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Technology

Development to Improve the Accuracy of Refining Control of Vacuum Argon Oxygen Decarburization (V-AOD)

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Abstract

The steelmaking plant of Hikari Area Yamaguchi Works, Nippon Steel Stainless Steel Corporation has been attempting to improve the accuracy of refining control by strengthening the Vacuum Argon Oxygen Decarburization (V-AOD) control system. As part of this effort, an intercommunication system between electricity-instrumentation-computer using a high-speed network was introduced. As a result, it is possible to improve the accuracy of refining control by calculating the heat and mass balance in the furnace and quickly reflecting it in the refining control of the actual furnace. The system for determining the end of decarburization of low carbon steel was constructed by observing the decarburization state successively by combining this system and an exhaust gas analyzer. As a result, variations in carbon concentration after refining were suppressed, and refining efficiency was improved. Furthermore, the nitrogen control accuracy of high nitrogen steel was improved by constructing a nitrogen reaction model formula considering various operating conditions and reflecting the measured operating data. These measures have enabled the manufacture of high-performance stainless steel with higher quality.

1. Introduction

In the steelmaking plant of Hikari Area Yamaguchi Works, Nippon Steel Stainless Steel Corporation (hereinafter referred to as the Hikari steelmaking plant), slabs, blooms and billets mainly of Ni-based stainless steel are produced. In the production of stainless steel that requires immense use of scarce resources such as rare metals represented by Cr, the establishment of environmentally harmonious type production technologies that are both resource-saving and energy-saving are required. Additionally, we need to contribute to the development of society by providing a stable supply of low cost, high-performance and high-function steel such as inclusion-eliminated high purity steel and super austenite stainless steel with high corrosion-resistance.[1] For stainless steel quality and resource and energy savings to compatibly exist, improvement in operation and technology development of the refining process are indispensable. This article reports the examples of technology development conducted over the past several years in the refining process of the Hikari steelmaking plant.

2. Outline of Hikari Steelmaking Plant

2.1 Production process of Hikari steelmaking plant

Figure 1 shows the manufacturing process of the Hikari steelmaking plant. Scrap arranged according to predetermined composition, alloying metals and auxiliary materials are melted in an electric arc furnace. The molten steel undergoes decarburization and reduction, composition adjustment and temperature adjustment in the Vacuum Argon Oxygen Decarburization (V-AOD) of the subsequent refining process. The molten steel composition and temperature are finely adjusted to be within the target range in the Ladle Furnace (LF), and subsequently continuously cast by the Continuous Caster (CC). There are vertical type CCs, one for slabs and another for blooms, and a horizontal type CC for billets, supplying materials to diversified types of products such as sheets, plates, bars and wire rods.

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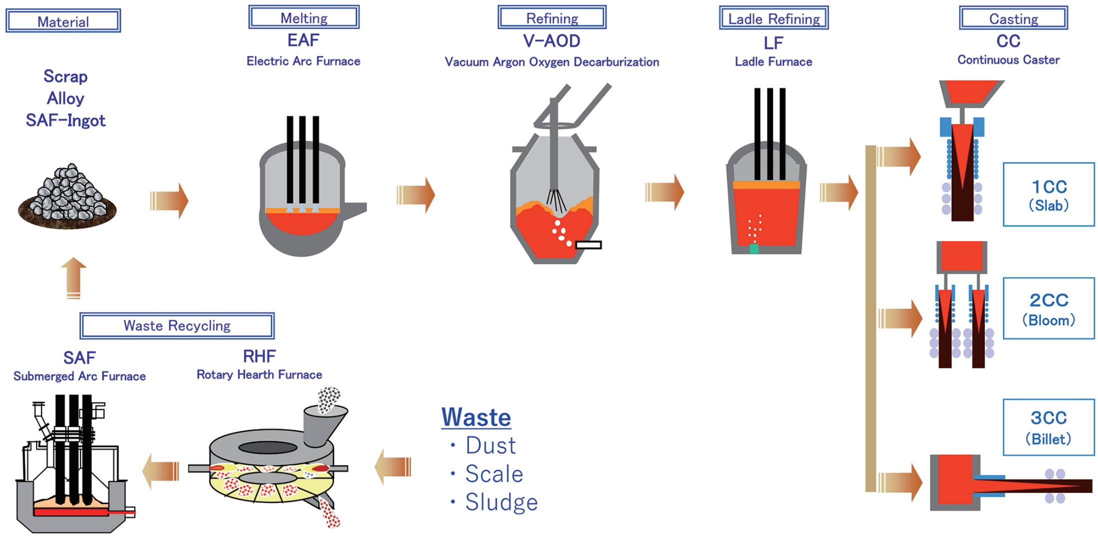

