

Development of Technology for Preventing Nitrogen Absorption by Using CaCO_3

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Abstract

To reduce the nitrogen content in high purity ferritic stainless steel, a method of placing CaCO_3 into a ladle has been developed to prevent nitrogen absorption on tapping at the converter. The key technology to prevent boiling of molten steel is preheating CaCO_3 in the ladle by a burner before tapping. By this method, nitrogen absorption is reduced. According to the analysis of gas composition in the upper part of the ladle during tapping, CO_2 remained at a high value during tapping. It is considered that the atmosphere around the ladle is replaced with CO_2 by decomposition of CaCO_3 , and nitrogen partial pressure is calculated to decrease from 0.8 atm to 0.15 atm and thus nitrogen absorption on tapping is reduced.

1. Introduction

In the steelmaking plant of the Shunan Area Yamaguchi Works of Nippon Steel Stainless Steel Corporation (hereinafter referred to as the Shunan area steelmaking plant), slabs of austenitic stainless steel and ferritic-martensitic stainless steel are produced by the production process of an electric arc furnace–KR (external desulfurization)–LD (converter)–VOD (vacuum degassing)–CC (continuous casting). The LD-VAC process is advantageous in reducing the carbon and nitrogen contents of products as refining is conducted under a vacuum condition, and appropriate for smelting high purity ferritic stainless steel for automotive exhaust gas system parts and/or roofing material. However, to further enhance its formability and oxidation resistance, the establishment of a technology to stabilize C and N at low levels is required. To achieve low N content in products, enhancement of the denitrification potential of the entire process and the minimization of N absorption on tapping are crucial.

In this report, N absorption on tapping from the converter was conducted by using calcium carbonate, and the reduction of the N content of high purity ferritic stainless steel was achieved, the process of which is reported hereunder.

2. Outline of Operation of Shunan Area Steelmaking Plant

2.1 Steelmaking process of Shunan area steelmaking plant

Figure 1 shows the production process of the Shunan area steelmaking plant. Firstly, scrap and alloys such as FeCr and FeNi are

melted in the electric arc furnace process, and stainless steel hot metal of [C]=3% is produced. Subsequently, the stainless steel hot metal is tapped to a ladle, and the desulfurization by KR is conducted and transferred to the following converter process. In the converter, the stainless steel hot metal is primarily decarburized to 0.2% carbon content by oxygen blowing. Subsequently, the final decarburization and composition-adjustment are conducted in the VOD process, and continuously cast to slabs in the CC process. Later on, slabs are hot-rolled, cold-rolled, annealed and pickled, and finished to various stainless steel sheet products via the finishing line.

2.2 Outline of operation of converter process

Figure 2 shows the outline of the operation of the converter process. In the converter, the stainless steel hot metal transferred from the electric arc furnace is charged, a water-cooled lance is lowered into the furnace and the primary decarburization by oxygen blowing is conducted. After the completion of the decarburization, a sample is taken from the molten steel and the blow end point compositions are confirmed. After composition adjustment upon necessity, the molten steel is tapped to a ladle. Then the ladle is transferred to the VOD process and the molten steel is treated. Since the tapped molten steel downflow is exposed to open air, and N absorption takes place, [N] before VOD treatment tends to increase from the converter blow end point [N]. Although the VOD process conducts refining under a vacuum condition and is advantageous in denitrification, the rise of [N] before the VOD treatment is linked to the rise of [N] after the VOD treatment, and the reduction of N absorption on tapping

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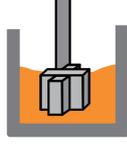
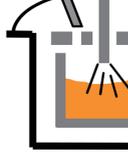
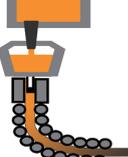
Process	EHF	KR	LD	VOD	CC
					
t / heat	160t, 2furnaces	80t	80t	80t	80t
Main specifications	Transformer No.6 EAF: 50,000KVA No.7 EAF: 60,000KVA	Rotation speed Max. 120rpm	Oxygen flow rate Max. 183Nm ³ /min	2 vessels 2 vacuum equipments	Type: Vertical bending

Fig. 1 Steelmaking process in Shunan Area Yamaguchi Works, Nippon Steel Stainless Steel Corp.

