#### Abridged version

### KAWASAKI STEEL TECHNICAL REPORT

No.6 (September 1982)

Metallurgical Characteristics of Combined-blown Converters

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#### Synopsis:

Kawasaki Steel Corporation has developed two different types of combined-blown processes for basic oxygen steelmaking; (1)inert gas-stirred LD(LD-KG) and (2)oxygen bottom-blown LD with the powdered lime injection (K-BOP). Small amount of bottom flows gas improves stirring intensity of steel bath and suppresses excessive oxidation of steel bath; hence LD-KG results in higher yields of iron and manganese than those of LD. K-BOP has shown much more advantages than other types of combined-blown processes, particularly in the removal of phosphorous and sulfur by the enhanced reaction with injected powdered lime.

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# Metallurgical Characteristics of

## **Combined-blown Converters\***

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Kawasaki Steel Corporation has developed two different types of combined-blown processes for basic oxygen steelmaking; ① inert gas-stirred LD(LD-KG) and ② oxygen bottom-blown LD with the powdered lime injection (K-BOP).

Small amount of bottom flows gas improves stirring intensity of steel bath and supresses excessive oxidation of steel bath; hence LD-KG results in higher yields of iron and manganese than those of LD. K-BOP has shown much more advantages than other types of combined-blown processes, particularly in the removal of phosphorous and sulfur by the enhanced reaction with injected powdered lime.

#### 1 Introduction

In the bottom-blown oxygen converters (Q-BOP, etc.), bath stirring intensity is much stronger than that in the top-blown converters (LD). As a result, the homogeneity of the metal bath is higher, with no slopping nor excessive oxidation occurring as does sometimes in the top-blown converters. Furthermore, the combined-blown converter is characterized by the low levels of (T.Fe) in slag and oxygen in steel and high partition ratios of [Mn], [S] and [P] at the blow end<sup>1)</sup>.

With the aim of fully utilizing such an advantage of the bottom-blown converter to improve the blowing characteristics of the top-blown converter, combined-blown process are developed at various steel works with an effort to intensify the both mixing<sup>2-8</sup>). Kawasaki Steel has also developed the following two combined-blown process and achieved some excellent results:

(1) LD-KG process in which an inert gas is blown at a small flow rate of 0.01 to 0.05 Nm<sup>3</sup>/min·t from

small-diameter single nozzles into the top-blown converter

(2) K-BOP process in which oxygen of a larger flow rate of 0.7 to 1.3 Nm<sup>3</sup>/min·t and powdered lime are injected through the coaxial-tube tuyere installed at the furnace bottom.

This report primarily describes metallurgical characteristics of the 250 t K-BOP converter equipped at No. 2 Steelmaking Shop of Mizushima Works.

#### 2 Top-blown Converter Facilities

In the LD-KG process which was applied to the 150 t converter at Chiba Works and 180 t converter at Mizushima Works, several small-diameter single nozzles are installed at the furnace bottom to allow injection of Ar or N<sub>2</sub> gas at a maximum flow rate of 0.05 Nm³/min·t. The K-BOP process is applied to Chiba 85 t converter and Mizushima 250 t converter. In the following, the specifications of the Mizushima 250 t K-BOP converter are described. Since the bottom of the K-BOP furnace is replaceable, two bottoms were used during the operation of one campaign. For the gas to cool and protect the coaxial-tube tuyere, propane is usually used and, in addition, other inert gases can also be mixed.

The amount of bottom-blown oxygen,  $Q_B$ , is limited by the number of tuyeres and can be increased up to

<sup>\*</sup> Originally published in Kawasaki Steel Giho, 14 (1982) 3, pp. 1-10

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40% of the total amount of oxygen ( $Q_A + Q_B$ ; where  $Q_A$  is the amount of top-blown oxygen). The amount,  $Q_B$ , has been selected on the conditions that the total amount of powdered lime can be injected and that the perfect mixing time of the metal bath predicted from equation (1)<sup>91</sup> is sufficiently short and approximates that in the Q-BOP:

$$\tau = 800 \dot{\epsilon}^{-0.4} N^{1/3}$$
  
= 800( $\dot{\epsilon}_{\rm T} N_{\rm T}^{-0.833} + \dot{\epsilon}_{\rm B} N_{\rm B}^{-0.833}$ )<sup>-0.4</sup> ····(1)

- τ: Perfect mixing time of metal bath (sec)
- è: Energy dissipation rate for mixing of metal bath (W/t-steel)
- N: The number of nozzles
- T, B: These suffixes indicate topblowing and bottom-blowing, respectively.