Fig. 1 Stainless steel manufacturing process at Hikari steelmaking plant

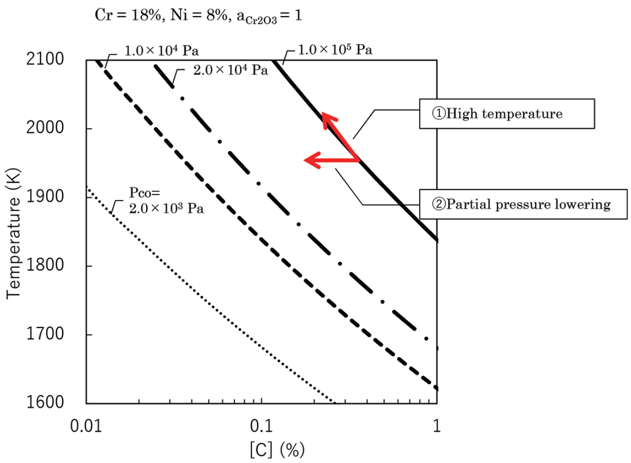

Fig. 2 Equilibrium relationship of oxidation reactions of C and Cr

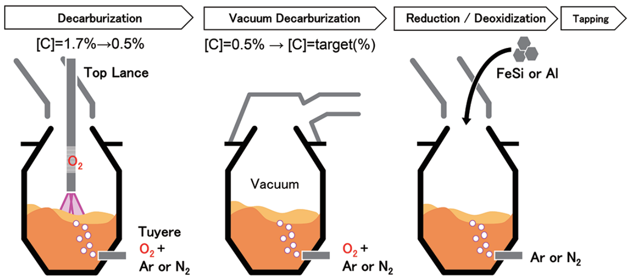

Fig. 3 Refining pattern of V-AOD operation

Furthermore, to correspond to resource-saving, valuable metals contained in the in-house dust and the sludge and scale generated in other plants are recovered in the Rotary Hearth Furnace-Submerged Arc Furnace (RHF-SAF) process, and reused as materials.

2.2 Refining of stainless steel in V-AOD

In the refining of stainless steel, to eliminate carbon that is inevitably brought into steel by alloying materials and so forth, the steel is decarburized by blown-in oxygen gas in the refining process. However, in Cr containing steel like stainless steel, in parallel with decarburization, the valuable metal Cr is also oxidized and migrates to slag in the form of oxide. Therefore, after decarburization, by using a reducing agent such as FeSi alloy and Al, the Cr oxide in the slag is reduced. Accordingly, to save the resources of Cr and the reducing agent, and to reduce the amount of the by-product slag, suppression of Cr oxidization during decarburization is important.

The equilibrium relationship of oxidization reactions of C and Cr is expressed by Equations (1) and (2) as follows:[2)]

