Some Thermochemical Discussions on the Oxidizing Refining of Steel*

By Takami IKEDA,** Masayuki TAGA,** Tohru MATSUO**
and Seiichi MASUDA**

Synopsis

In order to establish the basic concepts on oxidizing steelmaking processes, relationships among the oxidation, the decarburization and the dephosphorization were discussed with both thermochemical calculations and data in actual refining processes.

Decarburization reaction is promoted by reducing CO partial pressure. Thermochemical discussion shows the limit of decarburization by refining at one atmospheric pressure and the effect of refining at low CO partial pressure. The characteristics of actual decarburization reactions are described in such processes as VOD, AOD and other modified processes for stainless steel refining as well as LD, Q-BOP, the duplex blowing LD, VOD, Thomas, and DH Processes for carbon steel refining.

The other thermochemical importance is the balance between dephosphorization and decarburization in carbon steel refining. Discussion remarks the characteristics of dephosphorization reactions at one atmospheric pressure in LD, Q-BOP and the duplex blowing LD processes, the effectiveness of higher pressure for dephosphorization of high carbon steel and the usefulness of low temperature for dephosphorization of hot metal.

I. Introduction

Thermochemical calculations on the reactions occurring in steelmaking present some valuable suggestions to improve the refining processes. The most epoch-making process is the VOD stainless steelmaking process developed by Schmidt *et al.*¹⁾

Recently, the processes with gas injection into molten metal, such as AOD, Q-BOP, *etc.*, which accompany violent mixing of gas-metal-slag system, have been developed. In these processes, the reactions can reach more closely to the equilibrated state. Consequently, thermochemical calculations to clarify the equilibrium of reactions become more useful to improve the refining processes.

On the other hand, there have recently appeared new processes such as the dephosphorization of hot metal,^{2,3)} and the duplex blowing converter for carbon^{4,5)} and stainless steels.⁶⁾

It becomes now more important to understand the oxidizing reactions unitedly enough to establish the basic concept on the refining processes.

In this paper, some thermochemical calculations were performed to know the reaction limits of the metal oxidation, the decarburization and the dephosphorization which are most important reactions in carbon and stainless steelmakings. If the equilibrated state is favorable for the refining, the operation to get the reaction close to equilibrium can be applied; on the other hand if the equilibrated state is unfavorable, the operation to keep the reaction far from the equilibrium is suggested.

The reactions occurring actually in some new refining processes were compared with the results of the calculations.

II. Thermochemical Calculations

1. Decarburization and Metal Oxidation

First, the decarburization and the metal oxidation in stainless steelmaking is considered.

The relation between the decarburization and the chromium oxidation has been already investigated by Schmidt *et al.*¹⁾ The equilibriums among oxygen, carbon and chromium in liquid steel are represented by Eqs. (1) and (2), hence the equilibrium between carbon and chromium can be written as Eq. (3). Equation (3) can be rewritten into Eq. (4).

$$\begin{aligned} \underline{\text{C}} + \underline{\text{O}} &= \text{CO (g)}, \\ \log K_1 &= \log P_{\text{CO}}/a_{\text{C}} \cdot a_{\text{O}} = 1168/T + 2.07^n \dots (1) \\ 3\underline{\text{Cr}} + 4\underline{\text{O}} &= (\text{Cr}_3\text{O}_4), \\ \log K_2 &= \log a_{\text{Cr}_3\text{O}_4}/a_{\text{Cr}}^3 \cdot a_{\text{O}}^4 = 53520/T - 23.96^8) \\ &\dots\dots\dots (2) \\ 4\underline{\text{C}} + (\text{Cr}_3\text{O}_4) &= 4\text{CO (g)} + 3\underline{\text{Cr}}, \\ \log K_3 &= \log P_{\text{CO}}^4 \cdot a_{\text{Cr}}^3/a_{\text{C}}^4 \cdot a_{\text{Cr}_3\text{O}_4} = -48800/T \\ &\quad + 32.2 \dots\dots\dots (3) \\ [\% \text{C}]^4 &= (1/K_3) f_{\text{Cr}}^3 [\% \text{Cr}]^3 (P_{\text{CO}}^4/a_{\text{Cr}_3\text{O}_4})/f_{\text{C}}^4 \dots\dots (4) \end{aligned}$$

Here, a is either the activity of element on the weight percent basis or the activity of oxide on the mole-fraction basis, and f is the activity coefficient of element.

