Development of Steelmaking Process for Stainless Steel by Top and Bottom Blowing with Coke Addition in Converter*

By Noriyuki MASUMITSU,** Ryutatsu TANAKA,*** Takashi INOUE,***
Shingo SATO*** and Kiyoshi TAKASHIMA***

Synopsis

At Muroran Works, Nippon Steel Corporation, stainless steel has been produced by the LD-RH·OB process since 1972. This process has recently been improved by introducing the hot metal dephosphorization treatment and the top and bottom combination blowing of a LD converter. This paper shows the results when stainless steel scrap is used for the stainless steelmaking process by the addition of carbonaceous materials as an auxiliary heat source in the top and bottom blowing converter.

The results obtained are as follows:

(1) No significant difference in the heat efficiency is observed between the bottom injection of coke breeze and the top feeding of lump coke in the converter.

(2) The most effective way to high Cr yield is the additions of SUS scrap first separately before of HC-FeCr.

(3) The bottom gas injection accelerates the reactions to the thermodynamic equilibrium. For example, the (Cr_2O_3) content in the slag at the turn down is significantly lower than that in the conventional converter.

(4) The contents of [S] and [N] in molten steel at the turn down in the LD refining process increase with the addition of coke through the nitrogen bottom blowing. These impurity contents can be reduced to the normal level in the successive RH refining.

I. Introduction

The “hot metal pretreatment/combination blowing” process has become the main stream of the converter steelmaking technology for the integrated steelmakers.¹⁾

In stainless steel refining, particularly in the converter/vacuum decarburization process, efforts have been also made to introduce the single slag practice through the use of dephosphorized hot metal and to enhance the reduction refining through the combination blowing.²⁻⁵⁾ At Nippon Steel's Muroran Works, where stainless steels are produced by the LD-RH·OB process,⁶⁾ the various improvements such as process simplification and the realization of low-phosphorus stainless steel have been made through the introduction of hot metal dephosphorization.⁷⁾

Tests have recently been conducted in the new steelmaking process which uses stainless steel scrap as a source of chromium, and small lump cokes and coke breezes as a heat source for scrap melting. This report contains the metallurgical characteristics of the melting of stainless steel scrap by the carbonaceous materials in the combined-blown converter and its effects on the product quality.

II. Manufacturing Process and Its Features

Figure 1 shows the stainless steel production by the LD-RH·OB process developed at Muroran Works.

The operational conditions of the hot metal pretreatment, the converter and the RH degassing equipment are given in Table 1. The stainless steel manufacturing process consists of the following three steps.

(1) Hot Metal Pretreatment

Desiliconization is performed by injecting oxygen gas through the injection lance. After the removal of the desiliconization slag, dephosphorization is performed by injecting the CaO-CaF_2 powder as a dephosphorizing flux, together with oxygen gas and mill scales as oxidizers, through the injection lance. When an extra-low-sulfur hot metal is needed, desulfurization is further carried out by using an Na_2CO_3 flux. With these pretreatments, the hot metal with $[\text{P}] \leq 0.015\%$ and $[\text{S}] \leq 0.007\%$ is obtained.

(2) Chromium Melting in the Converter

The hot metal and high-carbon ferro-chromium (HC-FeCr) are added into the vessel for the decarburization. Since the refining is intended during the high carbon content at the high temperature in the converter to minimize the oxidation loss of chromium, the end-point carbon and the temperature are set to be $0.60 \sim 0.70\%$ and $1780 \sim 1800$, respectively.

(3) RH·OB Treatment

The liquid steel tapped from the converter is preferentially decarburized without the oxidation of chromium, by the injection of oxygen gas under the reduced pressure in the RH degassing equipment. After the decarburization period, silicon and aluminum are added for the deoxidation and the composition adjustment.

