$ increases as the flux becomes basic.

The activity coefficient of an element in pig iron, $f_M$, is expressed by the interaction coefficients, $\phi_i$. The value of $f_M$ increases by the addition of an element with large $\phi_i$. Unfortunately, it is difficult to find the element so as to increase $f_M$, to decrease $f_{M_b}$ and, at the same time, to be stable during the period of oxidation of silicon or niobium.

In this experiment, the effects of temperature, oxygen feeding rate, and kind of flux on the selective removal of silicon, niobium and manganese have been examined.

### III. Experimental

Mother alloys of Fe–C$_{sat}$ and Fe–C$_{sat}$–1%Nb were prepared from an electrolytic iron, an electrode graphite granule, and a Fe–Nb alloy (62% Nb). The mother alloys and electrolytic iron were melted in a graphite crucible or an alumina crucible (55 mmID, 190 mm in depth) by the use of an induction furnace in order to prepare the pig iron with desired concentration of carbon and niobium, and then, Fe–Si (77% Si), Fe–P (23% P) alloys and an electrolytic manganese were added to the pig iron in order to control the concentration of carbon and niobium. After keeping the molten pig iron at an experimental temperature for 10 min, the molten pig iron was stirred, and the sample for chemical analysis was taken with a silica tube by suction. The powder of Fe$_2$O$_3$ (1st chemical reagent grade) of a fixed weight was added onto the bath over the period of 5 min. Flux powder was mixed with Fe$_2$O$_3$ before adding. The powders of Fe$_2$O$_4$ (equivalent to the 1st chemical reagent grade) and FeO (reduced from the 1st chemical reagent grade Fe$_2$O$_3$, 93.8% in purity) were used for the comparison with Fe$_2$O$_3$. Fluxes used for the experiment, such as CaO, CaF$_2$, Na$_2$CO$_3$, B$_2$O$_3$ and Nb$_2$O$_5$ were of the 1st chemical reagent grade. The

### Table 2. Cation-oxygen anion attraction and melting points of oxides.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>I</th>
<th>M. P. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$O</td>
<td>0.29</td>
<td>685</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.38</td>
<td>920</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>0.45</td>
<td>1430</td>
</tr>
<tr>
<td>BaO</td>
<td>0.53</td>
<td>1925</td>
</tr>
<tr>
<td>CaO</td>
<td>0.71</td>
<td>2600</td>
</tr>
<tr>
<td>MnO</td>
<td>0.80</td>
<td>1785</td>
</tr>
<tr>
<td>MgO</td>
<td>0.91</td>
<td>2800</td>
</tr>
<tr>
<td>FeO</td>
<td>1.10</td>
<td>1378</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>1.52</td>
<td>(1457)</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>1.68</td>
<td>2030</td>
</tr>
<tr>
<td>Nb$_2$O$_5$</td>
<td>2.48</td>
<td>1490</td>
</tr>
<tr>
<td>B$_2$O$_3$</td>
<td>2.60</td>
<td>450</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2.74</td>
<td>(1610)</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>3.59</td>
<td>580</td>
</tr>
</tbody>
</table>
sample for chemical analysis was taken every 3 min from the beginning of Fe₂O₃ addition to 21 min. The experimental temperatures were mainly 1 300, 1 400 and 1 500 °C, and were monitored by a thermocouple inserted in a double tube of qualtz and graphite or an alumina tube. The experimental arrangement adopted in the present study is schematically shown in Figure 2.

IV. Results and Discussion

1. Selective Removal of Silicon in Excess of Niobium

The pig iron mainly used for the experiment was Fe-Csat-0.5% (Nb, Si, Mn, P). Generally, the amount of Fe₂O₃ added was 100 g.