Equations (3) and (4) show that the carbon content in the steel can be reduced as the temperature increases, the partial pressure of carbon mono-oxide decreases or the activity of chromium oxide increases. Using the following interaction parameters,¹⁾

$$\begin{aligned} e_{\text{C}}^{(\text{C})} &= 358/T, \quad e_{\text{C}}^{(\text{O})} = -0.31, \quad e_{\text{C}}^{(\text{Cr})} = -0.018, \\ e_{\text{O}}^{(\text{C})} &= -0.55, \quad e_{\text{O}}^{(\text{Cr})} = -0.027, \quad e_{\text{Cr}}^{(\text{Cr})} = 0, \end{aligned}$$

$$\text{and} \quad e_{\text{Cr}}^{(\text{C})} = -0.08$$

Figure 1 can be obtained from Eq. (4).¹⁾ When the P_{CO} is one atmospheric pressure, the carbon content in 18% chromium steel cannot be reduced to lower than 0.23% at 1700°C. However, if the P_{CO} is lowered to 0.1 atmospheric pressure, the carbon content can be reduced to 0.02%.

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** Central Research Laboratories, Sumitomo Metal Industries, Ltd., Nishinagasu-Hondori, Amagasaki 660.

Fig. 1. Equilibrium relationship between chromium and carbon in steel (After Schmidt *et al.*¹¹).

Next, the changes of metal and slag composition during the refining of 18% chromium steel are calculated on a condition that the reactions proceed with keeping the equilibrated state. Figure 2 shows the changes of the oxygen and the chromium contents in steel, of the chromium oxide activity in slag if slag exists and of the oxygen efficiency for decarburization when the flux is not added. It will be explained later how to calculate the oxygen efficiency. According to Fig. 2, the oxygen content is determined by the carbon content until the activity of chromium oxide reaches to unity, and since then no carbon in steel can be reduced further without the decreasing chromium content. The oxygen efficiency for decarburization decreases remarkably within the latter period even when the flux is not added.

Similarly the decarburization and the oxidation of carbon steel during the oxidizing refining are considered.

The equilibrium relations among oxygen and carbon in metal, iron oxide in slag and CO partial pressure are represented by Eqs. (5) and (6).

$$\begin{aligned} \underline{C} + \underline{O} &= \text{CO(g)}, \\ \log K_5 &= \log P_{\text{CO}}/a_{\text{C}}a_{\text{O}} = 1\,160/T + 2.003^{(9)} \dots\dots(5) \\ \text{Fe(l)} + \underline{O} &= (\text{FeO}), \\ \log K_6 &= \log a_{\text{FeO}}/a_{\text{O}} = 6\,150/T - 2.604^{(9)} \dots\dots(6) \end{aligned}$$

Combining these equations, Eq. (8) can be obtained through Eq. (7).

$$\begin{aligned} \underline{C} + (\text{FeO}) &= \text{CO(g)} + \text{Fe(l)} \\ \log K_7 &= \log P_{\text{CO}}/a_{\text{C}} \cdot a_{\text{FeO}} = -4\,990/T + 4.607 \dots\dots(7) \\ [\% \text{C}] &= (1/K_7)(P_{\text{CO}}/a_{\text{FeO}})/f_{\text{C}} \dots\dots\dots(8) \end{aligned}$$

Here, $\log f_{\text{C}} = 0.298[\% \text{C}]^{(9)}$.

Equations (7) and (8) show that carbon in steel can be reduced as the iron oxide content in slag increases and the partial pressure of carbon mono-oxide decreases. The effect of temperature on the reduction of carbon is small. For the calculation of [%C] through Eq. (8), it is necessary to know the activity of iron oxide in basic slag. The activity can be estimated from the iso-activity diagram after Turkdogan and Pearson.¹⁰ The calculation was carried out for a typical basic slag with a basicity (CaO/SiO₂) of 3.5. The result is shown in Fig. 3. At 1 atm P_{CO}, the carbon content cannot be reduced to lower than 0.013% at 1 600°C even if the FeO content reaches

Fig. 2. Equilibrated composition during refining of 18% chromium steel.

Fig. 3. Equilibrium relationship between iron oxide in slag, CO partial pressure and carbon in steel.

to 100%, while at 0.1 atm P_{CO} the carbon content can be easily reduced to lower than 0.01% even together with slag containing a small amount of FeO.

The oxygen efficiency for decarburization during the refining of carbon steel is calculated on a condition that the reactions proceed with keeping the equilibrated state. The oxygen is consumed for the decarburization (the formation of CO and CO₂), the dissolution into liquid steel (the dissolved oxygen in metal), and the oxidation of liquid iron (the formation of FeO in slag). Since the formation of CO₂ induces the decrease of the oxygen efficiency for decarburization calculated on the basis of CO formation, the following parameter α may be defined by Eq. (9) to correct the efficiency. The reason why the oxygen efficiency for decarburization is calculated on the basis of CO formation is merely more practical for the check of the operation, since the amount of decarburization is easily calculated by the amount of supplied oxygen.

$$\alpha \equiv (P_{CO} + P_{CO_2}) / (P_{CO} + 2P_{CO_2}) \dots\dots\dots(9)$$

Further, the weight percentage of oxygen of FeO in slag to liquid metal is written as $(\%O)_M$, then the oxygen efficiency F for decarburization is represented with Eq. (10) on the CO basis.