III. Test Method for the Use of Stainless Steel Scrap in the Converter

Figure 2 shows the outline of the equipment used in the tests. Stainless steel scrap was charged into the 120-t combined blown converter with the aid of scrap bags. The cokes used as a heat source for melting the scrap are of small lump and breeze, which are not suitable for the blast furnace. The lump coke was charged through the alloy addition chute, whereas the coke breeze was injected through the nozzles on the vessel bottom. The chemical composition and size of the coke added are given in Table 2. The stainless steel scrap used included the crops from the continuous casting process, the scrap from the slabbing mill, the both are almost in the as-generated forms.

* Based on the papers presented to the 108th ISIJ Meeting, October 1984, S1015 and S1016, at Hiroshima University in Hiroshima. Manuscript received on June 11, 1985; accepted in the final form on December 6, 1985. © 1986 ISIJ

** Carnegie-Mellon University, Pittsburgh, PA 15213, U.S.A. On leave from Muroran Works, Nippon Steel Corporation.

*** Muroran Works, Nippon Steel Corporation, Nakamachi, Muroran 050.

Fig. 1. Production of stainless steel by the LD-RH·OB process.

Table 1. Specification for equipment of LD-RH·OB process.

(i) Hot metal pretreatment		
Type	Injection lance	
Number of hopper	5 (CaO, CaF ₂ , FeO, Na ₂ CO ₃)	
Oxygen flow rate	1 500 Nm ³ /h	
Nitrogen flow rate (coolant gas)	250 Nm ³ /h	
Capacity	max. (100 t/ladle)	
(ii) LD furnace		
Items	No. 1 LD	No. 2 LD
Nominal capacity	110 t	120 t
Shell volume	166 m ³	203 m ³
Volume after lining	91 m ³	104 m ³
Oxygen flow rate	18 000 Nm ³ /hr	18 000 Nm ³ /hr
Bottom blowing	—	2 nozzles (N ₂ , CO ₂)
(iii) RH degassing unit		
Number	Twin (change of reactor)	
Shell dimension	2 450 mmφ × 10 080 m/m	
Gas exhausting system	6 stages ejector	
Exhaust gas rate	500 kg/h at 0.5 Torr	
Degree of vacuum	0.05 Torr 760 → 10 Torr 130 sec	
Oxygen flow rate	max. 2 000 Nm ³ /h	

The bottom-blown gases were Ar, N₂ and CO₂, depending on the grade of steel to be produced with regard to the nitrogen content limits, *i.e.*, mainly N₂ or CO₂ for the oxygen blowing period and Ar for the reduction period.

Fig. 2. Schematic flow diagram of coke addition in LD converter.

Table 2. Chemical composition and size of coke.

Chemical composition (%)						Size (mm)	
C	S	P	N	V.M.	Ash	Lump coke	Coke breeze
87.0	0.48	0.06	0.2	1.5	10.5	20~30	0.1~0.8

IV. Test Results

1. Scrap Melting Capacity of the Carbonaceous Materials

Various reports are available on the addition of carbonaceous materials into the converter as the heat source.⁸⁻¹⁰⁾ In these papers, the effects of the carbonaceous materials upon the increases in the liquid steel temperature in the converter are reported to be in the range of 5~7 °C/kg-C, depending on their kinds and the sizes, the carbon concentration in the steel bath, the intensity of the bottom stirring, the post-combustion rate of CO gas and the other factors. The enthalpy change in the liquid steel by the addition of the carbonaceous materials is calculated in Appendix mainly on the basis of sensible heat for heating the carbonaceous materials from the room

temperature up to the bath temperature, the heat of carbon solution, and the heat of carbon oxidation. When the coke containing 87 % C is used as a carbonaceous material, the amounts of heat generated by the lump coke charged into the vessel and the coke breeze injected through the vessel bottom are calculated to be 5.7 °C/kg-coke and 5.3 °C/kg-coke, respectively.