1. Temperature

Figure 3 shows the effect of temperature on both (a) the reduction rates and (b) the oxidation rates of elements in pig iron. The reduction rate of Nb₂O₅ or SiO₂ was determined by the addition of Nb₂O₅ or SiO₂ onto the bath. In this case, SiO₂ was hardly reduced and Nb₂O₅ was slightly reduced at 1 300 °C. At 1 500 °C, SiO₂ was slightly reduced and Nb₂O₅ became to be reduced easily. The powder of Fe₂O₃ added onto the surface of the bath stayed for a long time at 1 300 °C because of low reduction rate of Fe₂O₃. Although the oxidation rates of niobium, silicon and manganese increase with increasing temperature, there is no considerable difference in the oxidation rates of these elements at the same temperature.

2. Amount of Fe₂O₃ Added

Figure 4 shows the effect of the amount of Fe₂O₃ added on the oxidation rates of niobium and silicon in the carbon-saturated pig iron at 1 500 °C. Since the addition of Fe₂O₃ is always made over the period of 5 min, the change in the amount of Fe₂O₃ added corresponds to the change in the oxygen feeding rate. The oxidation rates of elements decrease with decreasing amount of Fe₂O₃ added. After the consumption of Fe₂O₃, manganese and niobium are recovered while silicon is still oxidized. Nb₂O₅ in slag seems to be reduced by silicon in pig iron.

\[
\text{Nb}_2\text{O}_5(s) + \frac{5}{2} \cdot \text{Si}(m) = 2\text{Nb}(m) = \frac{5}{2} \cdot \text{SiO}_2(s)
\]

\[
\Delta G_f^\circ = -83 269 + 25.38 T \text{[cal/mol]} \tag{5}
\]

\[
\Delta G_f^\circ = -RT \ln K \tag{6}
\]

\[
K = \frac{\theta_{\text{Nb}_2\text{O}_5}\theta_{\text{SiO}_2}^{5/2}}{\theta_{\text{Si}_2\text{O}_3}\theta_{\text{Nb}_2\text{O}_5}^{5/2}} \tag{7}
\]

By the use of the interaction coefficients\textsuperscript{15,17} for the calculation of \( f_{\text{Nb}} \) and \( f_{\text{Si}} \) and under the assumption of \( \theta_{\text{Si}_2\text{O}_3} = 0.7,15 \) \( \theta_{\text{Nb}_2\text{O}_5} \) is estimated to be \( 1.73 \times 10^{-6}, 4.73 \times 10^{-6} \) and \( 3.80 \times 10^{-5} \) at 1 300, 1 400 and 1 500 °C, respectively. From these results, it can be seen that the selective oxidation of silicon in excess of niobium in pig iron becomes to be facilitated at high temperatures. Furthermore, phos-

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phorus is scarcely oxidized and is transferred to slag.

The difference in the effects of iron oxides between Fe$_2$O$_3$, Fe$_3$O$_4$ and FeO on the oxidation of the elements in pig iron was not recognized when the amounts of oxygen in the iron oxides fed were the same.

Figure 5 shows the effect of the amount of Fe$_2$O$_3$ added on the removal rates of niobium and silicon from the carbon-saturated pig iron at 1 500 °C. The arrow mark indicates the lapse of the experimental time. It can be seen from the figure that the oxidation rate of niobium is almost the same as that of silicon during the period of oxidation, and that the recovery rate of niobium becomes much greater than that of silicon after oxidation. In order to obtain high desiliconization rate and low removal rate of niobium simultaneously, the oxygen feeding rate should be maintained at the optimum rate, 50 g of Fe$_2$O$_3$ as can be seen from Fig. 5. For the recovery of niobium in pig iron, silicon in pig iron acts very important role as a reductant of Nb$_2$O$_5$ in slag. In order to increase the recovery rate of niobium, it seems to be very effective to stir the slag-metal interface and to hold the melt at high temperatures.

Figure 6 shows the oxidation of niobium, silicon and manganese at a low temperature (1 350 °C), followed by the recovery of niobium and manganese at a high temperature (1 550 °C). This figure emphasizes the effective recovery of niobium. This method is difficult to be realized in a batch process but easy in a continuous one.