$$F = \frac{\frac{-\Delta[\%C]}{12}}{\frac{1}{\alpha} \times \frac{-\Delta[\%C]}{12} + \frac{\Delta[\%O]}{16} + \frac{\Delta(\%O)_M}{16}} \times 100$$

$$= \frac{100}{\frac{1}{\alpha} + \frac{12}{16} \left(\frac{\Delta[\%O]}{-\Delta[\%C]} + \frac{\Delta(\%O)_M}{-\Delta[\%C]} \right)} \dots\dots\dots(10)$$

The value of α is obtained from the relation written as Eq. (11).

$$\underline{C} + CO_2 = 2CO,$$

$$\log K_{11} = -7\,558/T + 6.765^9 \dots\dots\dots(11)$$

$\Delta[\%O]/-\Delta[\%C]$ is the gradient of the $[\%C]-[\%O]$ curve to be determined by Eq. (5). $(\%O)_M/-\Delta[\%C]$ can be obtained with the combination of the gradient of the $[\%C]-(\%FeO)$ curve and the weight ratio of slag to metal.

Figure 4 can be obtained through the calculation of the F value on the conditions that the weight percentage of the flux except FeO to the liquid metal is 7.5% and the basicity of the slag (CaO/SiO_2) is 3.5. The oxygen efficiency for decarburization begins to decrease at a higher carbon content in the refining with slag than that without slag. Also the efficiency keeps higher levels at lower P_{CO} than at one atmospheric pressure, even within a low carbon range.

Next, processes which are applicable to reduce

carbon with preventing the metal oxidation is considered for stainless and carbon steel refinings.

In the case of 18% chromium steel refining, three routes are possible as shown in Fig. 5(a). Route A is a process at one atmospheric pressure. To get the ordinary carbon content of lower than 0.06%, some reductant material like silicon to reduce chromium oxide is necessary after the decarburization, since the oxidation of large amount of chromium is inevitable. Route B is a process under a low P_{CO} condition in vacuum or dilution gas like argon. Route C is a combining process in which the refining is first carried out at one atmospheric pressure until the carbon content decreases to the point P and then the steel is treated without oxygen gas at lower P_{CO} condition where the oxygen for the decarburization is supplied from the oxide slag already formed during the first refining period.

In the case of carbon steel refining, four routes are possible as shown in Fig. 5(b). Route A is a process at one atmospheric pressure, and the carbon content cannot be reduced to an extremely low level without oxidizing the most of iron. Route B is a process at a low P_{CO} condition in vacuum or dilution gas. Route C is a combining process in which the refining is first carried out with flux at one atmospheric pressure until the carbon content decreases to the point Q, and then the steel is treated without oxygen gas at a lower P_{CO} condition where the oxygen for the decarburization is supplied from the FeO in the slag already formed at the first refining period. Route D is another combination process. However, the oxygen for decarburization is supplied from the oxygen dissolved in steel.

Routes A, B and C are equivalent each in stainless steel refining to each in carbon steel refining. Route

Fig. 4. Equilibrated composition during refining of carbon steel.

Fig. 5. Reaction routes in stainless and carbon steel refining.

D, however, is industrially valuable only in carbon steel refining, since the carbon content is much higher than the oxygen content near the point P in Fig. 5 in stainless steel refining.

In next chapter, actual reactions in various refining processes will be compared with those decarburization routes.

2. Dephosphorization

Regarding the dephosphorization reaction of carbon steel refining, many equilibrium equations have been reported up to this time. Here, the dephosphorization reaction is discussed with Healy's equation. Healy¹¹⁾ has lately presented the equilibrium equation (13) for the dephosphorization reaction written as Eq. (12), where the CaO content in slag is applicable from 0% to the saturation.

$$\log (\% \text{P}) / [\% \text{P}] = 22\,350 / T - 16 + 2.5 \log (\% \text{T.Fe}) + 0.08(\% \text{CaO})^{11)} \dots\dots(13)$$

First, the optimum slag composition, where the distribution ratio of phosphorus in slag to that in metal is a maximum, is calculated on the condition that the total content of CaO, SiO₂ and FeO in slag is equal to 90%. By changing (%T.Fe) to (%FeO) with the equation, (%T.Fe)=0.8(%FeO),¹¹⁾ and calculating Eq. (13) for different slag basicities and temperatures, Fig. 6 can be obtained. The optimum FeO content of slag which makes the maximum phosphorus distribution ratio becomes lower as the basicity increases. The influence of temperature is so remarkable that the ratio (%P)/[%P] decreases to about one fourth with a temperature increment of 100°C.