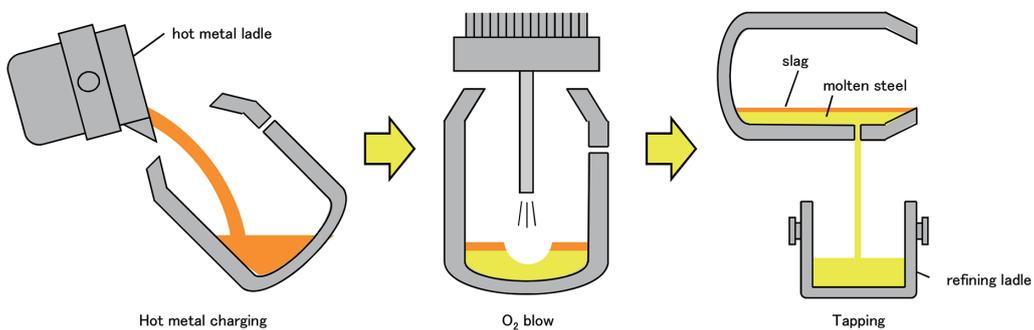


Fig. 2 Production steps at LD operation

is crucial for the high purity ferritic stainless steel that requires low N content.

2.3 Pursuit of N absorption reduction in converter

As a measure to reduce N absorption on tapping from the converter, up to the present, an operation of charging magnesium carbonate (hereinafter referred to as MgCO₃) to the refining ladle immediately before tapping (hereinafter referred to as input) has been practiced.¹⁾ MgCO₃ is thermally decomposed by contact with the high temperature molten steel, and CO₂ gas is produced. This operation prevents the absorption of N₂ in the air by the molten steel by sealing the tapped molten steel downflow with the CO₂ gas produced by the input of MgCO₃ in the ladle.

As a new means of reducing N absorption on tapping from the converter, we studied the effectiveness of the input of calcium carbonate (hereinafter referred to as CaCO₃) in the refining ladle.

CaCO₃ is also thermally decomposed at a high temperature similarly to MgCO₃, and produces CO₂ gas. To investigate the relationship between the holding temperature and the decomposition rate, samples of input materials were inserted to an elema furnace set at the respective predetermined temperature for four conditions as shown in Table 1. The mass was then measured at one minute intervals (0.2 min for Condition No.4), and the amount of the CO₂ gas produced was measured. Figure 3 shows the result. It is found that, in MgCO₃, the decomposition is completed within about two minutes when held at 1 570°C, while CO₂ gas continues to be discharged from CaCO₃ for longer than ten minutes when held at 1 570°C. The temperature of the tapped molten steel downflow from the converter is about 1 700 to 1 800°C, and the tapping time is about three minutes. Therefore, in the case of input of CaCO₃, the CO₂ discharging time when held at a high temperature is longer than that of MgCO₃,

Table 1 Experimental conditions for survey of gas composition

No.	Putting materials	Holding temperature
1	CaCO ₃	1 000°C
2	CaCO ₃	1 200°C
3	CaCO ₃	1 570°C
4	MgCO ₃	1 570°C

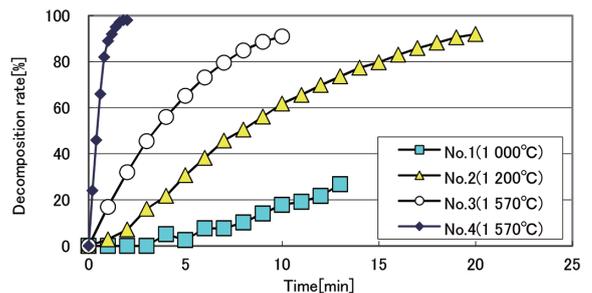


Fig. 3 Decomposition rate of CaCO₃ and MgCO₃ at each holding temperature

the discharge of CO₂ gas is not terminated during tapping and the sealing effect on the tapped molten steel downflow is considered to be maintained.