3. CaO/SiO$_2$ Ratio of Slag

Figure 7 shows the effect of the CaO/SiO$_2$ ratio of slag (1/4, 3/2) on the oxidation rate of niobium and silicon in the carbon-saturated pig iron at 1 500 °C. The CaO/SiO$_2$ ratio of slag was calculated under the assumption that all the silicon in pig iron was converted into SiO$_2$. The desiliconization rate is independent of the CaO/SiO$_2$ ratio of slag, but the removal rates of niobium and manganese are affected by the CaO/SiO$_2$ ratio. It is confirmed that Nb$_2$O$_5$ is relatively acidic, but that MnO is relatively basic as listed in Table 2. The CaO/SiO$_2$ ratio of slag was adjusted by the addition of CaO. Therefore, the slag with a high CaO/SiO$_2$ ratio has larger amount than that of the slag with a low CaO/SiO$_2$ ratio. Therefore, the dilution effect and the change in the viscosity by the addition of CaO also give large effect on the results.

4. Composition of Pig Iron

The oxidation rate of niobium decreases with decreasing initial content of niobium, but that of silicon does not change in spite of the decrease in initial content of niobium. The recovery rate of manganese increases with decreasing initial content of niobium because the slag formed has higher basicity and less weight.

The oxidation rate of silicon does not change in spite of the increase in the initial content of silicon, but the recovery rates of niobium and manganese changes with increasing initial content of silicon. The change in the recovery rates of niobium and manganese can be explained by the change in the basicity and the weight of the slag formed.

The experiments were made by using the pig irons of various initial carbon contents charged in alumina crucibles. The recovery rates of niobium and manganese at 4 %C were much lower than those at the content of saturation (4.6 %C at 1 300 °C). These results seems to be due to the adhesion of slag to the crucible wall.

2. Selective Removal of Niobium in Excess of Manganese

As described above, it is necessary to maintain the oxygen feeding rate at the optimum rate to obtain...
a high desiliconization rate and a low removal rate of niobium. Moreover, it is confirmed by the continuous treatment that the optimum silicon content after desiliconization is about 0.1%. Therefore, the pig iron with the composition of Fe-C sat-0.1%Si-0.5% (Nb, Mn, P) was mainly used in this work. Because of low silicon content in pig iron, for most of the cases 75 g of Fe₂O₃ was mainly added to the pig iron. As can be seen from Fig. 1, the value of ΔG° of niobium is nearly the same as that of manganese. Therefore, it seems very difficult to perform the selective removal of niobium in excess of manganese by controlling the temperature. Fortunately, Nb₂O₅ is relatively acidic but MnO is relatively basic, as can be seen from Table 2. Hence, the selective removal of niobium in excess of manganese with basic fluxes (CaO, Na₂CO₃) has been investigated in the current work.

1. Temperature

Figure 8 shows the effect of temperature on the oxidation rates of niobium and manganese in the carbon-saturated pig iron by the addition of Fe₂O₃ with 10 g of CaO. All the elements including phosphorus were oxidized at 1300 °C, while manganese and phosphorus were recovered greatly at 1500 °C. Therefore, the selective removal of niobium in excess of manganese can be achieved.

2. Basic Flux

Figure 9 shows the effect of (a) CaO (+CaF₂) and (b) Na₂CO₃ on the removal rates of niobium and manganese. The removal rate of niobium is nearly the same as that of manganese at 1400 °C by CaO (+CaF₂), while the removal rate of niobium is much greater than that of manganese at 1500 °C. The removal rate of niobium is more than 85% while that of manganese is less than 10%. By the addition of Na₂CO₃ it is possible to make a low melting point slag, and therefore, the selective removal of niobium in excess of manganese can be accomplished at 1300 °C.

3. Dephosphorization

Generally, the basic flux tends to oxidize phosphorus and to transfer phosphorus to slag. Phosphorus is considered to be harmful when the slag is utilized as the resources of niobium. The rephosphorization by stirring the slag-metal interface at high temperatures is necessary to maximize the removal rate of niobium in spite of the low removal rate of manganese by CaO (+CaF₂). When Na₂CO₃ is used, the removal rate of manganese becomes low. The oxides, Na₂O and P₂O₅ dissolve into water while Nb₂O₅ remains as the residue. From the amount of Nb₂O₅ remained as the residue, the content of Nb₂O₅ is calculated to be 30% when the removal rates of niobium, silicon and manganese are 85, 90 and 10%, respectively. Similarly, the content of Nb₂O₅ is calculated to be 70% when Na₂CO₃ is used after the separation of Na₂O and P₂O₅ by a wet process.