In the above discussion only the slag composition is considered, but the effect of carbon in metal should also be taken into account for the dephosphorization. Then the influence of carbon in steel equilibrating with slag on the phosphorus distribution is calculated on conditions that the slag basicity (CaO/SiO₂) is 3 and the total content of CaO, SiO₂ and FeO is similarly 90%. By defining that

$$a_{\text{FeO}} = f_{\text{FeO}}(\% \text{FeO}) / 100 \dots\dots\dots(14)$$

Fig. 6. Effect of slag composition on phosphorus distribution ratio calculated by Healy's equation.

and calculating the term (%T.Fe) in Eq. (13) through Eq. (7), Eq. (15) can be obtained.

$$\begin{aligned} \log (\% \text{T.Fe}) &= \log (0.8 \times a_{\text{FeO}} \times 100 / f_{\text{FeO}}) \\ &= \log P_{\text{CO}} / a_{\text{C}} + 4\,990 / T \\ &\quad - 2.074 - \log f_{\text{FeO}} \dots\dots\dots(15) \end{aligned}$$

By substituting Eq. (15) into Eq. (13) and rearranging it, the phosphorus distribution ratio can be obtained finally as follows.

$$\begin{aligned} \log (\% \text{P}) / [\% \text{P}] &= 34\,830 / T - 22.76 + 0.08(\% \text{CaO}) \\ &\quad + 2.5 \log P_{\text{CO}} / a_{\text{C}} - 2.5 \log f_{\text{FeO}} \dots\dots(16) \end{aligned}$$

By changing *a_C* into carbon percent by Eq. (8) and reading *f_{FeO}* in Fig. 3, the relation between the carbon percent and the phosphorus distribution ratio can be obtained under various *P_{CO}* as shown in Fig. 7. As the carbon content increases and the *P_{CO}* decreases, the phosphorus distribution ratio becomes smaller.

The above calculation shows that the refining at a higher pressure is favorable for the dephosphorization, especially within the high carbon content range. Then the oxygen content in steel, the FeO content in slag and the oxygen efficiency for decarburization are calculated on the condition that the reactions proceed with keeping the equilibrated state at high pressures. The results calculated at 1, 5 and 10 atmospheric pressures are shown in Fig. 8. According to the increasing pressure, both the oxygen content in steel and the FeO content in slag begin to increase earlier and reach to the FeO saturation at a higher carbon content. In accordance with these composition changes of steel and slag, the oxygen efficiency for the decarburization drops earlier within the high high carbon content range.

From these calculations, it can be concluded that the equilibrium state is unfavorable for the dephosphorization within the high carbon content range as long as the refining is carried out at one atmospheric pressure, and that the refining with slag whose oxygen potential is higher than that of metal should be intended if a high pressure refining cannot be applied. In the next chapter, reactions in some actual refining

Fig. 7. Equilibrium relationship between carbon in steel, CO partial pressure and phosphorus distribution ratio.

Fig. 8. Equilibrated composition during refining under high pressure.

processes will be compared with these calculations for a discussion.

III. Reactions in Actual Refining Processes

1. Decarburization of Stainless Steel

Reactions in some actual refining processes of stainless steel are compared with the thermochemical calculations based on the reaction routes previously mentioned in Fig. 5.

1. Route A

The refining process of stainless steel at one atmospheric pressure in an electric arc furnace has been established by Hilty *et al.*¹²⁾ In this process it is well known that the oxidation of a large amount of chromium is inevitable to reduce the carbon content to the level lower than 0.06%. Although the refining is carried out at a higher temperature over 1 800°C in order to accelerate the decarburization with preventing the chromium oxidation, it is necessary to reduce the chromium oxide by silicon after the decarburization.

2. Route B

AOD, VOD, CLU and some other modified processes are roughly classified into the route B.

In regard to VOD process, Schmidt *et al.*¹⁾ have presented the relation between the carbon and the oxygen contents before and after the refining in a 30 t VOD vessel as shown in Fig. 9. The oxygen content after the refining is on the carbon–oxygen equilibrium curve at 0.1 atmospheric pressure. This result supports that chromium oxide can be reduced into steel in the VOD process, even if chromium happens to be oxidized by the blowing oxygen. However, the amount of chromium oxidation is actually 1~2%.¹⁾

The authors have also investigated the change of the oxygen content during the refining by a 10 t

Fig. 9. Relation between oxygen and carbon in high chromium steel before and after VOD refining (After Schmidt *et al.*¹⁾).

Fig. 10. Change of oxygen in steel during VOD refining of 18% chromium steel.¹³⁾

VOD vessel,¹³⁾ and showed that the oxygen content of steel changes along the equilibrium curve at about 0.1 atmospheric pressure as shown in Fig. 10. The oxygen efficiency for decarburization is lower than the calculated value as shown in Fig. 11. This discrepancy is mainly owing to the fact that chromium oxide is likely to form rigid lumpy slag, and they cannot easily be reduced into metal.