2.4 Preliminary test of input of CaCO₃ in ladle

To confirm the applicability of input of CaCO₃ to practical operation, a test was conducted wherein CaCO₃ was put in the refining ladle immediately before tapping and then the molten steel was tapped. As a result, since boiling of the molten steel occurred immediately after tapping, the phenomenon of splashing to outside the la-

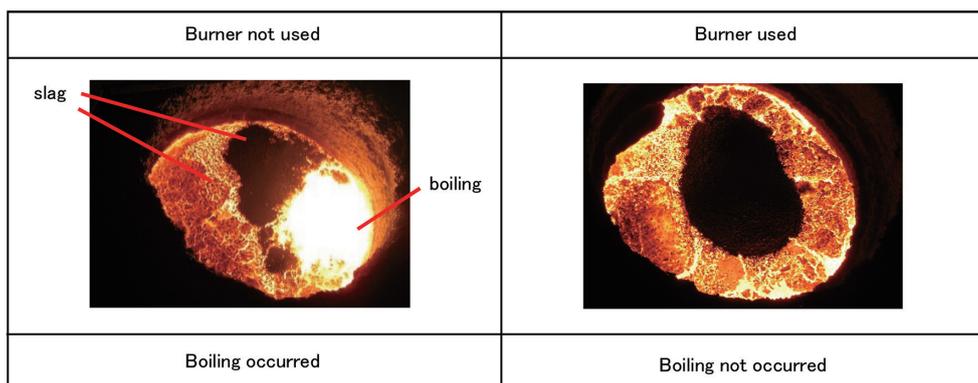


Fig. 4 Surfaces of molten steel with or without using burner

Table 2 Main chemical compositions of high purity ferritic grades

Steel grade	C	Ni	Cr	Mo	Ti	Nb	N
steel A	≤0.020	≤0.60	21.00–23.00	1.00–1.50	0.05–0.50	0.10–0.60	≤0.025
steel B	≤0.030	≤0.60	17.00–18.00	–	10×(C+N)–0.80	–	–

(mass%)

Table 3 Experimental conditions for putting materials in ladle

No.	Steel grade	Putting materials	Amount	Other condition
1	steel A	–	–	–
2	steel A	MgCO ₃	100 kg	–
3	steel A	CaCO ₃	300 kg	Burner heating (1000°C)
4	steel B	–	–	–
5	steel B	CaCO ₃	300 kg	Burner heating (1000°C)

dle was observed, and the application to practical operation was considered difficult from the safety viewpoint. As a countermeasure therefor, CaCO₃ in the ladle was preheated before tapping by a burner used for preheating the ladle, and the boiling caused by the rapid generation of CO₂ gas was suppressed. In Fig. 4, states of the surfaces of the molten steel in the ladle immediately after the end of tapping with and without the use of the burner are shown. By the heating of CaCO₃ with the burner, the boiling after tapping is suppressed, and safe operation has been achieved.

3. Experiment of Input in Ladle

3.1 Experimental condition

The major compositions of steel grades used in the experiment are shown in Table 2. Steel A is a high purity ferritic steel composed of 22%Cr-lowC-lowN, and steel B is also a high purity ferritic steel composed of 17%Cr-lowC-lowN.

Table 3 shows the experimental conditions of input of materials in the ladle. Five experimental conditions were set: in Condition No.1, no input material for steel A, in Condition No.2, 100 kg MgCO₃ input for steel A, in Condition No.3, 300 kg CaCO₃ input for steel A with preheating by a ladle-preheating burner at about 1000°C before tapping, in Condition No.4, no input material for steel B and in Condition No.5, 300 kg CaCO₃ input for steel B with preheating at about 1000°C. As the index for evaluating the amount of N absorption, the value of [N] before VOD treatment minus the

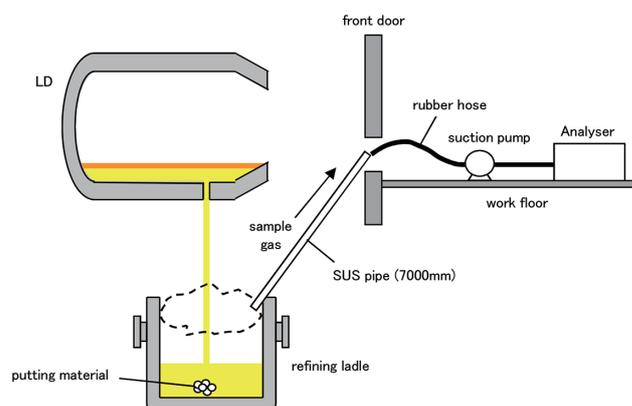


Fig. 5 Overview of gas analysis method in the upper part of the ladle

Table 4 Equipment and method for gas analysis

Gas component	Analysis equipment	Analysis method
CO	HORIBA VA3011	Non-dispersive infrared absorption analysis
CO ₂		
O ₂	Yanaco ECL88AO	Magnetic oxygen analysis

converter blow end point [N], which is the amount of increase during tapping ΔN ([N] before VOD treatment-converter blow end point [N]), is used.

