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MANGANESE PARTITION EQUILIBRIUM IN LESS SLAG BLOWING AT BOF

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Synopsis:The optimum operational conditions for high Mn yield and Mn equilibrium at the end point of BOF are discussed.High efficiency of Mn ore reduction and [Mn] control technologies are established by the study of Mn reaction mechanism from the aspects of both equilibrium and kinetics.By the improved operational conditions,Mn yield improvement effect is about 10% as compared with conventional average.Oxygen potentials of slag and metal at the end point,which influence Mn partition, are studied from equilibrium viewpoint.Comparing slag oxygen potential with metal oxygen potential,the former is higher than the latter.But its difference becomes small as decreasing the carbon content in metal.Mn partition depends on intermediate oxygen potential between those of slag and metal.

Key words:less slag blowing, hot metal dephosphorization,manganese equilibrium,
regular solution model

1. Introduction

With the “oil shock” as the turning point,demands for saving in resources and energy increased and demands for production of high quality steel also became severe.

In November,1986,Keihin Works has developed a hot metal dephosphorizing station called NRP(New Refing Process) which is capable of all hot metal from one blast furnace and has established less slag blowing process at BOF.

From the viewpoint of cost reduction,improvement of Mn yield in less slag blowing is considered most important.For achievement of high Mn yield,it has become important to improve the efficiency of Mn reduction and the accuracy of control of [Mn].

In this report,the following two items are discussed to improve the less slag blowing process.

1)Optimum operational conditions for high Mn yield during oxygen blowing

High efficiency of Mn ore reduction and [Mn] control technologies are established by the study of Mn behavior from the aspects of both equilibrium and kinetics.

2)Study of Mn partition equilibrium and oxygen potential at the end point

Reduction of the Mn partition ratio is necessary to improve Mn yield.
But,it is not adequately clarified whether Mn partition ratio is influenced by the oxygen potential of slag or that of metal.Oxygen potentials of slag and metal are studied from viewpoint of equilibrium.

2.Feature of hot metal dephosphorizing process and less slag blowing process

2.1 Production flow of steel making shop

Fig.1 shows the production flow of steel making shop.Hot metal is desiliconized at the tilting runner of BF and tranported to steel making shop by open ladle. The hot metal dephosphorizing station is capable of all hot metal from one blast furnace.Less slag blowing and Mn ore reduction are carried out at BOF.The each amount of desiliconization,dephosphorization and less slag blowing is 300KT/M

2.2 Feature of hot metal dephosphorizing process

Since hot metal dephosphorizing is carried out in open ladle with adequate mixing,low phosphorous hot metal is obtained at comparatively high temperature.

Fig.2 shows a schematic view of dephosphorizing station.This station has two oxygen blowing lance which enables total oxygen flow rate of $5000 Nm^3/Hr$.

The powdered flux feeding system is provided with four dispensers for optimum mixture depending on conditions such as the hot metal components.Four hoppers are also provided for lumpy flux.

An automatic lance handling unit is introduced to reduce loss time in lance replacement and replacement is now possible within five minutes.

By the effective use of less slag blowing slag and optimized conditions of oxygen feeding such as reduction of dynamic pressure,treatment time is now within 20 minutes.

2.3. Feature of less slag blowing

Table.1 shows the specification of BOF in Keihin Works.

Hot metal dephosphorization has enabled obtaining large stable amounts of low phosphorus hot metal.

One BOF can be used as an exclusive less slag blowing furnace to prevent coexistence of less slag blowing and conventional blowing.As a result,it is possible to reduce the amount of slag volume and to improve Mn yield.

Table.2 shows the typical operational conditions of less slag blowing.

Average end point [Mn] is 0.50%.Mn ore consumption is 12kg/T and burned lime consumption is 5kg/T.

3. Optimum operational conditions for high Mn yield during oxygen blowing

3.1. Actual Mn behavior during oxygen blowing

Fig.3 shows the blowing pattern and composition behavior during blowig.By observing [Mn] behavior,it is learned that [Mn] does not increase from middle stage of blowing and decreases near the end point of blowing.

3.2. Mn reaction mechanism

Fig.4 shows the Mn reaction mechanism in less slag blowing.

