Nitrogen adjustment in molten steel using rh vacuum degasser

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Technique for adjustment of nitrogen concentration [N] of molten steel in a RH degasser was improved to meet [N] specifications demanded for several kinds of case-hardening steel. To develop this technique, actual plant trials were carried out to investigate patterns of change in [N] under various RH treatment conditions. This investigation focused particularly on Sulfur content because it is a surface active element. The apparent equilibrium of [N] in molten steel increased with an increase in circulating of N2 gas flow rate, a decrease in degree of vacuum in the RH vessel and an increase in sulfur concentration [S]. The rates of [N] desorption and absorption both decreased with an increase in [S]. To determine appropriate RH treatment conditions according to the various [N] specifications, a prediction model was adopted. The calculation model includes various parameters, such as the interface area of circulating N2 or Ar gas bubbles, the surface area of molten steel in the RH vessel when using circulating N2 or Ar gas, and the mass transfer coefficient of [N] in molten steel. These parameter values were estimated by fitting calculated changes in [N] to actual measured data under a vacuum of 30 Torr and 0.5 Torr in the RH vessel. This model was used as guidance for the operators of RH to control [N] onsite. As a result, [N] adjustment could be done with high accuracy and case-hardening steel having the various [N] specifications was successfully manufactured using RH with only N2 gas flow.

INTRODUCTION

Iron and steelmaking processes in Kobe Works were shut in November 2017 to be consolidated into Kakogawa Works for strengthening of cost competitiveness of special steel wire rods and bars. Therefore, steel blooms and billets manufactured in Kobe Works have to be done in Kakogawa Works. One of these steels is high nitrogen steel, for example case-hardening steel. This is for making gears used for sliding parts, for example transmission gears, differential gears and so on. [N] is added because these parts need to be tough and long-lasting.

Molten steel for case-hardening steel was refined by ASEA-SKF in Kobe Works and needed vacuum treatment to decrease [H] to prevent hair cracks. Table 1 shows a comparison of ASEA-SKF and RH. [N] desorption in the vacuum degasser (VD) process where ASEA-SKF is smaller than RH because the whole surface of molten steel is covered with molten slag and the surface area of the molten steel under vacuum is small. Nitride alloys were used to adjust [N] in molten steel in ASEA-SKF. On the contrary, in the RH vessel the surface area of molten steel exposed to vacuum atmosphere is large because the surface of the molten steel is not covered with molten slag and is bursted by circulating gas. Figure 1 shows the comparison of [N] de-sorption using ASEA-SKF and RH. [N] is decreased rapidly using RH even when [N] is added in the previous process, for example converter and Ladle Furnace (LF). Therefore, in RH Ar gas was used instead of N2 gas as the circulating gas to adjust [N].

In RH there were some research and prediction models of [N] behavior(1-6). However, there were few reports that [N] was controlled for various [N] specifications in RH. In present study, patterns of change in [N] were investigated under various conditions to develop a prediction model of [N] in RH to provide guidance for the operators of RH to control [N] onsite. Among them, high nitrogen steel, for example, case-hardening steel is one of the steel grades that Kakogawa Works had not manufactured.

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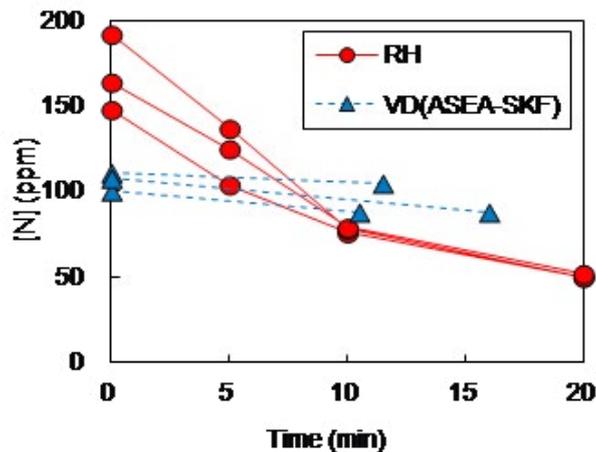|	VD(ASEA-SKF)	RH
Apparatus		
Way of [N] addition	Nitride alloys	Nitride alloys with circulating Ar gas
[N] desorption in vacuum degasser process	10 ppm	~ 150 ppm