3.2 Analysis of composition of gas in upper part of ladle

In conducting the experiment, to confirm the compositions of the atmospheric gas near the molten steel on tapping, in the experimental conditions of Nos. 1, 2 and 3, samples of the gas in the upper part of the ladle were continuously taken during tapping, and the transitions of the gas compositions from the start of tapping to the end of tapping were investigated. In Fig. 5, the gas analysis method for the gas in the upper part of the ladle, and in Table 4, the gas analysis equipment and the gas analysis method are shown, respectively.

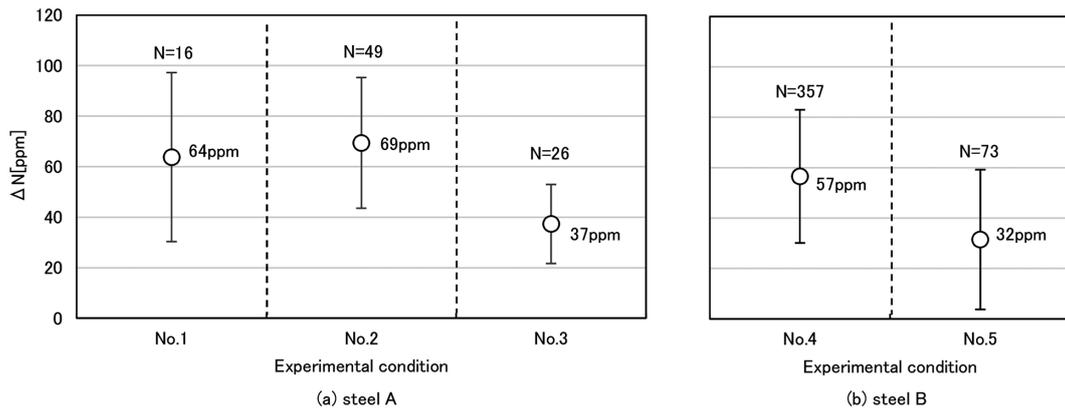


Fig. 6 Comparison of nitrogen absorption from end of tapping to start of VOD treatment by each experimental conditions

4. Result of Experiment

4.1 Comparison of amount of N absorption

Figure 6 shows the comparison of ΔN ([N] before the VOD treatment-converter blow end point [N]) of Conditions No. 1 to 5. In steel A, ΔN of Condition No.3 is the smallest. In steel B, as compared with Condition No. 4, ΔN of Condition No. 5 is smaller.

4.2 Comparison of composition of gas in upper part of ladle

Transitions from the start of tapping until the completion thereof of the gas in the upper part of the ladle in Condition Nos. 1, 2 and 3 are shown in Figs. 7, 8 and 9, respectively. In each condition, CO gas detected in the initial stage of tapping is considered to be produced by the coke placed in the ladle to add carbon to the molten steel. In Fig. 7, the amount of CO_2 gas produced is about 5% at most. In Fig. 8, CO_2 gas starts to be produced immediately after the start of tapping, and after reaching its peak of 12%, decreases gradually. In Fig. 9, CO_2 gas starts to be produced about 10 seconds after the start of tapping, reaches about 50% in the middle term of tapping and stays above 5% until the end of tapping.

From Fig. 8, MgCO_3 is considered to discharge CO_2 sharply by the reaction in the initial stage of tapping, and end its reaction very soon thereafter. In addition, in Fig. 9, CaCO_3 is considered to discharge CO_2 gas from the initial stage of tapping, and continue to discharge CO_2 gas until the end of tapping. Compared with MgCO_3 , CaCO_3 discharges CO_2 gas for a longer time. This result shows a similar trend to that of the investigation experiment (Fig. 3) conducted with respect to the decomposition rate before the test of input of material in the ladle.