Figure 3 shows the relationship between the amount of coke added and the stainless steel scrap ratio. With an approximately 30 kg/t of coke addition, the approximately 10 % (100 kg/t) of stainless steel scrap was melted, with no scrap left unmelted. No significant difference in the melting capacity was observed between the lump coke and the coke breeze, contrary to the expected difference in the melting capability between them because of longer melting time required for the lump coke than for the coke breeze and therefore the lower yield for the lump coke. This is probably due to the fact that the lump coke can also completely melt within the scrap melting time of 7~10 min, and this nearly 100 % yield is proved by the oxygen and carbon balance at the blow off point of the scrap melting period. According to Fig. 3, the coke has a scrap melting capability of 3.0~3.5 kg per unit weight of coke (5.4~6.3 °C/kg-coke, assuming that 1 % of scrap ratio is equivalent to 18 °C) in fair agreement with the calculated values in Appendix and with the reported values.⁸⁻¹⁰⁾

2. Heat Efficiency with and without Coke Addition

Figure 4 shows the relationship between the amount of the coke added and the partition of the heat input into the steel, the slag the out gas, etc. With increase in the amount of the coke added, the partition of the heat, η_H to the molten steel (broken line in the figure) decreases. With 25 kg/t of the coke added, it lowers by 14 %. This is because the total heat input in the converter increases with the coke consumption whereas the heat output to the molten steel is kept constant as the blow-end temperature in the converter is almost constant. The 120-t converter at Muroran No. 2 steelmaking plant is of the boiler type where the heat of the secondary oxidation reaction of carbon is recovered as steam. This steam recovery and the

Fig. 3. Relationship between amount of coke added and the stainless steel scrap ratio.

sensible heat of steel are the effective energy. A coke addition of 25 kg/t causes an approximately 4 % drop in the effective energy as shown in Fig. 4.

This decrease is attributable, firstly to the increase in the loss of the waste gas sensible heat with the increase in the amount of the waste gas, secondly to the loss of the sensible heat associated with the increase in the amount of the slag due to the ash content (15~17 %) of the coke, and thirdly to the increase in the radiation heat from the furnace in the prolonged blowing time caused by the increase in the amount of the coke added.

Figure 5 shows the typical heat balances in the stainless steel refining with and without the coke addition. In the heat with a coke addition of 24 kg/t, the steam generation is more than twice, and the loss as the sensible heat of the waste gas is more than one and half times bigger than that without the addition. The heat efficiency including the steam recovery, is 58.6 % with the coke addition, and 60.5 % without the addition.

3. Scrap Melting Patterns

Table 3 shows the scrap melting patterns. In the conventional practice, HC-FeCr is added in two equal lots to prevent oxygen blowing at the low temperature. On the present tests, on the other hand, three scrap melting methods were compared. For Method A, HC-FeCr, stainless steel scrap, and coke were added simultaneously at the initial stage of the blowing.

Although this method allows a short operation time, it inherently includes the oxygen blowing at the low temperature and the low carbon condition. Method B consists of an addition of coke at the initial stage of the blowing and a subsequent simultaneous addition of HC-FeCr and stainless steel scrap in the intermediate stage. This method is characterized by the oxygen blowing at the high temperature in the high carbon region since it consists of an advance addition of coke and the subsequent separate additions of HC-FeCr and stainless steel scrap.

Figure 6 shows the relationship between the stain-

Fig. 4. Relationship between the partition of heat and coke consumption.

Fig. 5. Heat balances in SUS refining with and without coke addition.

Table 3. Patterns of scrap and HC-FeCr melting.

pattern	Start	End	Characteristics
Conventional	<div>FeCr</div> <div>FeCr</div>		•Divided charge of FeCr
A	<div>Coke</div> <div>Scrap</div> <div>FeCr</div>		•Charging together of FeCr and Scrap •Melting in low temp. and low [%C] range
B	<div>Coke</div> <div>Scrap</div> <div>FeCr</div>		•Charging together FeCr and Scrap •Melting in low temp. and high [%C] range
C	<div>Coke</div> <div>Scrap</div> <div>FeCr</div> <div>FeCr</div>		•Separate charging of Scrap and FeCr •Melting in high temp. and high [%C] range

less steel scrap ratio and the Cr₂O₃ content in the slag at the blow-end.