$$3\underline{C} + (Cr_2O_3) = 3CO(g) + 2\underline{Cr} \quad (1)$$

$$\Delta G°(\mathrm{J/mol}) = 776\,510 - 486.82T \quad (2)$$

Furthermore, **Fig. 2** shows Equations (1) and (2) based on SUS304 composition. To suppress Cr oxidization, or to promote the decarburization reaction preferentially, ① increase of refining temperature and ② reduction of CO partial pressure are effective. However, since the upper refining temperature is limited from the viewpoint of preventing refractory erosion, in practical operation, control of CO partial pressure is crucial. There are two methods for the control of CO partial pressure. One is to lower the CO partial pressure by using Ar gas (or N_2 gas) simultaneously with O_2 gas as a dilution gas as in the operation of Argon Oxygen Decarburization (AOD), and the other is to lower the pressure of the entire atmosphere by using vacuum equipment as in the operation of Vacuum Oxygen Decarburization (VOD). In the Hikari steelmaking plant, advantages of both methods were exploited and a V-AOD technology was established based on AOD in which the internal furnace pressure is reduced by starting and using vacuum equipment after a middle timing during the refining operation.[3)] With this technology, oxidization of Cr was reduced and the amount of O_2 gas used was also reduced, and highly efficient decarburization treatment is conducted.

Figure 3 shows the stainless steel manufacturing process of the Hikari steelmaking plant. In the first place, decarburization is conducted by top and bottom blown oxygen under atmospheric pressure. When [C] is decreased to a predetermined level, the operation mode is switched to the vacuum refining operation mode. During the vacuum refining, decarburization is conducted while controlling the O_2 gas dilution ratio and the internal furnace pressure based on the estimated [C]. After the completion of decarburization, reducing material is charged into the furnace to reduce the Cr oxide in the slag, and for the deoxidization and the desulfurization of the molten steel. After reduction, the molten steel composition is confirmed and the molten steel is tapped to a ladle.

3. Equipment Measures to Improve Refining Control Accuracy

3.1 Improvement of function of control system

In the Hikari steelmaking plant, aiming at higher efficiency of V-AOD operation, measures for improving the refining control accuracy were implemented. As a part thereof, intensification of the sensing of the internal furnace conditions and the refining control system was implemented. **Figure 4** shows the outline of the refining control system. This system features: ① Precise refining control by means of an intercommunication system between electricity-instrumentation-computer using a high-speed network (integration of EIC), ② Optimization of operating condition per heat amount by means of successive calculation of heat and material balances using a high-performance computer, ③ Alleviation of work load of operators and reduction of operators' work skill dispersion by standardizing the refining operation, and reduction of operators' work dispersion by providing operator guidance. This system is hereinafter referred to as the Advanced System for Top Runner of AOD (ASTRA). By introducing ASTRA, calculation of heat and material balances in the furnace at 3-second intervals became possible, and by incorporating the result quickly into the refining control of the actual machine, the refining control accuracy was improved, and redundant alloying metals and energy consumption were eliminated. Furthermore, the obscure and unwritten part of operation techniques that relied on the operator's skill was visualized and standardized, and the discrepancies in refining operation skill were complemented by standardization. Thus, stabilization of quality and enhancement of productivity were achieved.

The following chapters introduce two concrete examples of efforts made for refining control accuracy improvement by using ASTRA.

4. Measures for Improving Decarburization Control Accuracy of Low Carbon Steel

4.1 Problem of decarburization control in V-AOD

During the vacuum refining in V-AOD, since the furnace throat is capped by a vacuum sealing cover, composition values cannot be captured by sampling. Therefore, in the past operation, due to concerns about the case of [C] exceeding the upper limit due to insufficient decarburization, O_2 gas was blown excessively and [C] was decreased, which was adjusted later on by adding carburizer based on the analysis values. For these reasons, the amounts of O_2 gas and the reducing agent increased, and the refining efficiency deteriorated. Additionally, the refining time was prolonged, and this was one of the factors that deteriorated productivity. To solve this problem, we endeavored to develop measures to improve decarburization control accuracy by using an exhaust gas analyzer.

4.2 Outline of exhaust gas analyzer

An overview of the exhaust gas analyzer is shown in **Fig. 5**. During the vacuum refining, a small amount of exhaust gas is sampled continuously, and analyzed by an infrared absorption type gas analyzer to determine the concentrations of CO_2 gas and CO gas. Herein, in order for the gas analyzer to analyze the gas at a constant flow rate, by not depending on the internal furnace pressure, back pressure control is conducted, which also prevents the reverse flow of air when the sampling gas pressure is low.