3. Selective Removal of Manganese in Excess of Niobium

Similarly to the selective removal of niobium in excess of manganese, the composition of pig iron after desiliconization was Fe-C sat-0.1%Si-0.5% (Nb, Mn, P). Because MnO is basic oxide, B₂O₃ is used as an acidic flux with low melting point.

1. Temperature

Figure 10 shows the effect of temperature on the oxidation rates of niobium and manganese in the carbon-saturated pig iron by the addition of Fe₂O₃ with 20 g of B₂O₃. Although all the elements except for phosphorus are oxidized at 1300 °C, phosphorus is not oxidized at low temperatures. The oxidation rate of niobium is low and at the same time the recovery rate of niobium is very high at 1500 °C while the oxidation rate of manganese is high.

2. Amount of B₂O₃

Figure 11 shows the effect of the amount of B₂O₃ on the removal rates of niobium and manganese.
The selective removal rate of manganese in excess of niobium increases with increasing amount of B$_2$O$_3$ added. At 1300 °C the recovery rate of niobium is much greater than that of manganese after the oxidation of both niobium and manganese. On the other hand, the oxidation rate of niobium is low at 1500 °C.

3. Amount of Fe$_2$O$_3$

Figure 12 shows the effect of the amount of Fe$_2$O$_3$ added with 20 g of B$_2$O$_3$ on the removal rates of niobium and manganese. The melting point of B$_2$O$_3$ slag is low, and the recovery rate of niobium is high at 1400 °C. When the amount of Fe$_2$O$_3$ added is small, that is, the oxygen feeding rate is low, the selective oxidation of manganese in excess of niobium becomes to be possible.

4. Composition of Pig Iron

As the content of silicon in pig iron increases from 0.1 to 0.5 %, the melting point, the viscosity, and the amount of slag formed increase, and the acidity of slag also increases. As a result, the recovery rate of niobium decreases, and the selective removal rate of manganese in excess of niobium decreases with increasing initial content of silicon. The low content of silicon in pig iron is suitable for the selective removal of manganese in excess of niobium by the addition of Fe$_2$O$_3$ with B$_2$O$_3$.

Since the content of niobium can be raised up to 0.2 % in China, the selective removal of manganese in excess of niobium from the pig iron containing 1.5% Mn-0.2% Nb has been studied in this work. Figure 13 shows the effect of the amounts of Fe$_2$O$_3$ and B$_2$O$_3$ added on the removal rates of niobium and manganese at 1400 °C. The selective removal rate of manganese in excess of niobium increases with increasing amount of B$_2$O$_3$ added. The oxidation rates of niobium and manganese increase with increasing amount of Fe$_2$O$_3$ added. After oxidation, niobium can preferably be recovered.

V. Conclusion

In order to utilize as the mineral resources, the recovery of such valuable elements as niobium and manganese, from pig iron containing large amount of niobium has been studied in the current work. The selective removal of silicon, niobium or manganese has been studied to recover the one element prior to the removal of the other element by means of a multi-stage continuous treatment. The results obtained are summarized as follows:

(1) Silicon is most easily oxidized. The selective removal of silicon in excess of niobium has been accomplished by the addition of the optimum amount of Fe$_2$O$_3$ at a high temperature and by stirring the slag-metal interface.

(2) The selective removal of niobium in excess
of manganese from pig iron after desiliconization can be achieved by adding a basic flux. The rephosphorization becomes high at high temperatures by the addition of CaO, and phosphorus is restrained from transferring into the slag formed.

(3) The selective removal of manganese in excess of niobium from pig iron after desiliconization is realized by the addition of Fe$_2$O$_3$ with B$_2$O$_3$ as an acidic flux.

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