Fig. 1 – Comparison of [N] desorption using ASEA-SKF and RH

EXPERIMENTAL

We carried out some actual plant trials to investigate patterns of change in [N] under various RH treatment conditions. Table 2 shows the experimental conditions of RH. Initial [N], circulating N2 gas flow rate, degree of vacuum in RH vessel and [S] were changed. We focused on [S] content because it is a surface active element[1, 2]. Some samples were taken from molten steel in a ladle during RH treatment and [N] was analyzed by insert gas fusion – using the thermal conductivity method.

Tab. 2 – Comparison of [N] desorption using ASEA-SKF and RH

Heat size	250 ton
Initial [N] concentration	65 ~ 180 ppm
Circulating N_2 gas flow rate	1,500 ~ 5,000 NL/min
Degree of vacuum in RH vessel	0.5 and 30 Torr
[S] concentration	0.003 ~ 0.055 %

RESULTS

Effect of circulating N$_2$ gas flow rate

Figure 2 shows the behavior of [N] when the circulating N$_2$ gas flow rate was varied from 1,500 to 5,000 NL/min under a vacuum of 30 Torr and [S] was 0.008 to 0.010 %. Apparent equilibrium [N] were about 105 ppm, about 135 ppm and over 150 ppm when circulating N$_2$ gas flow rate was 1,500 NL/min, 3,000 NL/min and 5,000 NL/min respectively. It increased with an increase in circulating N$_2$ gas flow rate because the rate of [N] absorption from N$_2$ gas bubbles increased.
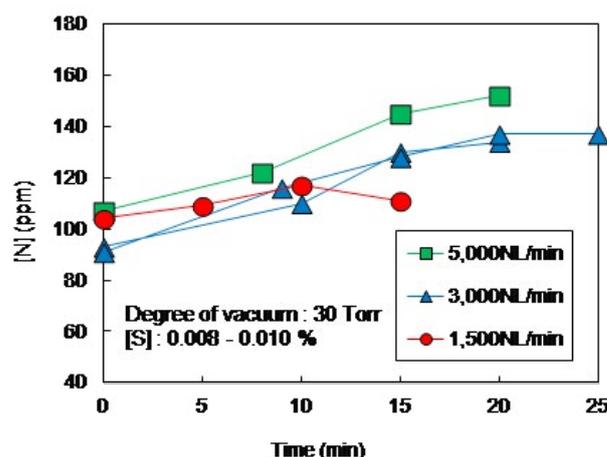

Fig. 2 – Influence of circulating N2 gas flow rate on [N] behavior

Effect of vacuum degree

Figure 3 shows the influence of [N] when degree of vacuum was 0.5 and 30 Torr where circulating N2 gas flow rate was 3,000 NL/min and [S] was 0.003 - 0007 %. Apparent equilibrium [N] was about 60 ppm when degree of vacuum was 0.5 Torr and about 120 ppm under a vacuum of 30 Torr. It increased with as the degree of vacuum decreased because the rate of [N] desorption from surface of molten steel in the RH vessel decreased.
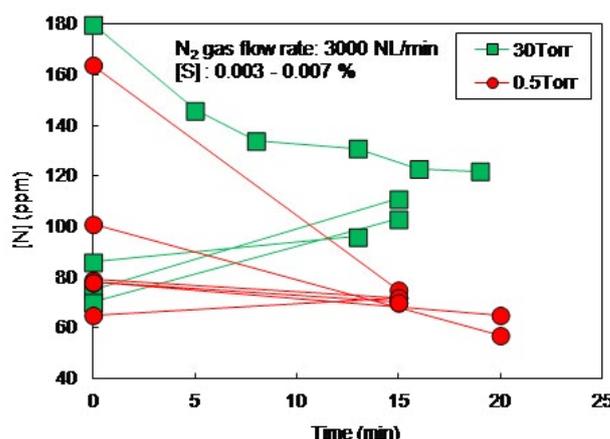