As shown in this Fig.,equations (1) to (4) may be considered as Mn reaction in BOF.It is believed that oxidation reaction(1) normally proceeds to the right during oxygen blowing. In relation to reduction reactions,equations(2)and(3) proceed dominantly at high [C] area and equation(4) proceeds at low [C] area with increase in (FeO).

During oxygen blowing,[Mn] in BOF is determined by the simultaneous reaction of oxidation reaction(1) at the fire spot and reduction reactions(2)and(3) at the slag/metal boundary.

Kinetic study is necessary to decide the optimum operational conditions and carried out as follows.

3.3 Kinetic studies

Fig.5 shows the Mn reaction model.

The Mn reaction model and parameters are obtained by the assumption based on [Mn] balance in the bulk metal.The [Mn] behavior can be described by the balance between reduction rate of (MnO) and oxidation rate of [Mn] by the above studies.

For calculation of reduction rate parameter,rate-controlling step of mass transfer at the slag/metal boundary is assumed and for calculation of oxidation rate parameter,rate-controlling step of oxygen flow rate is assumed.

By the calculations using actual operational data,it is determined that K_R is proportional to 1/3 power of bottom blowing gas flow rate and that K_O remains almost constant value.

3.4 Improvement of Mn yield

3.4.1 Conditions of yield improvement

Fig.6 shows the yield improvement conditions derived from the Mn reaction model. The following general conditions are necessary to improve Mn yield.

1) Strong agitation
2) Decreasing the oxygen flow rate near the end point of blowing
3) Mn ore addition at the early stage of blowing

Furthermore,conditions for realizing over 80% of Mn yield are also shown in this Fig..

3.4.2. Test of Mn yield improvement

The test is carried out with an actual BOF under conditions shown in Table.3. The test conditions are based on conditions of high Mn yield obtained from a model.

Bottom gas flow rate at first stage increases from $0.03Nm^3/min.T$ to $0.15Nm^3/min.T$.The top oxygen gas flow rate at latter stage decreases from $35000Nm^3/Hr$ to $22000Nm^3/Hr$.The timing of Mn ore addition changes from "5 min. after blowing start" to "just after blowing start".

3.4.3. Test results

Fig.7 shows the relationship between Mn yield and [C]E.P..High yield as predicted is obtained as a result of improved conditions.Yield improvement is about 10% as compared with conventional average.

4. Study of Mn partition equilibrium and oxygen potential at the end point

[Mn]E.P. in BOF is determined by the amount of input [Mn],slag volume and Mn partition ratio.Increase of the input [Mn],reduction of slag volume and reduction of Mn partition ratio are important to improve Mn yield.There is little allowance in increase of the input [Mn] and reduction of slag volume.

Therefore reduction of Mn partition ratio is necessary to improve Mn yield. But,it is not adequately clarified whether Mn partition ratio is influenced by the oxygen potential of slag or that of metal.Oxygen potential of slag and metal are studied from viewpoint of equilibrium.

4.1 Relationship between Mn partition ratio and oxygen activity in steel

Fig.8 shows the relationship between Mn partition ratio(L_{Mn} =(MnO)/[Mn]) and oxygen activity in steel(a_O).Calculated LMn of γ'_{MnO}=0.013 and 0.023 are indicated in this Fig..γ'_{MnO} is obtained from iso-activity curves in CaO-FeO-MnO system[1] and from regular solution model of CaO-MgO-SiO2-FeO-MnO-P2O5 system proposed by Suito et al[2].Although the correlation is observed between a_O and L_{Mn}, the actual L_{Mn} is higher than the calculated value.In other words,it is considered that the L_{Mn} is determined by the oxygen potential which is higher than the metal oxygen potential. Studies are therefore conducted on slag oxygen potential which is considered higher than metal oxygen potential.

4.2 Relationship between Mn partition ratio and oxygen potential of slag

Fig.9 shows the relationship between logPO2 and [C] in metal.

PO_2(a) ;calculated oxygen potential of slag using a regular solution model proposed by Banya et al[3].
PO_2(b) ;actual measured oxygen potential of metal
PO_2(c) ;calculated oxygen potential balanced with [Mn]
PO_2(d) ;calculated oxygen potential balanced with [C]

PO_2(c) and PO_2(d) are obtained by the equations (1),(2),(3).