5. Consideration

Based on this experimental result, it is considered that N absorption is reduced by the effect of CO_2 gas discharged by CaCO_3 on the sealing of the tapped molten steel downflow. Then to evaluate the sealing effect of CaCO_3 on the tapped molten steel downflow, the amount of the decrease of the N_2 partial pressure in the atmosphere in the neighborhood of the tapped molten steel downflow was estimated based on the amount of the decrease of N absorption on tapping. Then, with respect to the target steel grade of B, to analyze the N absorption on tapping in more detail, CaCO_3 input experiments based on Conditions Nos.4 and 5 were repeated, such repeated experimental conditions hereinafter being referred to as Condition No. 4' and Condition No. 5'. In the experiments, samples were taken from the molten steel immediately before the start of tapping from the converter, and ΔN_{Tap} was defined anew as follows, and compared.

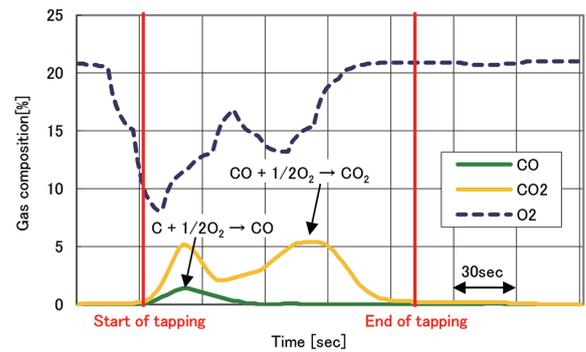


Fig. 7 Change of gas composition without putting materials in ladle

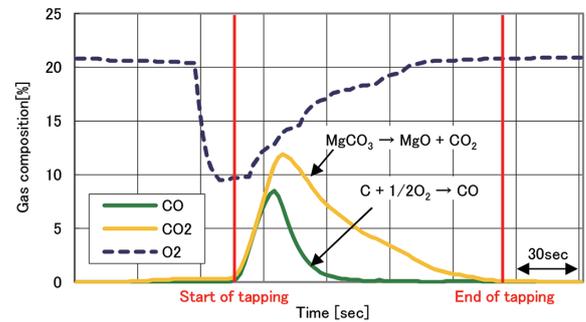


Fig. 8 Change of gas composition with putting MgCO_3 in ladle

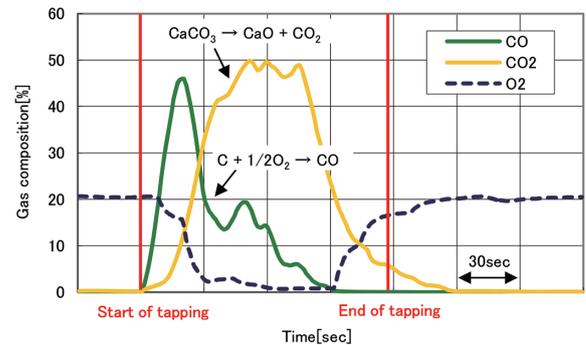


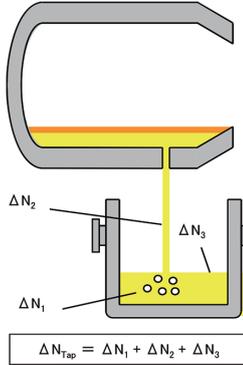
Fig. 9 Change of gas composition with putting CaCO_3 in ladle

$$\Delta N_{\text{Tap}} = [\text{N}] \text{ before VOD treatment} - [\text{N}] \text{ before tapping from converter}$$

The actual result of ΔN_{Tap} is shown in Table 5.