Next, in regard to AOD process, the behavior of oxygen in steel during the refining has not been investigated so much. According to the authors investigation in a 2.5 t AOD furnace,⁶⁾ as shown in Fig. 12, the oxygen content changes from the equilibrated value at 1 atm P_{CO} to that at 0.1 atm P_{CO} during the refining. Since the oxygen level is still lower than the solubility limit with chromium oxide, the decarburization can be performed with a small amount of chromium oxidation of 2%.⁶⁾

Fig. 11. Oxygen efficiency for decarburization during VOD refining of 18% chromium steel.¹⁸⁾

Fig. 12. Oxygen content of 18% chromium steel during AOD refining and the modified AOD refining where oxygen is supplied continuously by top blowing lance in LD.⁶⁾

Schürmann and Rosenbach¹⁴⁾ have investigated one of the modified AOD process in a 8 t ladle where argon gas is injected through the tuyeres constantly while oxygen gas is supplied intermittently through a top blowing lance to get enough time to reduce chromium oxide by carbon. Their result is shown in Fig. 13. The P_{CO} corresponding to the oxygen content changes from 1 to 0.1 atm during the refining. In spite of the fact that the oxygen level is close to the solubility limit with chromium oxide, the amount of oxidized chromium during the refining is as much as 2%.¹⁴⁾ In this process, the dilution of CO gas with argon gas can be achieved by supplying oxygen and argon separately. This point is very like that in VOD process where the oxygen gas supply and the pressure reduction by vacuum are given separately.

The authors⁶⁾ have recently investigated another modified AOD process in a 2.5 t LD converter where argon gas is injected through the tuyeres into the metal bath and oxygen is supplied continuously through a top blowing lance. The change of the oxygen content during this refining process is shown in Fig. 12, compared with that in AOD process. The oxygen level in this process is almost similar to that in AOD. 2~3% of chromium oxidation in this pro-

Fig. 13. Oxygen content in high chromium steel during the modified AOD refining where oxygen is supplied intermittently by top blowing lance (After Schürmann and Rosenbach¹⁴⁾).

cess is also similar to that in AOD.⁶⁾ This result shows that the reduction of carbon is possible within a small amount of chromium oxidation by the continuous oxygen top blowing method if argon is supplied appropriately through the tuyeres. This process has the advantages that stainless steel can be refined even in a LD converter and that rapid refining is possible within the high carbon range since the oxygen flow rate can be increased easily.

CLU (Creusot-Loire-Uddeholm) process¹⁵⁾ is also in this Route B group. In this process, oxygen-steam mixture is injected within the high carbon range and only steam within the low carbon range. Although steam reacts with steel to make hydrogen and CO or chromium oxide and the hydrogen dilutes CO gas, the maximum dilution of CO obtained by pure steam is similar to the Ar-O₂ mixture with a ratio of

Fig. 14. Oxygen content of high chromium steel before and after VODC refining comparing with VOD refining (Bauer *et al.*¹⁶⁾).

2 to 1. Since this CO dilution does not seem enough to prevent chromium oxidation, the process seems inferior to AOD process, especially within the low carbon range. The oxygen content during the refining has not been presented. The amount of chromium oxidation is as much as 3~4%,¹⁵⁾ and this result seems to support the above discussion.

3. Route C

The VODC (VOD-Converter) process developed by Bauer *et al.*¹⁶⁾ is corresponding to the route C. In this process, metal is first refined in a LD converter at one atmospheric pressure until the carbon content decreases to the content when chromium begins to be oxidized remarkably, and then the melt is treated under vacuum in the same furnace to decarburize further with the oxygen in the slag already formed. The changes of the oxygen contents before and after the vacuum treatment in a 55 t furnace are shown in Fig. 14. The oxygen content is beneath the equilibrated value at 0.1 atm of P_{CO} . From this figure, it is considered that about 0.3% of the oxygen in the slag is useful. This means that 0.5% of chromium is reduced in the second refining period. The oxidized amount of chromium is near 2%.¹⁶⁾ In this process, there is a suggestible point that even such rigid slag formed during the refining under one atmospheric pressure can act as the source of oxygen for decarburization through the mixing by the argon injection under vacuum.

As mentioned above, VOD and AOD (route B) and VODC (route C) have been applied for the industrial stainless steel refining with a small amount of chromium oxidation. In VOD process the reaction proceeds along the route B, but in AOD it proceeds through the route A within the high carbon range and the route B within the low carbon range. The latter is based on the reason that the low CO partial pressure is not always necessary within the high carbon range in order to prevent the chromium oxidation. However, the amount of chromium oxide reduced by carbon in the metal is very small as shown in VODC process, so it seems better to keep the chromium oxidation as low as possible even within the high carbon range.

2. Decarburization of Carbon Steel

Reactions in some actual refining processes of carbon steel are compared with the thermochemical calculations based on the reaction routes in Fig. 5, just as those in stainless steel.

Fig. 15. Oxygen in metal and total iron in slag during LD refining.¹⁷⁾

1. Route A

The processes at one atmospheric pressure such as LD and OBM including Q-BOP are corresponding to the route A.