(MnO)=[Mn]+O logK=-12760/T+5.64 [4] (T=1923K, γ'_{MnO}=0.013/0.023) (1)
$C+1/2O_2(g)=CO(g)$ logK=1160/T+2.003 [4] (P_{CO}=1atm, T=1923K) (2)
$1/2O_2(g)$ =O logK=6070/T+0.21 [4] (3)

As shown in this Fig.,PO_2(a) is almost constant and PO_2(b) is near [C]-[O] equilibrium.When PO_2(a) is compared with PO_2(b) , PO_2(a) is higher than PO_2(b) in high [C] area.But its difference becomes small as decreasing the carbon content in metal and approaches the balanced state of [C]-[O] equilibrium.

PO_2(c) which influences Mn partition is positioned intermediate oxygen potential between those of slag and metal.

5. Conclusion

(1) Keihin works has developed a hot metal dephosphorizing process called NRP(New Refining Process) and has established less slag blowing process at BOF.

As a result,NRP has contributed greatly to high Mn yield and production of low-phosphorus steel.

(2) Optimum operational conditions for high Mn yield during oxygen blowing

By the study of Mn reaction mechanism from the aspects of both equilibrium and kinetics, the following conditions are necessary to improve Mn yield.

1)Strong agitation 2)Decreasing the oxygen flow rate near the end point of blowing 3)Mn ore addition at the early stage of blowing

By the improved operational conditions,yield improvement is about 10% as compared with conventional average.

(3) Study of Mn partition equilibrium and oxygen potential at the end point

Oxygen potentials of slag and metal in less slag blowing,which influence Mn partition, is studied from equilibrium viewpoint.When slag oxygen potential is compared with metal oxygen potential,the former is higher than the latter.But its difference becomes small as decreasing the carbon content in metal.Mn partition in less slag blowing depends on intermediate oxygen potential between those of slag and metal.

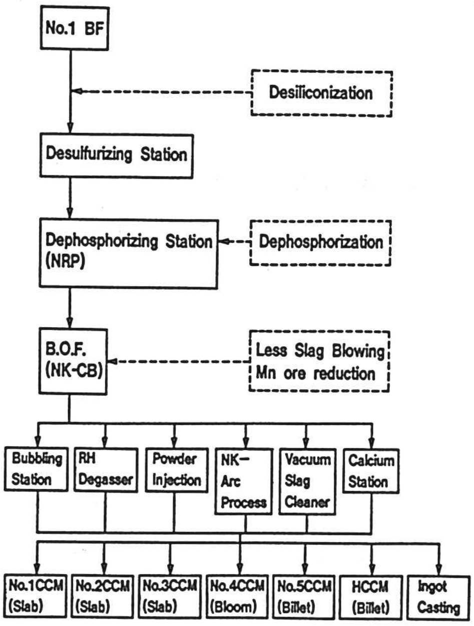

Fig.1 Production Flow Chart of Steel Making Shop

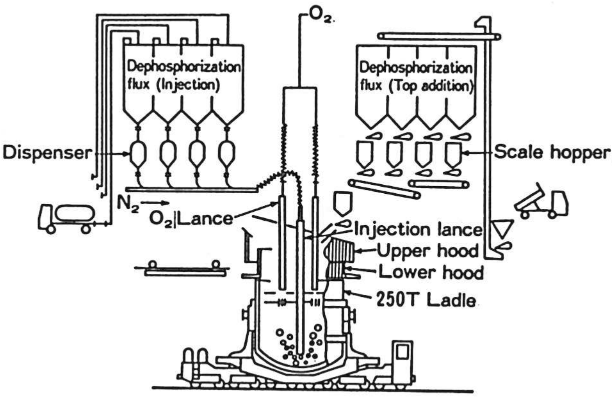

Fig. 2 Schematic view of dephoshorization process

Table 1. Specification of BOF in Keihin Works

Item	Content
Type of BOF	Top and bottom blowing (NK-CB)
Kind of bottom tuyere	Multiple hole plug
Kind of bottom blowing gas	N_2, Ar
Bottom blowing gas flow rate	0.02~0.15 $Nm^3/min.t$