Fig. 1 shows the relation between the perfect mixing time and the bottom-blowing oxygen ratio  $Q_{\rm B}/(Q_{\rm T}+Q_{\rm B})$ , where the total oxygen feed is kept at a constant value. The perfect mixing time conspicuously shortens until the bottom-blowing oxygen ratio rises up to about 30%, but this shortening effect seems to become unappreciable at if the oxygen ratio above 30%.

Fig. 2 shows the relation between the bottom gas blowing rates and the perfect mixing time of the steel bath in LD-KG and K-BOP in comparison with other combined-blown processes. As for the processes which blow oxygen gas from the bottom, factor 2 is taken into consideration for the bottom gas-blowing rate

shown in Fig. 2. The combined-blown processes executed in various steel-works are classified into the following three types:

- Processes in which an inert gas is blown at a maximum flow rate of 0.1 Nm³/min⋅t (LD-KG, STB, NK-CB, LD-AB and LBE).
- (2) Processes in which the O<sub>2</sub> gas is blown at a flow rate of 0.07 to 1.0 Nm<sup>3</sup>/min·t (LD-OB, and LD-OTB).
- (3) Process in which O<sub>2</sub> is blown at a flow rate of 0.7 to 1.3 Nm<sup>3</sup>/min·t together with powdered lime (K-BOP).

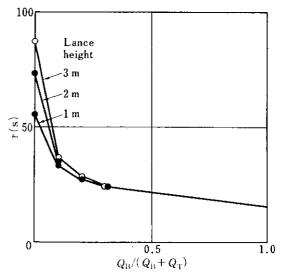


Fig. 1 Relation between time, τ, for perfect mixing of the bath and bottom blowing ratio of oxygen in 250 t K-BOP

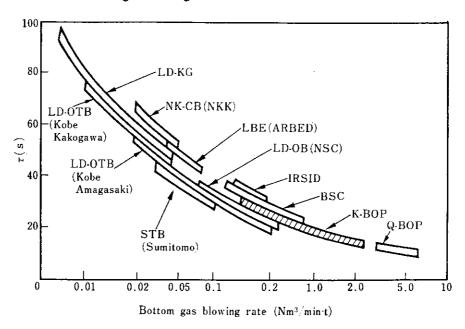


Fig. 2 Effect of bottom gas blowing rate on the mixing time of metal bath

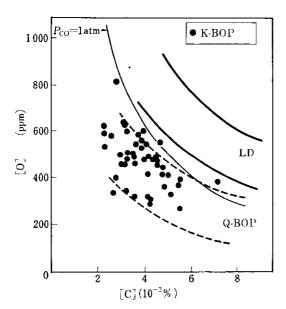


Fig. 3 Relation between [C] and [O] at blow end

## 3 Metallurgical Characteristics of Combined-blown Converter

#### 3.1 Outline of Metallurgical Reaction

As the stirring intensity of the metal bath increases, the excess oxidation of the metal bath experienced in the LD decreases, and the metallurgical characteristics of the K-BOP become similar to those of the Q-BOP. In the following, major features of metallurgical reactions in the K-BOP and LD-KG are described.

#### 3.1.1 Decarburization and metal bath oxidation

The critical carbon concentration—at which the rate determining step for decarburization changes from oxygen supply to carbon diffusion—decreases with an increase of the bath stirring; namely, the critical carbon concentration in the LD is 0.8 to 1.0% [C], whereas it is 0.6 to 0.9% [C] in the LD-KG, 0.35 to 0.55% [C] in the K-BOP, and 0.3 to 0.5% [C] in the Q-BOP. The possible lowest carbon level is 0.025% in the LD, whereas that of the K-BOP is 0.01%, which is close to that of the Q-BOP. At the carbon content of 0.05%, the oxygen unit consumption is reduced by 1.2 Nm³/t in comparison with that of the LD¹0).