Furthermore, as a countermeasure to reduce the time lag caused by the delayed arrival of the sample gas at the analyzer due to passage through the internal space of the piping, the suction gas flow rate is adjusted to the optimum speed by the unit control of sub pumps on the downstream side of the sampling pump. By revising the mass balance by using the result of the gas analysis and the exhaust gas flow rate measured by a pitot tube, the amount of C discharged out of the furnace as exhaust gas, and the decarburization rate can be grasped.

4.3 Low carbon steel decarburization completion assessment technology

The decarburizing reaction in the final stage of decarburization of low C steel ([C]≤0.034%) is considered to be dependent on the transfer limitation of [C] in molten steel.[4] The decarburization rate depends on [C] of molten steel as expressed by Equation (3).

$$-\frac{d[C]}{dt} = k_C[C] \quad (3)$$

where t is time (s), k_C is the decarburization rate constant (s^{-1}).

Since the decarburization rate can actually be measured by exhaust gas analysis, [C] in molten steel in the final stage of decarburization can be estimated by using this relational equation.

Furthermore, in the decarburization of V-AOD-processed stainless steel, we considered that the target composition in each charge and the difference in operation condition among charges have to be reflected, and therefore parameters and their coefficients were taken

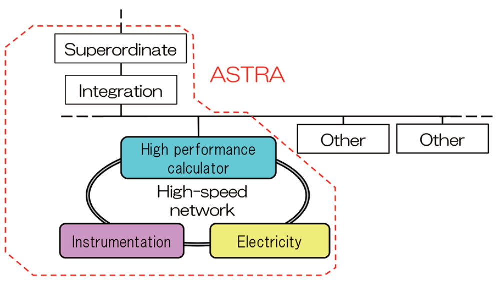

Fig. 4 System configuration of ASTRA

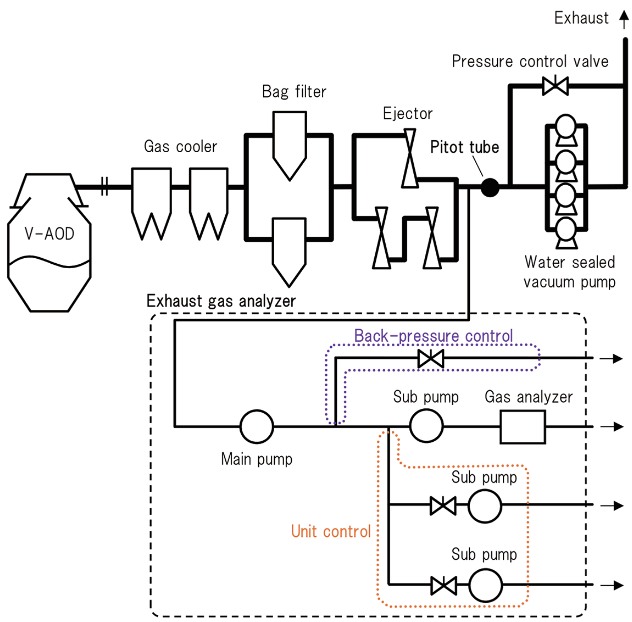

Fig. 5 Overview of exhaust gas analyzer

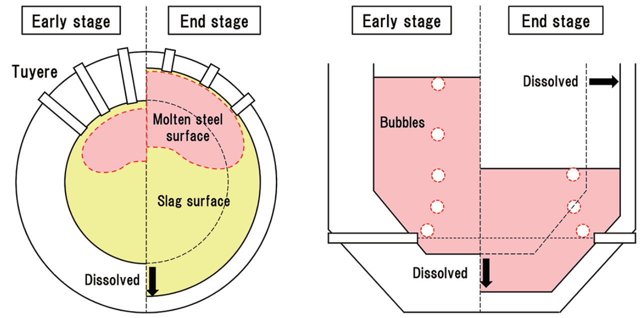

Fig. 6 Relationship between furnace refractory dissolved loss and effective interfacial area

into consideration. As parameters, the pressure and the activity coefficient of C were considered. Furthermore, since the internal effective reaction interface area of the furnace and the stirring power energy density vary depending on the progress of erosion of the furnace refractories, the amount of heat after a relining of internal refractories was taken into consideration as a parameter (**Fig. 6**). The respective coefficient to be set on each parameter was determined according to the dilute gas type. The estimation equation of [C] is shown as Equation (4) below.