Concerning LD process, many investigations have been performed. As an example, the results obtained about the oxygen content in steel and the iron oxide content as the total iron in slag during the refining in an 160 t LD converter by the authors¹⁷⁾ are shown in Fig. 15. The oxygen content changes along the carbon-oxygen equilibrium curve at one atmospheric pressure, but the actual content of oxygen is a little higher than the equilibrated value. The content of iron oxide in the slag is remarkably higher than the equilibrated value. These results show that the oxygen potential, especially of the slag, is higher than that determined by the carbon content of the metal and the P_{CO} . The oxygen efficiency for decarburization in another 70 t LD converter¹⁸⁾ is shown in Fig. 16. It is shown that the efficiency is lower than that in equilibrium in the case with the addition of a large amount of lime. This discrepancy is caused mainly by the fact that the oxygen potential of slag is higher than the equilibrated value and that the gradual dissolution of lime into the slag makes the efficiency decrease remarkably in the case with the addition of

Fig. 16. Oxygen efficiency for decarburization in LD converter measured by waste-gas analysis.¹⁸⁾

a large amount of lime.¹⁸⁾ In the LD converter, the carbon content cannot be reduced to lower than 0.03% due to the remarkable iron oxidation without decarburization.

In the Q-BOP process, as Pearce¹⁹⁾ have reported, both the oxygen content of steel and the FeO content of slag at turn down are lower than those in a LD converter. The oxygen content is close to the equilibrated value at one atmospheric pressure and is rather lower than that especially within the low carbon range. The latter is caused by the dilution of CO gas with the coolant gas containing hydrogen.²⁰⁾ The change of oxygen in metal and the total iron in slag obtained during the refining in a 2.5 t Q-BOP converter by the authors⁵⁾ are shown in Fig. 17. The oxygen content of steel in Q-BOP is lower than that in LD, and it is very close to the equilibrated value at one atmospheric pressure. The total iron content of slag in Q-BOP is also lower than that in LD as shown in Fig. 17, but it is still higher than the equilibrium value especially within the high carbon range. The oxygen efficiency for decarburization of Q-BOP, as shown in Fig. 18, becomes rather close to the value calculated on the condition that the FeO in slag is equilibrated with carbon in metal. From these results, it is considered that the reactions in Q-BOP proceed close to the equilibrium state by the effect of the violent mixing induced by the bottom blowing. Since the metal oxidation in this process is smaller than in LD, the carbon content can be reduced to a level of 0.015%,⁵⁾ which is in good agreement with the limit of decarburization previously calculated.

The authors have investigated the duplex blowing process in a 2.5 t converter where oxygen is supplied through a top blowing lance while a small amount of argon gas is injected through the bottom for the bath agitation.⁵⁾ The change of the oxygen content of metal and the total iron content of slag during the

Fig. 17. Oxygen in metal and total iron in slag during Q-BOP refining comparing with LD refining.⁵⁾

Fig. 18. Oxygen efficiency for decarburization in Q-BOP refining comparing with LD refining.

refining are shown in Fig. 19. Both the contents in the duplex blowing process are very similar to those

Fig. 19. Oxygen in metal and total iron in slag during duplex blowing LD refining.⁵⁾

in Q-BOP process. This means that the reactions in a LD converter approach closely to the equilibrium state by the help of injecting a small amount of gas into bath. Consequently, the carbon content can be reduced to about 0.015% in this process.⁵⁾

2. Route B

The authors have investigated the VOD refining of carbon steel in a 10 t VOD vessel without addition of flux.¹³⁾ The change of the oxygen content of steel during the refining is shown in Fig. 20. The oxygen content changes along the equilibrated value at 0.1 to 0.2 atmospheric pressure of CO, and the carbon content can be easily reduced to a level of 0.005%. The oxygen efficiency for decarburization is shown in Fig. 21. It is rather lower than the value calculated on the condition that the reactions proceed with keeping the equilibrium state. This discrepancy is caused mainly by the simultaneous oxidation of silicon and manganese together with carbon and the dissolution of oxygen into the slag formed.¹³⁾

The refining of carbon steel in the process using dilution gas like argon has not been investigated. An air blowing process in a Thomas converter can be included in this group. In Thomas process, high phosphorus hot metal is refined. Therefore, the slag composition in a Thomas converter is different from the slag which is formed from low phosphorus hot metal. However, the oxygen content of steel in a Thomas converter seems worth while discussing. The oxygen content of steel at turn down in a Thomas converter summarized by Koch *et al.*²¹⁾ is shown in Fig. 22. The oxygen level is corresponding to the equilibrium value at 1/3~1/6 atmospheric pressure of CO. The ratio of O₂ to N₂ in air is about 1/4, that is the P_{CO} in the reacted gas is 1/3 atm if the oxygen efficiency for decarburization is 100%. If the efficiency becomes lower within the low carbon range mainly with the formation of FeO in the slag, the P_{CO} in the reacted gas can decrease to lower than 1/3 atm. Consequently, it may be explained that the P_{CO} at turn down in a Thomas converter is actually 1/3~1/6 atmospheric pressure.