Fig. 3 shows the relation between [C] and [O] at the blow end. In the K-BOP, [O] is lower than the equilibrium line ( $P_{CO} = 1$  atm) and slightly higher than that in the Q-BOP. At the carbon concentration of 0.05%, Oxygen falls on the [C]-[O] equilibrium line at  $P_{CO} = 0.75$  atm. This is probably due to the fact that  $P_{CO}$  drops owing to decomposition of the propane gas. During blowing, (T.Fe) in slag shows a similar behavior to that of oxygen in steel, and at the blow end the relation shown in Fig. 4 is obtained. Namely, the

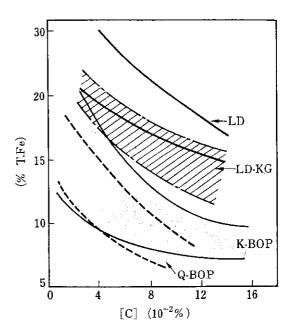


Fig. 4 Relation between (T. Fe) and [C] at blow end

more intense the bath stirring, the lower (T.Fe) in slag, and this fact can be clearly interpreted in terms of the parameter ISCO<sup>11)</sup> which indicates the degree of preferential oxidation of carbon.

As shown above, the K-BOP can easily produce ultra-low carbon steel and permits the achievement of stabilized quality without increasing oxygen concentration in the steel.

#### 3.1.2 Slag-metal reaction

Fig. 5 shows the relation between [C] and [Mn] at the blow end. Because of the intensive stirring, [Mn] in the K-BOP becomes higher about 0.07% than in the LD at the blow-end [C] of 0.04 to 0.08%, thereby permitting to reduce the addition of ferromanganese

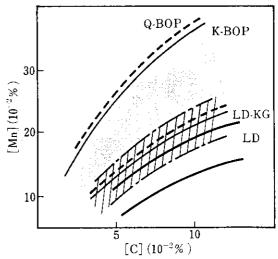


Fig. 5 Relation between [Mn] and [C] at blow end

alloy by about 1 kg/t. Moreover, at the time of producing low-carbon steel, low-cost high-carbon ferromanganese alloy can be used, instead of the expensive low-carbon ferro-manganese alloy. The reason for the higher recovery of [Mn] is that (T.Fe) in slag drops by intensified stirring and that the reaction in the following eq. (2) closes to equilibrium:

$$(FeO) + [Mn] = (MnO) + [Fe] \cdot \cdot \cdot \cdot \cdot \cdot (2)$$

Desulfurizing reaction in the K-BOP is excellent and similar to that of the Q-BOP as shown in Fig. 6, because the oxigen potential of the metal bath of the K-BOP is lower than that of the LD, as can be estimated from the following eq. (3):

$$[S] + (O^{2-}) = (S^{2-}) + [O] \cdots (3)$$

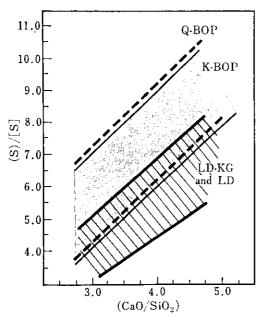


Fig. 6 Relation between sulfur partition and slag basicity

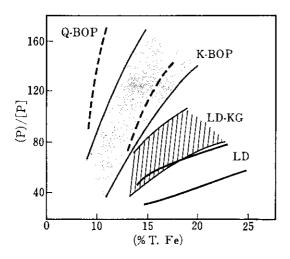


Fig. 7 Relation between phosphorus partition (T. Fe)

There is no appreciable difference in the [S] behavior between LD-KG and LD; thus the contribution of powdered lime injection seems significant in the K-BOP and Q-BOP, in addition to the above-mentioned stirring effect.

Fig. 7 shows the relation between (T.Fe) in the slag and the [P] partition ratio. At a same (T.Fe) content, the stronger the stirring force, the higher the [P] partition ratio. The decrease in the temperature difference between slag and metal might also play a role on this; namely, the temperature difference between

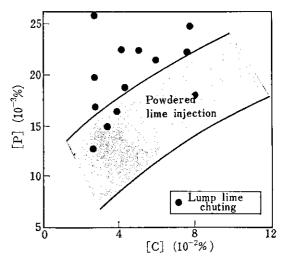


Fig. 8 Effect of powdered lime bottom injection on phosphorus content at blow end in K-BOP

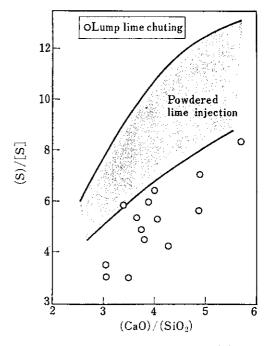


Fig. 9 Effect of powdered lime bottom injection on sulfur partition as a function of slag basicity in K-BOP

slag and metal in the K-BOP is within 10°C and is smaller than that of 20 to 40°C in the LD. In the examples of other steel works, it is reported that the temperature difference was reduced from 40-70°C to 20-30°C in the STB process<sup>12</sup> and from 10-30°C to -10-10°C in the NK-CB process<sup>13</sup>.