Table 5 Experimental conditions and results of ΔN_{Tap} (steel B)

No.	Putting materials	Burner	Number of tests	ΔN_{Tap} [ppm]
4'	–	Not use	2	40
5'	CaCO ₃	Use	6	12


Fig. 10 Schematic view of sites of nitrogen absorption on tapping

In **Fig. 10**, N absorption sites on tapping are shown. The amount of N absorption on tapping (ΔN_{Tap}) is considered to be the total of: N absorption from the bubbles of entrained air in the refining ladle (ΔN_1), N absorption through the surface of the tapped molten steel downflow (ΔN_2) and N absorption through the surface of the molten steel in the refining ladle (ΔN_3).

$$\Delta N_{\text{Tap}} = \Delta N_1 + \Delta N_2 + \Delta N_3 \quad (1)$$

N absorption from the bubbles of entrained air (ΔN_1) is expressed by the following expressions.¹⁾

$$\Delta N_1 = \eta_B \cdot k_N / k_{N_0} \cdot \Delta N_0 \quad (2)$$

$$\Delta N_0 = 34.1 \cdot P_{N_2} \cdot G / (T_G \cdot M_1) \quad (3)$$

where η_B : N absorption efficiency from air bubbles, k_N : apparent nitrogen mass transfer coefficient [cm/s], k_{N_0} : k_N when [%O]=0 [cm/s], ΔN_0 : N absorption when [%O]=0, P_{N_2} : N₂ partial pressure in the atmospheric gas [atm], G : total volume of entrained gas [m³], T_G : entrained gas temperature [K], M_1 : weight of molten steel [T]. Assuming herein that all nitrogen of the bubbles of entrained air is absorbed, η_B is taken as 1 ($\eta_B = 1$), and taking $k_N = 0.012$ and $k_{N_0} = 0.035$, and by inserting these figures, the following expression was obtained.

$$\Delta N_1 [\%] = P_{N_2} \cdot 2.47 \times 10^{-3} \quad (4)$$

With respect to N absorption through the surface of the tapped molten steel downflow (ΔN_2), the N absorption rate is expressed by the following expressions.^{2,3)}

$$\frac{dN}{dt} = \frac{F}{V} \cdot k_N \cdot ([\%N]_e - [\%N]) \quad (5)$$

By rearranging Expression (5), the following expression is obtained.

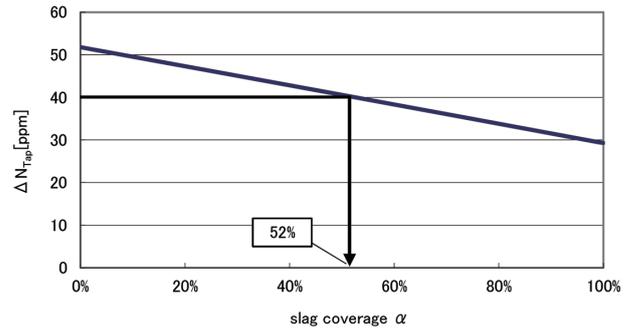
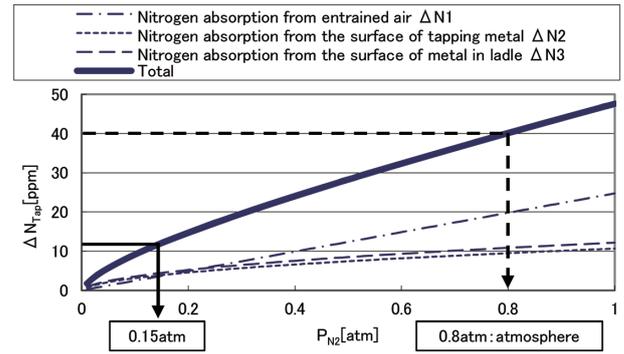
$$[\%N] = [\%N]_e - ([\%N]_e - [\%N]_0) / \exp\left(-\frac{F}{V} \cdot k_N \cdot t\right) \quad (6)$$

where F : surface area of tapped molten steel downflow [cm²], V : volume of molten steel [cm³], $[\%N]_e$: equilibrium N concentration of molten steel, $[\%N]$: N concentration of molten steel, $[\%N]_0$: N concentration of molten steel in the initial stage, t : time required for tapping [s]. In addition, $[\%N]_e$ is obtained by the following expression.

$$\log[\%N]_e = \frac{1}{2} \log P_{N_2} - \log f_N - 518/T - 1.063 \quad (7)$$

By defining the amount of N absorption (ΔN_2) as

$$\Delta N_2 = [\%N] - [\%N]_0 \quad (8)$$


Fig. 11 Relation between slag coverage (α) and nitrogen absorption

Fig. 12 Relation between N₂ partial pressure and nitrogen absorption ($\alpha = 52\%$)

and by assuming and inserting $[\%N]_0 = 0.007$, $t = 180$, the following expressions were obtained from Expressions (6) and (7).