$$[C] = a \times \frac{d[C]}{dt} + b \times P + c \times N_h + d \times f_C + e \qquad (4)$$

where, P: internal furnace pressure (Pa), N_h: amount of heat of a furnace after relining of refractories, f_C: activity coefficient of C, a, b, c, d, e: constants determined for each type of gas

By incorporating this estimation equation into ASTRA, the system of estimating [C] wherein the operating condition of the respective charge and the characteristics of subject steel are taken into consideration, and the decarburization completion assessment system were constructed.

4.4 Effect of improvement of decarburization by exhaust gas analysis

Figure 7 shows the result of a comparison of [C] estimated by the exhaust gas analysis and the actually measured [C]. The estimation error of the estimated [C] is $1\sigma=0.0024\%$, and well achieved the target estimation accuracy of $3\sigma \leq 0.010\%$ that is applicable to stainless steel refining in the Hikari steelmaking plant.

As the continuous capture of [C] transition at the decarburization completion stage with a target accuracy of within ±0.010% has become possible, completion of decarburization was assessed, exploiting the estimated [C]. Taking into consideration the [C] estimation accuracy and [C] pick-up after tapping from AOD, estimated [C]≤(target upper limit [C]−0.010%) was taken as the decarburization completion assessment condition, and the oxygen blowing was terminated. As a result of the implementation of the measures, and as compared with the operation before taking the measures, the refining time of the low carbon steel was shortened by 6.7%, and the productivity was enhanced (**Fig. 8**). Furthermore, by reducing the dispersion of [C], excessive decarburization was suppressed, and the amounts of O_2 gas and the reducing agent used were reduced (**Fig. 9**).

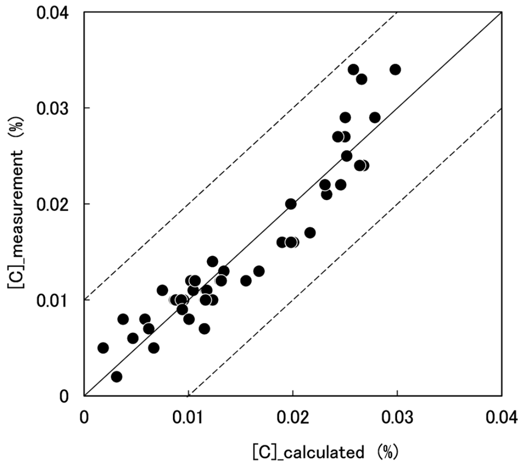

Fig. 7 Comparison calculated [C] and measurement [C]

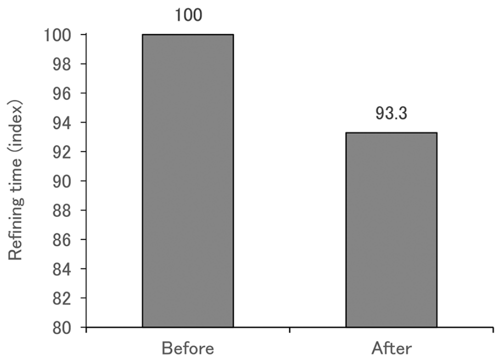

Fig. 8 Effect of shortening refining time

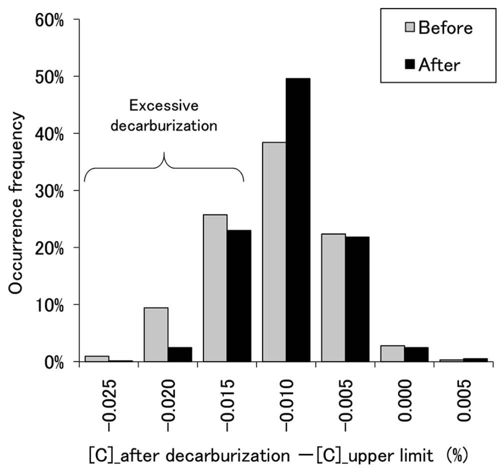

Fig. 9 Effect of suppression of excessive decarburization by decarburization completion judgment system