Since the K-BOP has a function of powdered lime injection which is not performed in other combined-blown processes, dephosphorization and desulfurization in the K-BOP are superior to the conventional method of adding lump lime on the metal bath surface. The effects of lump lime addition and powdered lime injection are compared in the K-BOP for dephosphorization and desulfurization; the results are shown in Figs. 8 and 9, respectively. The difference between two methods may be attributable to the transient reaction of powdered lime floating up in the metal bath and also to a quick slag formation.

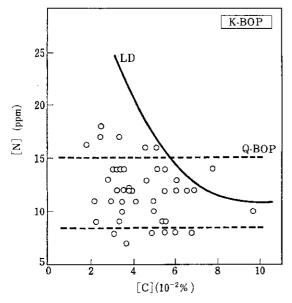


Fig. 10 Relation between [N] and [C] at blow end in K-BOP

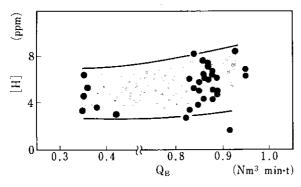


Fig. 11 Influence of bottom oxygen flow rate with constant propane ratio on hydrogen content at blow end in K-BOP

#### 3.1.3 Gas contents in metal bath

Fig. 10 shows the relation between blow-end [C] and [N]. In the K-BOP, [N] is lower than in the LD and is close to that in Q-BOP, thereby proving an advantage in producing low-carbon, low-nitrogen steel.

Hydrogen concentration at the blow end in the K-BOP is 2 to 4 ppm higher than that in the LD due to the effect of propane gas. If the propane ratio (ratio of propane gas rate to bottom-blowing oxygen rate) is constant, hydrogen concentration in the K-BOP becomes similar to that in the Q-BOP, dependent on the bottom-blowing oxygen rate (refer to Fig. 11). This phenomenon indicates that hydrogen concentration in steel is determined by the partial pressure of hydrogen in CO gas bubbles, and not by the absolute quantity of hydrogen brought in by propane. The hydrogen can be reduced, even without resorting to RH degasser, by performing dehydrogenation treatment by Ar or N2 gas in the converter before tapping, or by performing low-hydrogen partial pressure blowing explained later. Furthermore, degassed steel by the K-BOP poses no problem on achieving highquality steel, because the difference between the degassed steel in the K-BOP and that in the LD is negligible.

#### 3.2 Control of Total Iron in Slag

Although the dephosphorization function of the K-BOP is superior to that of the LD, this superiority is reduced at high temperature and high carbon content region, like other combined-blowing processes, because (T.Fe) in slag for the K-BOP is lower. When the apparent dephosphorization equilibrium is expressed by the multiple regression equation of the Balajiva type<sup>14</sup>, the following eqs. (4) and (5) are obtained for the K-BOP and LD, respectively.

$$\log \frac{(\%P_2O_5)}{[\%P]^2(\%T \cdot Fe)^5} = 0.07 \, (\%CaO)$$

$$+ \frac{36\,941}{T} - 24.29 \, \cdots \text{(4)}$$

$$\log \frac{(\%P_2O_5)}{[\%P]^2(\%T \cdot Fe)^5} = 0.076 \, (\%CaO)$$

$$+ \frac{32\,507}{T} - 22.49 \, \cdots \text{(5)}$$

Using three equations, the relation between temperature at which blow-end [P] is made 0.015%, and (T.Fe) in slag is obtained as shown in Fig. 12. K-BOP can achieve the target [P] at a lower (T.Fe) content in slag than that in the LD at an arbitral temperature. When the blow-end temperature rises in both processes, it becomes necessary to increase (T.Fe) in slag, or to increase the consumption of lime. (T.Fe) in slag