For Methods A and B, the Cr₂O₃ content in the slag increases with increase in the stainless steel scrap ratio. For Method C, however, the Cr₂O₃ content in the slag remains constant at the range of 4~8 % even when the stainless steel scrap ratio is increased. This can be qualitatively understood by the schematic diagram, Fig. 7 where the trajectory of the temperature and the carbon content is depicted for each pattern in the C-Cr-temperature equilibrium curve.¹¹⁾ It is clear from the figure that for Method C the steel experiences less time to go through the region where the chromium oxidation is predicted by the thermodynamic calculation, thus resulting in the less chromi-

Fig. 6. Effect of scrap melting pattern of (% Cr₂O₃) at turn down.

Fig. 7. Schematic diagram of refining pattern in C-Cr-temperature equilibrium curve.

um oxidation in accord with the experimental results shown in Fig. 6.

4. The Effect of Bottom Stirring

1. Improvement of Decarburization Reaction

Figure 8 shows the relationship between [C] and (Cr₂O₃) at the blow-end for the conventional LD and the combined-blown LD converters. In a high-carbon region of [C]≥0.60 %, (Cr₂O₃) remains at the same level of 3~7 % for both the top and the combination-blown practices. In an low-carbon region of [C]<0.6 %, however, the bottom blowing at a flow rate of over 0.20 Nm³/t-min remarkably decreases the (Cr₂O₃) content in the slag. For example the (Cr₂O₃) in the slag at the blowing end of SUS430 steel with the [C] content of 0.25 % is approximately 10 % for the combination blowing whereas approximately 20 % for the top blowing. Kai *et al.*⁵⁾ reported that the combination blowing has an effect of the reducing (Cr₂O₃) in the slag even at such a low flow rate of the bottom-blown gas as 0.06 Nm³/t-min or below. The present tests, however, show that the effect of the bottom blowing becomes pronounced at the flow rates over 0.20 Nm³/t-min. The need for the higher flow rate of the bottom

Fig. 8. Influence of bottom blowing gas on the relationship between [% C] and (% Cr₂O₃) at turn down.

gas in our case may be attributable to the higher inhomogeneity of the chromium distribution in the bath due to the use of cold HC-FeCr (Cr≈52 %) as the source of chromium.

For the EF-LD process used by Kai *et al.*, the decarburization is performed for the high-carbon, high-chromium liquid steel that has been prepared by the proceeding EF process.

2. Elimination of Unmelted Scrap

In the present study using the combined blown converter, even when 10~12 t/heat of stainless steel scraps weighing 300~500 kg/piece were added to the base metal at approximately 1 650 °C, no unmelted scrap was observed after 8 to 10 min of the oxygen blowing. In the conventional top-blown converter, on the other hand, it has been experienced that the refining time of 8 to 10 min is not enough to the complete melting of such amount and size of the scraps even if the thermal balance is maintained at a proper level. This shows that the bottom stirring is quite effective to eliminate the unmelted scraps.

3. Reduction of (Cr₂O₃)

As noted earlier, one of the objectives of the intense bath stirring by the bottom gas blowing is to promote the reduction of the chromium oxide formed during the melting and decarburization periods. Figure 9 shows the relationship between the (Cr₂O₃) in the slag at the blow-end and after the reduction. With an addition of ferrosilicon as the reducing agent at constant levels of 0.5~1.0 kg/t, the (Cr₂O₃) in the slag after the reduction is 1.0 to 1.5 % lower in the combined-blown converter, compared with that in the top-blown converter.

Figure 10 shows a comparison of the relationship between the [C] and the (Cr₂O₃) at the end of the reduction refining in the conventional and the combined-blown converters. With the same [C] value, the (Cr₂O₃) in the combined-blown converter is approximately 2 % lower than that in the top-blown converter. In other words, the combined-blown converter is capable of the reducing blow-end [C] by 0.2 % at the same chromium loss, thus reducing the load for the subsequent decarburization in the RH unit.