$$\Delta N_2 [\%] = ([\%N]_e - 0.007) \cdot (1 - e^{-0.0056}) \quad (9)$$

$$\log[\%N]_e = \frac{1}{2} \log P_{N_2} - 0.701 \quad (10)$$

With respect to N absorption through the molten steel surface in the refining ladle (ΔN_3), by taking F in Expression (6) as the molten steel surface in the ladle [cm²], and by inserting the respective figure to Expression (6) similarly, the following expression was obtained.

$$\Delta N_3 [\%] = ([\%N]_e - 0.007) \cdot (1 - e^{-0.0133}) \quad (11)$$

By using Expressions (4), (9), (10) and (11), and assuming $P_{N_2} = 0.8$ [atm] in Condition No. 4, ΔN_{Tap} was calculated, and ΔN_{Tap} of 53 ppm was obtained. For this however, the actual amount of N absorption in Condition No. 4' was 40 ppm, which was much smaller as compared with the calculated value. As a reason thereof, it was considered that the molten steel surface in the refining ladle was partly covered by slag on tapping, and the molten steel surface wherein N absorption takes place was smaller.

Then, the slag coverage ratio α of the molten steel in the refining ladle was defined as

$$\alpha = (1 - F) / F_0 \times 100 [\%] \quad (12)$$

and α was determined based on the F value that satisfies the amount of N absorption in Condition No. 4'. Herein F_0 is the area of molten steel surface in the ladle [cm²] when the slag coverage ratio is 0. In **Fig. 11**, the relationship between the slag coverage ratio α and the total amount of N absorption on tapping ΔN_{Tap} is shown when P_{N_2} is 0.8 atm. From the result of Condition No. 4', as the total amount of N absorption during tapping is 40 ppm, $\alpha = 52\%$ is obtained.

Furthermore, **Fig. 12** shows the relationship between N₂ partial pressure in the atmospheric gas and the total amount of N absorption on tapping (ΔN_{Tap}) under the condition of $\alpha = 52\%$. In Condition No. 5', as N absorption is 12 ppm, N₂ partial gas pressure of the at-

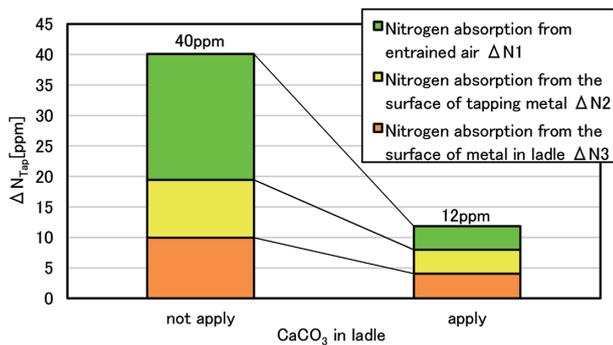


Fig. 13 Comparison of nitrogen absorption with or without putting CaCO₃ in ladle (steel B)

atmospheric gas is 0.15 atm. From this calculation result, with the application of input of CaCO₃ to the sealing of tapped molten steel downflow, P_{N₂} of 0.8 in atmospheric air is reduced to 0.15 atm, and from the change of P_{N₂}, 81% of air in the neighborhood of tapping molten steel downflow is considered to have been replaced by CO₂. As a result thereof, the reduction of N absorption is considered to

have been achieved.

Figure 13 shows a comparison of nitrogen absorption broken down to N absorption sites. All of N absorption from the bubbles of entrained air (ΔN₁), N absorption through the surface of tapped molten steel downflow (ΔN₂) and N absorption through the molten steel surface in the refining ladle (ΔN₃) are reduced by input of CaCO₃, among them, reduction of ΔN₁ in particular was the largest.

6. Conclusion

- (1) In converter operation, by input of CaCO₃ in the refining ladle and heating it by a burner before tapping, N absorption on tapping was reduced while suppressing boiling.
- (2) By the CO₂ gas produced by the decomposition of CaCO₃, P_{N₂} is reduced to 0.15 atm from 0.8 atm, and 81% of the air in the neighborhood of tapped molten steel downflow is considered to be replaced by CO₂.

References

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