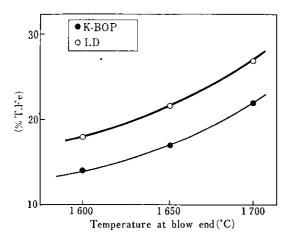


Fig. 12 Relation between (T. Fe) and bath temperature for the aimed [%P] of 0.015 at blow end

is empirically expressed by eq. (6) for the K-BOP, and the major factor is its first term,  $\Delta t_0$ , which is oxygen blowing time (min) after completion of powdered lime injection.

$$(\%T \cdot Fe) = a \cdot \Delta t_{O_1} + b \cdot W_{ore} + c\Delta t_{ore} + d\frac{1}{C_F} + e \cdot \tau + f \quad \dots (6)$$

a, b, c, d, e, f: Constants

 $W_{\text{ore}}$ : Amount of ore added (t)

 $\Delta t_{\text{ore}}$ : Time from ore addition to blow-end (min)

 $C_{\rm F}$ : Blow-end [C] concentration  $(10^{-2})$ %

When top-blowing is ended immediately after completion of powdered lime injection and only oxygen is bottom-blown, (T.Fe) in slag drops according to each level of [C], as  $\Delta t_{0}$ , becomes longer, as shown in Fig. 13. Namely, (T.Fe) in slag—while powdered lime is being injected—is higher than while only oxygen is being blown. This indicates that while lime is injected, Ca-ferrite<sup>15)</sup> is immediately formed above tuyeres and that reduction of iron oxide is retarded.

On the other hand, as shown in Fig. 14, when lumpy lime is added on the bath surface of the K-BOP, (T.Fe) in slag becomes lower than that with powdered lime injection. Therefore, the K-BOP process which is accompanied with powdered lime injection has an advantage over other combined-blowing processes without powdered lime injection in that (T.Fe) in slag is controllable in a wide range and in a stable manner.

#### 3.3 Behavior of Hydrogen in Steel

In order to lower the blow-end hydrogen in steel, the behavior of hydrogen in the K-BOP has been

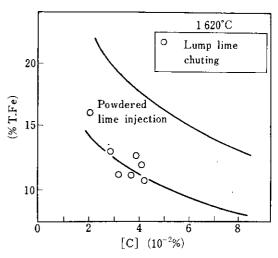
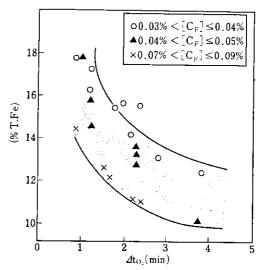


Fig. 13 Effect of oxygen bottom blowing time,  $\Delta t_{0_2}$ , without top blowing on (%T. Fe) as a function of blow end carbon,  $[C_f]$ , in K-BOP



• Fig. 14 Effect of powdered lime bottom injection of (%T. Fe) as a function of [C] at blow end in K-BOP

investigated. Fig. 15 shows the relation between the propane ratio and hydrogen in steel; obviously hydrogen in steel becomes higher as the propane ratio increases or blow-end [C] drops. In Fig. 15, equilibrium contents are calculated from eq. (8), where the partial pressure of hydrogen in a CO bubble is evaluated by eq. (7).

$$P_{\rm H_2} = \frac{4\gamma \cdot Q_{\rm O_1}}{4\gamma \cdot Q_{\rm O_1} + 2\eta_{\rm O_1} \cdot Q_{\rm O_1}} \cdot \cdots (7)$$

y: Propane ratio

η<sub>0</sub>.: Decarburization efficiency of bottom-blown oxygen

 $Q_{o_*}$ : Bottom-blown oxygen quantity

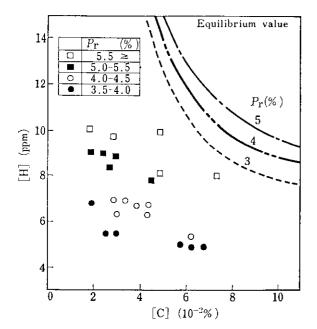


Fig. 15 Influence of [C] and propane ratio,  $P_r$ , on [H]

$$\log a_{\rm H}^2/P_{\rm H_2} = -1.905/T - 1.591 \cdots (8)$$

As a result, the calculated hydrogen content affected by the propane ratio shows a same tendency as the observed one. A rather large discrepancy, however, exists between the two quantitatively.