4. Optimum Bottom Stirring Power

In order to determine the optimum reduction refin-

$$\eta_{Red} = \frac{(\%Cr_2O_3) \text{ turn down} - (\%Cr_2O_3) \text{ after reduction}}{(\%Cr_2O_3) \text{ turn down}}$$

Fig. 9. Relationship between (% Cr₂O₃) at turn down and (% Cr₂O₃) after reduction.

Fig. 10. Relationship between (% Cr₂O₃) in slag and [% C] in molten steel after reduction.

ing conditions, the total stirring energy is calculated from the following two equations.

$$\varepsilon_B = \frac{0.0285 \times Q_B \times 10^3 \times T}{W} \log \left(1 + \frac{L_0}{1.48} \right) \text{ (W/t)}$$

.....(1)¹²⁾

$$E = \varepsilon_B \times t \text{(2)}$$

- where, ε_B : physical stirring energy (W/t)
 T : steel bath temperature (°K)
 L_0 : steel bath depth (cm)
 E : total stirring energy (J/t)
 Q_B : flow rate of bottom blowing gas (Nm³/min)
 W : weight of liquid steel (t)
 t : reduction time (sec).

Figure 11 shows the relationship between the total stirring energy calculated from the above equations and the efficiency of ferrosilicon as the reducing agent for (Cr₂O₃). The reduction efficiency first increases with increase in the total stirring energy and then saturates at the total stirring energy of about 7×10⁵ J/t. It is found that, at a bottom-blown gas flow rate of 0.15 Nm³/t-min, for example, approximately

Fig. 11. Effect of bottom stirring on the (Cr₂O₃) reduction efficiency by FeSi.

4.5 min is sufficient for the reduction refining.

Figure 12 shows the changes in the chemical composition of the slag during the reduction refining. Almost 70 % of the (Cr₂O₃) is reduced in 2 min and the value of the (Cr₂O₃) becomes virtually constant after 6 min. The value of the (T.Fe) behaves similarly to of the (Cr₂O₃). The value of the (MgO), on the other hand, increases as the reduction reaction proceeds due to the refractory wear enhanced by the reduced basicity which is caused with SiO₂ formation by the reduction reaction and also enhanced by the bottom stirring.

5. Effects of Coke Addition on Steel Quality

1. Behavior of [S]

(1) Sulfur

Judging from the approximately 0.5 % S content of the coke used as the heat source and the low desulfurization ratio in the converter, most of the sulfur is considered to be captured in the liquid steel. Figure 13 shows a typical example of the sulfur balance when 24 kg/t of the coke is added.

Approximately 60 % of the input sulfur comes from the coke and 17 % from the HC-FeCr ([S] ≈ 0.10 %). This means that approximately 80 % of sulfur is brought into the liquid steel from the sources other than the base metal. Consequently, desulfurization of the liquid steel after the refining in the converter is essential to ensure the sulfur concentration obtained so far by the conventional process.

(2) Desulfurization during Oxygen Blowing in Converter

Figure 14 shows the relationship between the slag basicity and the desulfurization ratio during the oxygen blowing. The desulfurization ratio increases with increase in the slag basicity. However, the optimum slag basicity is 1.3 to 1.4 in terms of the yield of chromium, so much desulfurization during the oxygen blowing can not be expected.

(3) Desulfurization during Reduction Period

Figure 15 shows the relationship between the [S] at the end point of the oxidizing refining and the desulfurization ratio in the reduction refining. The desulfurization ratio increases with increase in the blow end [S] and the slag basicity. The effect of the basicity is remarkable for the case when the

Fig. 12. Change of slag composition during reduction by bottom blowing.

Fig. 13. Sulfur balance in LD refining.

Fig. 14. Relationship between basicity and desulfurization ratio in LD refining.

Fig. 15. Desulfurization ratio during reduction period.

desulfurization ratio is improved to 37 % by increasing the basicity up to 1.8. To improve the desulfurization ratio during the reduction refining, the liquid steel is better to be fully killed by the [Si] of 0.4~0.6 %.