5. Measures to Improve Nitrogen Control Accuracy for High N Steel

5.1 Problem of nitrogen control for high N steel in V-AOD

Nitrogen can be added intensively to stainless steel as the steel contains a high Cr content and a high N-solubility. As a γ phase stabilizing element substituting costly Ni, it can also be used to enhance strength and corrosion resistance. For example, in high-function steel such as super austenite stainless steel and duplex stainless steel as shown in **Table 1**, there are a number of steel grades that contain N of higher than 0.1%. Therefore, in the refining of stainless steel, control of N in high N steel is crucial technology.

In V-AOD, N is added by bottom-blown N gas. In this operation, the yield of N_2 gas with respect to molten steel varies, being influenced by such operating conditions as refining temperature and in-

Table 1 Standard composition of typical high nitrogen stainless steel grade

Grade	Standard component (%)									
	C	Si	Mn	P	S	Ni	Cr	Mo	Cu	N
SUS312L (NSSC™ 270)	≤0.020	≤0.80	≤1.00	≤0.030	≤0.015	17.50–19.50	19.00–21.00	6.00–7.00	0.50–1.00	0.16–0.25
SUS821L1 (NSSC 2120™)	≤0.030	≤0.75	2.00–4.00	≤0.040	≤0.020	1.50–2.50	20.50–21.50	≤0.60	0.50–1.50	0.15–0.20
SUS316LN	≤0.030	≤1.00	≤2.00	≤0.045	≤0.030	10.50–14.50	16.50–18.50	2.00–3.00	–	0.12–0.22

ternal furnace pressure. Since these operating conditions can be captured by the ASTRA function, construction of an N control system for high N steel by using ASTRA was tackled.

5.2 N transition estimation equation and N control technology

To grasp the transition of [N] during refining, the equation of [N] saturation concentration in molten steel and the equation of the rate of reaction of N absorption by N_2 gas and denitrification by Ar gas are solved. The saturation [N] follows Sieverts' law, and is expressed by the equilibrium relation of [N] in molten metal and N_2 partial pressure as shown by Equations (5) and (6).[2)]

$$[\%N]_{eq} = \frac{K\sqrt{p_{N_2}}}{f_N} \tag{5}$$

$$\log K = -\frac{518}{T} - 1.063 \tag{6}$$

where $[\%N]_{eq}$: equilibrium nitrogen concentration (mass%), K: equilibrium constant, p_{N_2}: N_2 partial pressure (Pa), f_N: activity coefficient of N, T: molten steel temperature (K). These values are estimated by ASTRA at 3-second intervals.

Furthermore, since the N absorption reaction rate and the denitrification reaction rate are considered as a first-order reaction[5)] and second-order reaction respectively,[6–8)] they are expressed as Equations (7) and (8), respectively where the N-adding N_2 gas volume $V_{g.N_2}$ (Nm^3) and the denitrification Ar gas volume $V_{g.Ar}$ (Nm^3) are used as functions for the convenience of operation.

N absorption reaction rate equation

$$\ln\frac{[N]_{eq}-[N]_0}{[N]_{eq}-[N]} = k'\frac{A}{V_m}\frac{V_{g.N_2}}{Q} \tag{7}$$

Denitrification reaction rate equation

$$\frac{1}{[N]_0} - \frac{1}{[N]} = k''\frac{A}{V_m}\frac{V_{g.Ar}}{Q} \tag{8}$$

where k': N absorption reaction rate constant (m/s), k'' denitrification reaction rate constant (m/s), A: reaction interface area (m^2), V_m: amount of molten steel (m^3), Q: gas flow rate (Nm^3/h), $[N]_0$: nitrogen concentration in molten steel at start of calculation.