As shown in Fig. 22, the carbon content can be

Fig. 20. Oxygen content of carbon steel during VOD refining.¹³⁾

Fig. 21. Oxygen efficiency for decarburization during VOD refining of carbon steel.¹³⁾

Fig. 22. Carbon and oxygen content of steel at turn down of Thomas converter (Abstracted from Koch *et al.*²¹⁾).

reduced nearly to 0.006% during the refining in a Thomas converter. Such easy decarburization is owing to the dilution of CO with nitrogen, but the maximum dilution of CO is similar to that with the Ar-O₂ mixture with a ratio of 4 to 1.

3. Route C

In OBM process including Q-BOP, argon gas is injected after the end of the oxygen blowing in order to reduce the carbon content to such an extraordinary

Fig. 23. Change of metal and slag composition by argon injection after oxygen blowing in Q-BOP.

low level of 0.01%.²²⁾ This is one of the superior functions of OBM, compared with LD.

According to the authors' investigation in a 2.5 t Q-BOP converter, the reactions during the argon gas injection proceed along the route C. As shown in Fig. 23, the oxygen content of steel and the total iron content of slag do not change at all during the decarburization to 0.005% by the argon injection. This result shows that the oxygen for decarburization is supplied from the large amount of FeO in the slag. Since the oxygen in steel keeps a constant value, the reduction of the FeO into the steel seems rapid enough to compensate the oxygen content in steel consumed for the CO formation at the surface of argon bubbles.

Duplex blowing LD converter previously mentioned has the same function for the decarburization by the argon injection after the end of the oxygen top blowing. From the authors' investigation in a 2.5 t duplex blowing converter,²³⁾ the similar decarburization reaction can be obtained as shown in Fig. 24. Consequently, the decarburization to the level as low as 0.005% can be achieved by only one converter having argon injecting tuyeres.

4. Route D

The route D is well known for the decarburization reaction of steel in a ladle by vacuum treatment like DH or RH process. One example of DH process²⁴⁾ is shown in Fig. 25. Since the decarburization proceeds by the reaction with oxygen in steel itself, the carbon

Fig. 24. Decarburization reaction by argon injection after oxygen top blowing in duplex blowing LD refining.⁵⁾

RF: Recirculation factor

Fig. 25. Decarburization reaction in DH process after LD refining (After Umeda *et al.*²⁴⁾).

and the oxygen contents decrease simultaneously in the direction of the nearly atomic ratio of CO formation. This process has been widely used for the production of extraordinary low carbon steel, but the process has the shortcoming to need two reactors like LD-DH.

As discussed above, processes like OBM or duplex blowing LD converter can reduce the carbon content to a lower level than LD converter, because the reactions proceed closely to the equilibrium by the violent mixing. However, the limit of decarburization in the oxygen refining process at one atmospheric pressure (route A) is about 0.015%. In order to reduce the carbon content further to a level of lower than 0.010%, the decrease of CO partial pressure by vacuum or argon dilution in VOD (route B), argon injection after oxygen blowing in OBM or duplex blowing LD converter (route C), or DH succeeding LD converter (route D) is necessary. Among these processes, the converter with argon injection in which

the decarburization proceeds along route C seems the most suitable for the economical mass production, since the decarburization can be achieved from hot metal to an extraordinary low level in the one reactor.

3. Dephosphorization of Carbon Steel

Reactions in the following actual refining processes are compared with the thermochemical calculations; (1) the dephosphorization in oxygen converters, (2) the refining of steel under high pressures and (3) the dephosphorization of hot metal outside the converter.

1. Dephosphorization in Oxygen Converter

The FeO content of slag in LD process is much higher than that equilibrating with carbon in metal. On the other hand, the FeO in Q-BOP process is rather close to the equilibrated value. The FeO content in low carbon steel refining is near to the optimum level for dephosphorization both in LD and Q-BOP processes, while the FeO content in high carbon steel refining is not enough for good dephosphorization in both the processes, especially in Q-BOP process. Although Q-BOP process has advantages, such as small metal oxidation and good decarburization, the most inferior point of Q-BOP to LD is this unsatisfactory dephosphorization in high carbon steel refining. Comparison between LD and Q-BOP in regard to the dephosphorization is shown in Fig. 26 after the authors' investigation in a 2.5 t converter.⁵⁾ Dephosphorization proceeds to a lower level in LD than in Q-BOP. The result in a duplex blowing LD converter is also shown in this figure. With injecting the gas from the bottom under the optimum flow rate, the dephosphorization in this process proceeds along the lower level of LD. This reason is that the slag-metal reaction and the slag formation are promoted by the suitable agitation.