According to the report on the operation data from the AOD vessel,¹⁶⁾ desulfurization is effectively accomplished in the high-[Si], low-[O] region, *i.e.*, the end-point temperature of 1 745 °C [Si]=0.66 %, [O]=160 ppm after the chromium reduction; and end-point temperature of 1 690 °C, [Si]=0.52 %, [O]=40 ppm after the desulfurization, respectively. On the other hand, in the LD-RH·OB process at Muroran Works, a vacuum decarburization by RH is conducted after the converter blowing. Figure 16 shows the relationship between the [Si] concentration in the steel before RH treatment and the oxygen efficiency for decarburization in the RH process. As the [Si] concentration before the RH treatment increases, the oxygen efficiency for the decarburization decreases. To cope with this, the upper limit for the [Si] before the RH treatment has to be set at 0.15 %. So the refining in the converter is conducted at the elevated temperature to inhibit the oxidation loss of chromium, the [Si] content in the molten steel at the blow-end is in the range of 0.05~0.08 %. From the equations given below, the oxygen concentration is calculated to be 530~800 ppm at 1 780 °C, [Cr]=16.5 % and [C]=0.5~0.8 %.

$$\begin{aligned} \text{C} + \text{O} &\rightarrow \text{CO} \log K = \log \frac{P_{\text{CO}}}{a_{\text{C}} \cdot a_{\text{O}}} \\ &= 1\,160/T + 2\,003^{13-15)} \\ e_{\text{C}}^{\text{O}} &= 0.298, \quad e_{\text{O}}^{\text{C}} = -0.316, \quad e_{\text{Cr}}^{\text{C}} = -0.024 \\ e_{\text{O}}^{\text{O}} &= -0.421, \quad e_{\text{O}}^{\text{O}} = -1\,750/T = 0.76, \quad e_{\text{Cr}}^{\text{O}} = -0.040 \end{aligned}$$

For these reasons, the desulfurization during the

reduction refining in the converter can not be expected.

In the present tests, therefore, the desulfurization is carried out by using a CaO–CaF₂ flux after the decarburization and the deoxidation in the RH.¹⁷⁾

2. Behavior of Nitrogen

The nitrogen content in the molten steel at the oxygen blow end in the present converter tests was in between 150~250 ppm, which was larger than that (60~80 ppm) in the conventional process partly because the coke used contains 1.2 % N and partly because N₂ gas was used as the coke breeze carrier gas.

Figure 17 shows the behavior of nitrogen during the refining in the converter. The figure indicates that the denitrification reaction, together with the decarburization reactions, take place during the oxygen blow. It can be also seen that the nitrogen absorption proceeds when the blowing is interrupted for the scrap and Fe–Cr addition. After the repeated increase and decrease, the nitrogen concentration at the end of the blowing becomes 150~250 ppm.

Figure 18 shows the yield of nitrogen gas in the converter. The yield of nitrogen gas at the end of the blowing decreases from 11 to 4 % as the volume of bottom blown nitrogen gas increases. Nitrogen input includes 0.03 % from the coke (with 25 kg/t of coke containing 1.2 % N) and 0.2~0.4 % from the bottom-blown gas (1.2~2.8 Nm³/t). Thus the nitrogen input from the coke stands for approximately 10 % of the total input and, therefore, causes no problem of the high nitrogen concentration for virtually all stainless steel grades.

Figure 19 shows the changes in the nitrogen concentration during the RH refining. As can be seen in the figure, even for a nitrogen concentration of 400 ppm before the RH treatment, therefore, the

Fig. 16. Effect of [Si] content at RH start on the efficiency of oxygen for decarburization.

Fig. 17. Change of [N] in molten steel during LD blowing.

Fig. 18. Relationship between volume of nitrogen gas and ratio of nitrogen absorption in LD converter.

concentration can be reduced to less than 150 ppm after the RH refining by ensuring the sufficient decarburization. Thus, the nitrogen absorption from the coke and the bottom blowing nitrogen gas can be offset by degassing in the RH.

Stainless steels with a nitrogen specification of $[N] \leq 100$ ppm can be successfully produced by using gases other than N_2 , such as CO_2 and Ar, for the bottom-blown gas in the combined-blown converter.