Thus, an analysis based on the kinetic theory of chemical reaction has been performed on the basis of assumptions shown below:

- (1) Hydrogen generated by decomposition of propane is all absorbed into molten steel.
- (2) Dehydrogenation is performed by CO bubbles generated at the location immediately above the tuyere.

In order to denote the deviation from the equilibrium, a parameter  $\eta$  is defined by eq. (9).

$$P'_{\mathrm{H}_{\bullet}} = \eta \cdot \left(\frac{\left[\frac{\%}{6}H\right]}{K_{\mathrm{H}}}\right)^{2} \quad \cdots \qquad (9)$$

 $K_{\rm H}$ : Equilibrium constant ( $\frac{9}{10}/\text{atm}^{1/2}$ )

Assuming that the gas bubbles follow the behavior of the ideal gas, the material balance of hydrogen in molten steel will be as follows:

$$\frac{d[\%H]}{dN} = \frac{-0.2P_{H_1}}{(P'_0 - P'_{H_1})W} \cdots (10)$$

P<sub>0</sub>: Gas bubble pressure when bubbles escape from molten steel (atm)

N: Cumulative Avogadro's number of generated CO gas

W: Weight of molten steel (t)

Eventually, the following eq. (11) is obtained:

$$\frac{d[\%H]}{89.3Q_{o_1} \cdot \eta_{o_2} \cdot dt} = \frac{0.2\eta[\%H]^2}{\{K_H^2 \cdot P_0 - \eta[\%H]^2\}W} \cdot \cdot \cdot \cdot (11)$$

By using eq. (11), hydrogen contents during blowing has been estimated at propane ratios of 4%, 5%, and 6% taking into consideration the oxygen efficiency for decarburization during blowing when blow-end [C] is 0.04%, and the results are shown in Fig. 16. These estimated values show good agreement with measured values at the blow end, if  $\eta = 0.5$  is assumed.

On the basis of this computation, Ar-or N<sub>2</sub> rinsing has been performed in a practical operation; this provided an effective dehydrogenation of the bath.

As an alternative way, the hydrogen reducing method in which hydrogen partial pressure of the bottom blowing gas is decreased during blowing has been examined by mixing propane gas with  $N_2$  or  $CO_2$ . As shown in Fig. 17, it is possible to give a

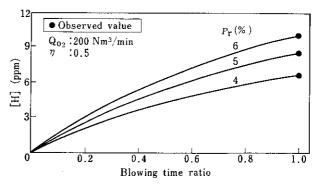


Fig. 16 Effect of propane ratio on hydrogen absorption during blowing

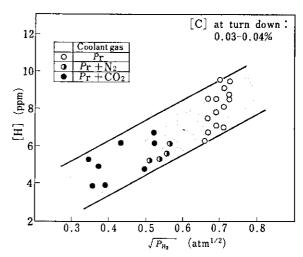


Fig. 17 Relation between (H) at turn down and partical pressure of H<sub>z</sub> within bottom blown gas in K-BOP

reasonable explanation by using the relation in which blow-end hydrogen concentration is proportional to the square root of the partial pressure of hydrogen in the bottom-blown gas, whichever gas may be used, and it is found that the reducing of hydrogen partial pressure method by mixing propane with Ar,  $N_2$  or  $CO_2$  is effective.

#### 3.4 K-BOP and Hot Metal Pretreating Process

In order to reduce the cost of the steelmaking process and to meet the demand for ultra-low sulfur and phosphorous steel, active research has been carried out recently on the external treatment of hot metal; substantially hot metal is stepwisely desiliconized, phorized and desulfurized.

Concerning the steelmaking process accompanied with hot metal pretreatment, the following two methods are considered:

- Method in which, after desiliconization and desulfurization treatments, blowing with minimum slag is performed for decarburization in the converter.
- (2) Method in which, after desiliconization, desulfurization and supplemental dephosphorization treatments, decarburization and final dephosphorization are performed in the converter.

The effectiveness of the K-BOP in the abovementioned two methods have been examined.