Upon applying the above equations to the actual machine, the settings of each parameter and constant were studied. Firstly, the reaction rate constants are influenced by the extent of deoxidization,[9–13)] and by taking the state of deoxidization as a parameter, the value was determined based on the result of sampling from the actual machine. Next, regarding the reaction interface area, the amount of furnace heat after a relining of refractories was taken as a parameter since it is influenced by the heat of the furnace as described above.

The nitrogen transition estimation equation was built into ASTRA, and the optimization of N control was promoted.

5.3 Improvement effect of nitrogen control model

Figure 10 shows a comparison of the calculated result by the N transition estimation equation and the result of analysis of samples taken from the actual machine. In both steel grades of A and B, it is confirmed that the result of [N] analysis in the actual machine is in good agreement with the calculation result. Additionally, in **Fig. 11**, the dispersion of [N] before tapping from V-AOD is compared with respect to before and after the application of this calculation model. The [N] dispersion was reduced and the N control accuracy was improved by the introduced calculation model, and contributed to the stabilization of quality. In addition, the frequencies of prolonged V-AOD refining time for N adjustment and/or long N adjustment time in the subsequent process of LF were reduced, and the productivity of high N steel was significantly enhanced.

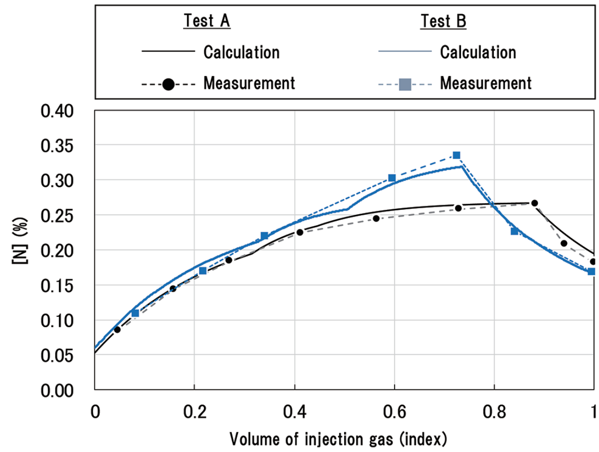

Fig. 10 Comparison of calculation results and measured results

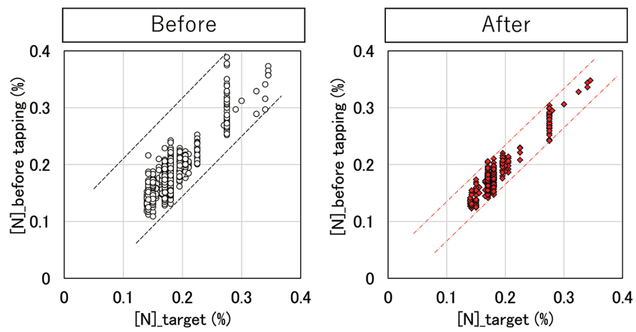

Fig. 11 Comparison of variations of [N] before V-AOD tapping before and after measures

6. Conclusion

Efforts made in the Hikari steelmaking plant to enhance the accuracy of refining control are summarized as below.

(1) By intensifying the system function (ASTRA), the state of refining in the furnace has been grasped successively with high accuracy.

(2) A decarburization completion assessment system for low C

steel by exploiting exhaust gas analysis and the ASTRA function was constructed, and reductions of the refining gas and reducing agent were achieved by suppressing excessive oxygen blowing.

(3) The N transition estimation equation for high N steel was constructed, and by incorporating it into ASTRA, shortening of the refining time and the reduction of the dispersion of N in high N steel were achieved.

Through a series of efforts made for enhancing refining control accuracy, resource-saving and energy-saving were achieved. Furthermore, the production, with decreased composition dispersion and high quality, of high-performance and high-function low C and high N steels such as duplex stainless steel and super austenite stainless steel has been realized.

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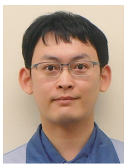

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