V. Conclusion

(1) No significant difference in scrap melting capacity has been observed between the bottom injection of coke breeze and the top feeding of lump coke as the heat source. The scrap melting capacity of the coke is 3.0~3.5 kg-scrap/kg-coke (5.4~6.3 °C/kg-coke).

(2) With increase in the coke addition, the thermal efficiency of the converter is lowered, e.g., approximately 4 % low at the coke addition of 25 kg/t when the steam recovery is included in the effective energy.

(3) The optimum scrap melting pattern for refining stainless steel is the one in which carbonaceous materials are added before solid iron source (HC-FeCr, stainless steel scrap), and the stainless steel scrap and the HC-FeCr are separately added. This practice allows the oxygen blowing to be carried out under the high-temperature and high-carbon condition.

(4) Bottom blowing is effective in improving the decarburization reaction in the low-carbon region of $[C] \leq 0.6$ %. Furthermore, the reactions between the (Cr_2O_3) in the slag and the reducing elements can be enhanced by ensuring stirring energy $E \geq 7 \times 10^5$ J/t during the reduction refining.

(5) The increase in the sulfur and nitrogen contents caused by the coke and the bottom-blown gas can be compensated by the subsequent RH refining process, thus making the same quality of the stainless steel as that in the conventional ones.

According to the results obtained by the test described in this report, the new process has been put into operation since 1983. In the new process lump coke is added in 10 % SUS scrap melt from the top of the converter with the bottom blowing.

Fig. 19. Nitrogen removal during RH treatment.

REFERENCES

- 1) T. Ueda, K. Marukawa and M. Anezaki: *Tetsu-to-Hagané*, **69** (1983), 24.
- 2) I. Tanaka, K. Kanekogi, U. Gondoh, T. Uchimura, T. Inatomi and M. Tsuchinaga: *Tetsu-to-Hagané*, **69** (1983), S143.
- 3) S. Murakawa, N. Satoh, T. Uchimura, H. Aoki, M. Tsuchinaga and M. Kobayashi: *Tetsu-to-Hagané*, **70** (1984), S1017.
- 4) Kawasaki Steel Corp.: Report to the 67th Special Steel Comm., Joint Research Soc., ISIJ, March 1982.
- 5) T. Kai, F. Hoshi, Y. Uedate and T. Yamagami: *Tetsu-to-Hagané*, **70** (1984), 680.
- 6) Y. Kamii, S. Ohkubo and A. Etoh: *Tetsu-to-Hagané*, **63** (1977), 2064.
- 7) S. Ono, T. Itoh, S. Satoh, T. Inoue, N. Masumitsu and T. Hasegawa: *Tetsu-to-Hagané*, **68** (1982), S296; *Trans. ISIJ*, **22** (1982), B381.
- 8) Y. Ohnishi, M. Kawasaki, W. Takagi, Y. Igai, J. Katsuta and M. Aoki: *Tetsu-to-Hagané*, **70** (1984), S264.
- 9) Kawasaki Steel Corp.: Report to the 84th Steelmaking Comm., Joint Research Soc., ISIJ, March, 1983.
- 10) Karl Brotzmann: JOURNEES SIDERURGQUES ATS, 1981, SESSION 8.
- 11) D. C. Hilty, H. P. Rassbach and W. Crafts: *JISI*, **180** (1955), 6, 116.
- 12) N. Nakanishi, T. Fujii and J. Szekely: *Ironmaking Steelmaking*, (1975), No. 3, 193.
- 13) The 19th Committee (Steelmaking), Japan Soc. Promotion of Science (JSPS), Recommended Equilibrium Values in Steelmaking Reactions, Nikkan Kogyo Shinbunsha, Tokyo, (1968).
- 14) Y. Kojima and K. Sano: *Tetsu-to-Hagané*, **50** (1964), 888.
- 15) T. Fuwa, S. Ban-ya and K. Suzuki: The 19th Committee (Steelmaking), Japan Soc. Promotion of Science (JSPS), Rep. No. 8132 (May, 1966).
- 16) K. Yamada, H. Higashi, T. Hiyama and K. Sugimura: *Tetsu-to-Hagané*, **67** (1981), 2145.
- 17) S. Satoh, T. Inoue, N. Masumitsu and K. Kinoshita: *Tetsu-to-Hagané*, **69** (1983), S180; *Trans. ISIJ*, **23** (1983), B405.
- 18) M. Ohtani: Thermodynamics in Iron Metallurgy, Nikkan Kogyo Shinbunsha, Tokyo, (1971), Appendix 1.
- 19) Handbook on Physical Properties of Molten Iron and Slags, ed. by ISIJ, ISIJ, Tokyo, (1972), 184.