In the LD and general combined-blown converters, addition of lumpy lime on the bath surface of externally desiliconized hot metal (Si: 0.01 to 0.1%, P: 0.12 to 0.15%), makes slag formation difficult, whereas in the K-BOP, this drawback is eliminated by the injection of small amount of powdered lime as

shown in **Table 1**. Furthermore, method (2) coupled with the K-BOP enables cutting down of the overall lime consumption by more than 5 kg/t.

To suppress the dissolution of MgO out of furnace refractories, calcined dolomite is commonly added to the slag. The externally desiliconized hot metal reduces the consumption of calcined dolomite required as shown in Fig. 18. It is also found that since (T.Fe) in slag of the K-BOP is lower than that of the LD, the K-BOP requires less calcined dolomite.

When hot metal containing 0.2 to 0.3% Si is externally pre-dephosphorized, the K-BOP can easily blow low phosphorus iron ([%P] = 0.01%) with a lime consumption of 20 kg/t.

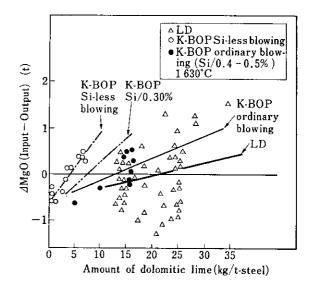


Fig. 18 Influence of burnt dolomitic lime addition on MgO balance

Table 1 An example of blowing performance of desiliconized hot metal

Hot		С	Si.	Mn	P	s	Temp.	H.R.
Met	al (%)	4.65	0.07	0.36	0.137	0.018	1 240°C	96.5
		Fl	ux materi	al	Lime (	F/I)	10.6	kg/t
		and oxygen			Dolomite		3.4	kg/t
		consumption			Ore		27.8	kg/t
7	7	<u></u>	(K-BOP)		O <sub>2</sub>		45.7	Nm³/t
	Metal	С	Mn	P	S	Temp	<u> </u>	
Blow	(%)	0.088	0.23	0.019	0.011	1 632°	c	
end	Slag	T.Fe	CaO	SiO <sub>2</sub>	MnO	$P_2O_5$	MgO	s
	(%)	14.7	46.7	10.9	5.9	5.61	8.8	0.122

Table 2 Metallurgical advantages of K-BOP and LDKG over LD in blowing low carbon killed steel

	LD-KG	K-BOP		
Steel yield (%)	+0.15	+1.0		
(%Mn) at blow end	+0.03	+0.07		
Lime + Dolomitic lime (kg/t)	-2	-5		
Aluminum addition (kg/t)	-0.05	-0.2		
Gas recovery (Mcal/t)		36		

#### 4 Evaluation of Top-blown Converters

Table 2 shows a comparison of operational data between the LD-KG, and the K-BOP. For both LD-KG and K-BOP, the slag and the metal are less oxidized than those of the LD, due to intensified stirring; hence these combined processes are preferable in metallic yields.

Besides, the K-BOP has the advantages of reduction in the consumption of desulfurization flux and an increase in off-gas recovery.

The refractory cost of the K-BOP is slightly higher than that of the LD, because the wear of the bottom in the K-BOP is higher than that in the LD. However, since various operational causes for the bottom wear have now been clarified, much improvement has been made in this respect compared with the condition at the initial stage of the K-BOP operation.

Judging from dephosphorization characteristics, the LD-KG is recommendable to the shop which mainly produces high carbon steel, whereas the K-BOP is suitable for the production of low carbon steel.

Metallurgical effects of powdered lime have been compared between the bottom injection from tuyeres and the injection from the top lance at a constant blowing ratio of top to bottom; the former has turned out much superior to the latter.

Because of the surplus of scraps, the U.S. and European countries have much interest in the capability of scrap melting in basic oxygen processes. The post-combustion of CO gas is easily controlled in the K-BOP, and the intensified stirring enhances the melting rate of scraps; hence the scrap ratio can be increased in the K-BOP rather than in the LD.

#### 5 Conclusion

The outline of combined-blown converters developed by Kawasaki Steel, i.e., the LD-KG and the K-BOP processes, and their metallurgical characteristics have been described.

Small amount of bottom blown gas improves stirring intensity of steel bath and supresses excessive oxidation of steel bath; hence the LD-KG and the K-BOP result in higher yields of iron and manganese than those of the LD. The K-BOP has shown much more advantages than any other type combined-blown processes, particularly in the removal of phosphorus and sulfur by enhanced reaction with injected powdered lime.

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