Consequently, processes like Q-BOP getting the reactions close to equilibrium state are unfavorable for the dephosphorization in high carbon steel refining. In LD process, on the other hand, it is possible to increase the iron oxide content of slag within the high carbon range by such means as soft blowing. Thus, non-equilibrated refining is recommended for the high carbon steel refining in converters operated at one atmospheric pressure.

2. Refining of Steel under High Pressures

Trials of refining steel under high pressures have scarcely been investigated, since the process is difficult and dangerous to be operated. Kazakow *et al.*²⁵⁾ has shown in a 80 kg LD converter that the iron oxide content in slag at the blowing end increases from 20~35% at one atmospheric pressure to 30~45% at 4 atmospheric pressure. The authors²⁶⁾ have also tested at 3 atmospheric pressure in a 60 kg LD converter. The result obtained is shown in Fig. 27. Although both the oxygen content of metal and the total iron content of slag are higher than those equilibrated with carbon in metal even at one atmospheric pressure, the tendency that both the oxygen in steel and the total iron in slag increase remarkably by rising the vessel pressure can be observed clearly. The optimum dephosphorization is achieved in this furnace

Fig. 26. Dephosphorization reaction in duplex blowing LD refining comparing with LD and Q-BOP refinings.⁵⁾

Fig. 27. Oxygen in metal and total iron in slag during LD refining under high pressure.²⁶⁾

at 1.5 atmospheric pressure at the carbon content of 1%.²⁶⁾ This result verifies that the refining under high pressures can be one method to promote dephosphorization for high carbon steel production as has been presumed by the previous calculation. However, it is considered that many problems have to be solved for the industrial application.

3. Dephosphorization of Hot Metal

Since low temperature is favorable for dephosphorization reaction, attempts to dephosphorize hot metal in a ladle have been carried out recently^{2,3)} before the refining in an oxygen converter. The authors^{3,27)} have investigated the process in which hot metal is treated at about 1300°C with CaO-FeO flux in a 45 t ladle with a mechanical stirrer and a small amount of oxygen injection. The result has the similar tendency with Healy's equation as shown in Fig. 28. High phosphorus distribution ratio can be obtained even in acid or weak basic slag. The

Fig. 28. Phosphorus distribution ratio in hot metal dephosphorization treatment.²⁷⁾

optimum content of iron oxide in slag decreases as the slag basicity increases. However, the constant term in Eq. (13) should be changed from -16.0 to -17.5 in the hot metal dephosphorization at 1330°C .²⁷⁾

In this process, the iron content of slag can be kept as high as $10\sim 50\%$ during the treatment. Thermochemically such high iron oxide slag cannot coexist with high carbon hot metal. Considering that the decarburization of hot metal during treatment is smaller than 1% , the reaction seems to be suppressed in this process. Thus, this process may be realized owing to the extremely non-equilibrated state between slag and metal.

The introduction of the hot metal dephosphorization process has great influences on overall steelmaking process. If most of phosphorus is removed at the stage of hot metal, the function of oxygen converter will become a reactor for mere decarburization. At that time, the oxygen converter should have the function to decarburize steel to an extraordinary low level without metal oxidation. For this purpose, oxygen converter in which argon can be injected after oxygen blowing will be the most suitable reactor. This reactor can also refine alloy steels with including a reducing period.

IV. Summary

Relationships among the metal oxidation, the decarburization and the dephosphorization in stainless and carbon steel refinings were thermochemically calculated. These calculated were compared with the actual reactions in various refining processes.

For decarburization reaction, refining under low CO partial pressure is favorable because of being able to reduce oxidation. The limit of decarburization in the refining at one atmospheric pressure and the effectiveness for decarburization in refining under reduced CO partial pressure by vacuum or dilution with argon have been discussed in regard to such processes as electric furnace process, VOD, AOD including modified process like duplex blowing LD process and CLU for stainless steel as well as LD, OBM(Q-BOP), duplex blowing LD process, VOD, Thomas and DH for carbon steel. The duplex blowing LD process has been emphasized to be useful for decarburization in stainless and carbon steels.

For dephosphorization reaction of carbon steel,

refining with slag of optimum iron oxide content and refining at low temperature are favorable. Dephosphorization in such refining processes at one atmospheric pressure as LD, Q-BOP and duplex blowing LD process, the effectiveness of refining under high pressure for dephosphorization of high carbon steel and hot metal dephosphorization at low temperature have been discussed. If any CO partial pressure can be selected, both decarburization and dephosphorization can be achieved satisfactorily by refining close to equilibrium state. However, if refining under high pressure cannot be realized, non-equilibrium state is recommended for high carbon steel refining. In this point, LD process is preferable to Q-BOP process, since the oxygen potential of slag can be increased more in LD than in Q-BOP. Further, dephosphorization of hot metal is useful, and this process can be carried out with the suitable dephosphorizing slag which is in extreme non-equilibrium state at low temperature as far as decarburization is concerned. Overall steelmaking process when hot metal dephosphorization process is adopted has been also discussed.

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