Appendix

1. Heat of Oxidation of Carbon

When the composition of waste gas of LD is assumed to be $\text{CO}=85\%$ and $\text{CO}_2=7.5\%$, the heat of carbon oxidation is calculated as

$$\begin{aligned} 2\,450 \times \frac{85}{85+7.5} + 8\,080 \times \frac{7.5}{85+7.5} \\ = 2\,906 \text{ kcal/kg-C} \end{aligned}$$

from Eqs. (A-1) and (A-2).

Fixed carbon of coke is 87% , so the heat of coke oxidation is

$$2\,906 \times 0.87 = 2\,528 \text{ kcal/kg-coke} \dots\dots(\text{A-3})$$

2. *Sensible Heat of Coke*¹⁸⁾ ($25^\circ\text{C} \rightarrow 1\,600^\circ\text{C}$)

$$\begin{aligned} C_p^c = 4.10 + 1.02 \times 10^{-3} T - 2.10 \\ \times 10^5 \times T^{-2} \text{ cal/mol } ^\circ\text{K} \end{aligned}$$

$$\int_{298}^{1873} C_p \cdot dT = 7.62 \text{ kcal/mol}$$

$$7.62 \times \frac{1\,000}{12} \times 0.87 = 552 \text{ kcal/kg-coke} \dots\dots(\text{A-4})$$

3. *Heat of Solution of Carbon*¹⁹⁾

4. *Sensible Heat of N_2 Carrier Gas* ($25^\circ\text{C} \rightarrow 1\,600^\circ\text{C}$)

$$C_p^{\text{N}_2} = 6.66 + 1.02 \times 10^{-3} T \text{ cal/mol } ^\circ\text{K}$$

$$\int_{298}^{1873} C_p \cdot dT = 12.3 \text{ kcal/mol}$$

As the solid / gas ratio of coke injection is 5, the sensible heat of N_2 for 1 kg coke injection is

$$1 \times \frac{1}{5} \times \frac{1}{28} \times 10^3 \times 12.3 = 88 \text{ kcal/kg-coke} \dots\dots(\text{A-6})$$

5. *Sensible Heat of O_2* ($25^\circ\text{C} \rightarrow 1\,600^\circ\text{C}$)

$$C_p^{\text{O}_2} = 7.16 \times 1.00 \times 10^{-3} T - 0.4 \times 10^5 \times T^{-2}$$

$$\int_{298}^{1873} C_p \cdot dT = 13.01 \text{ kcal/mol}$$

$$\begin{aligned} \frac{1\,000}{32} \times 13.01 \times \frac{16}{12} \times 0.87 = 472 \text{ kcal/kg-coke} \\ \dots\dots\dots(\text{A-7}) \end{aligned}$$

6. *Specific Heat of Steel*

$$210 \text{ kcal/t} \cdot ^\circ\text{C} \dots\dots\dots(\text{A-8})$$

In the case of lump coke addition from vessel top, the amount of heat generated by coke is calculated by Eqs. (A-3)~(A-5), (A-7) and (A-8), and is $5.7^\circ\text{C/kg-coke}$.

In the case of coke breeze injection through vessel bottom, the amount of heat generated by coke is calculated by Eqs. (A-3) to (A-8), and is $5.3^\circ\text{C/kg-coke}$.