Table 2. Typical operating conditions of less slag blowing

<table>
<tr><th>Item</th><th>Content</th></tr>
<tr><td>Chemical composition and temperature</td><td><table>
<tr><th></th><th>C %</th><th>Si %</th><th>Mn %</th><th>P %</th><th>Temp. ℃</th></tr>
<tr><td>H.M.</td><td>3.8</td><td>tr.</td><td>0.15</td><td>0.015</td><td>1250</td></tr>
<tr><td>E.P.</td><td>0.15</td><td>tr.</td><td>0.50</td><td>0.012</td><td>1645</td></tr>
</table></td></tr>
<tr><td>Flux consumption (kg/T)</td><td><table>
<tr><td>Mn ore</td><td>12</td></tr>
<tr><td>Burned lime</td><td>5</td></tr>
<tr><td>Soft burned dolomite</td><td>3.5</td></tr>
<tr><td>Iron ore</td><td>12</td></tr>
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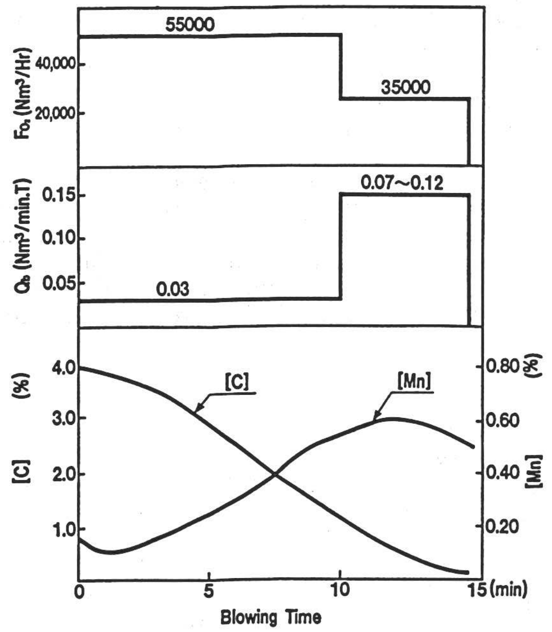
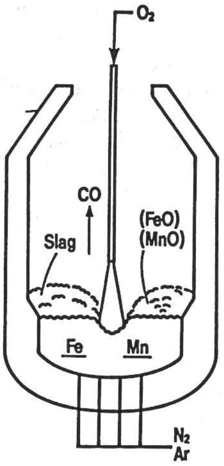


Fig. 3 Blowing pattern and composition behavior



- O_2 gas / metal reaction (at fire spot)

$\underline{Mn} + \frac{1}{2}O_2 \rightarrow (MnO)$ (1)

- Slag / metal reaction

$(MnO) + \underline{C} \rightarrow \underline{Mn} + CO$ (2)

$(MnO) \leftrightarrows \underline{Mn} + \underline{O}$ (3)

$(MnO) + \underline{Fe} \rightleftarrows \underline{Mn} + (FeO)$ (4)

Fig. 4 Mn reaction mechanism in less slag blowing

[Mn] balance in the bulk metal.

Accumulated [Mn] in metal=Input[Mn] — Output[Mn]
(Reduction) (Oxidation)

$$\frac{d[Mn]}{dt} = K_R\{(MnO) - (MnO)^*\} - K_O V_{O_2}$$

K_R : Reduction rate parameter
K_O : Oxidation rate parameter
$(MnO)^*$: Equilibrium (MnO) content
V_{O_2} : Oxygen flow rate (Nm³/min.T)

$K_R = 2.0 \times \left(\frac{Q}{0.08}\right)^{1/3}$ (min⁻¹)

$K_O = 0.017$ (T.%/Nm³)

Q : Bottom blowing gas flow rate

Fig. 5 Mn reaction model

$$\frac{d[Mn]}{dt} = K_R((MnO) - (MnO)^*) - K_O V_{O_2}$$

① Increasing the reduction rate parameter (K_R)	→	Strong agitation
② Decreasing the oxidation term ($K_O V_{O_2}$)	→	Decreasing the oxygen flow rate near the end point of blowing
③ High [C] content and enough reducing time are necessary to satisfy the reaction, $(MnO) + C \rightarrow Mn + CO$	→	Mn ore addition at the early stage of blowing

⇩

Conditions for realizing over 80% of Mn yield.

Item	Details	Conditions
Strong agitation	K_R to 1.3 times	Double amount of agitating gas
Decreasing the oxygen flow rate	$K_O V_{O_2}$ to 0.7 times	End oxygen flow rate to 0.7 times
Initial addition of Mn ore	Initial addition	Addition of just after blowing start

Fig. 6 Mn yield improvement conditions.

Table. 3. Experimental conditions

Item	Case	Conventional condition	Test condition
Bottom gas flow rate (Nm^3/min.T)	First stage	0.03	0.15
	Latter stage	0.07~0.12 Last 4 min.	
Top oxygen flow rate (Nm^3/Hr)	First stage	50000 ~ 58000	
	Latter stage	35000	22000
Mn ore addition	Timing	5min. after blowing start	Just after blowing start

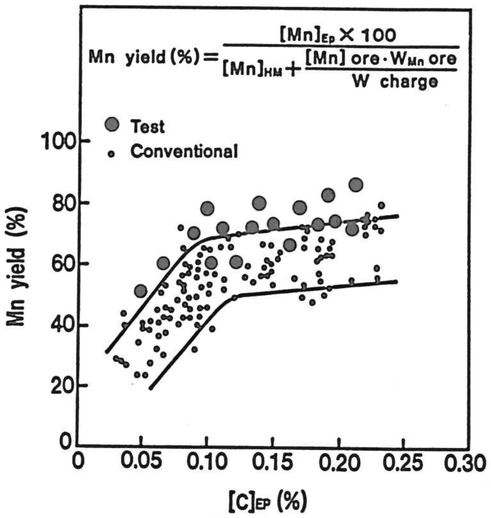


Fig. 7 Relationship between Mn yield and $[C]_{E.P.}$

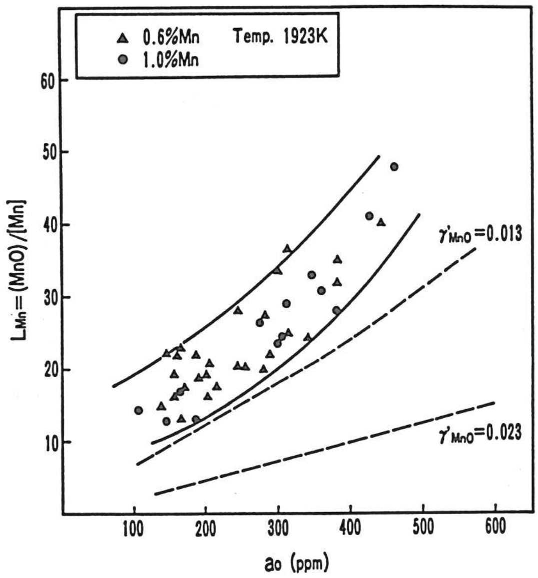


Fig. 8 Relationship between L_{Mn} and a_o in steel

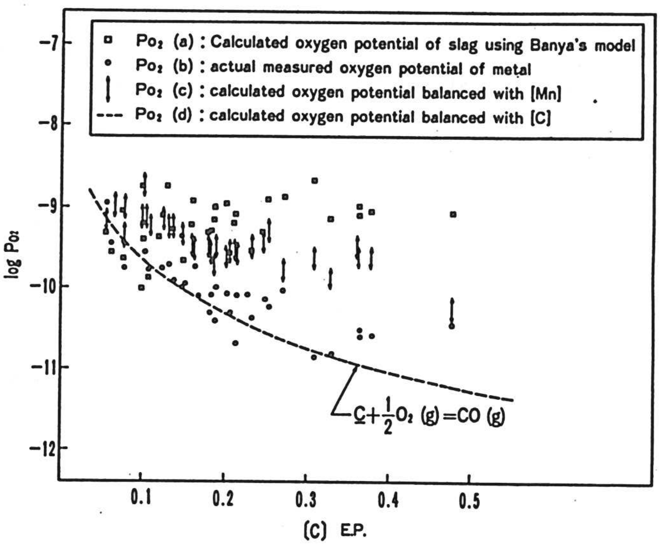


Fig. 9 Relationship between $\log P_{O_2}$ and (C) E.P.

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