Fig. 3 – Influence of degree of vacuum on [N] behavior

Effect of sulfur concentration

Figure 4 shows the influence of [N] when [S] was varied from 0.003 to 0.055 % where circulating N2 gas flow rate was 3,000 NL/min and the degree of vacuum was 0.5 Torr. Apparent equilibrium [N] were about 80 ppm, 110 ppm and 120ppm when [S] was 0.003%, 0.015 % and 0.055% respectively. It increased with an increase in [S]. And the rate of change in [N] was decreased with an increase in [S]. These results suggest that the rates of [N] desorption and absorption were decreased because sulfur acted as a surface active element. Figure 5 shows the reaction sites of [N] in RH. The reason why apparent equilibrium [N] was changed by [S] is that balances between the rates of [N] desorption from the surface of molten steel and absorption from N2 gas bubbles is changed. We assumed that

the surface area of molten steel in the RH vessel is larger than interface area of N2 gas bubbles and molten steel. Therefore, the decrease in the rate of [N] desorption is larger than the decrease in the rate of [N] absorption.
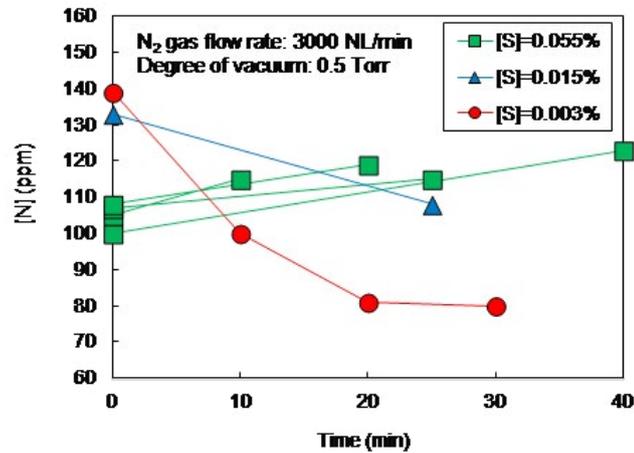

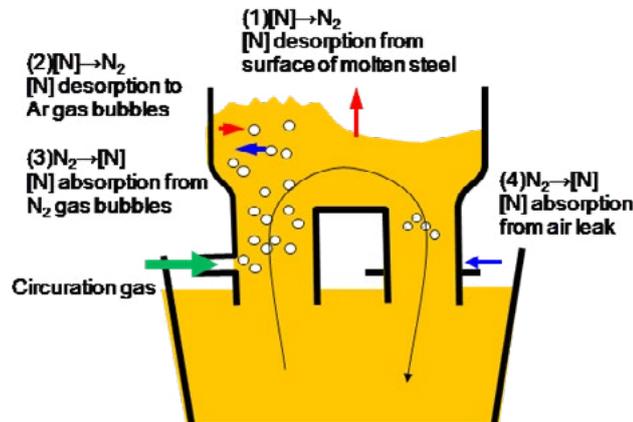
Fig. 4 – Influence of [S] on [N] behavior

Fig. 5 – Reaction sites of [N] in RH

MODEL OF [N] BEHAVIOUR
Details of model
[N] needs to be adjusted within a limited time in RH to be in time to start casting. This prediction model was adopted to determin appropriate RH treatment conditions, for example the kind of circulating gas, circulating gas flow rate and degree of vacuum, according to the various [N] specifications, the concentration of other components and RH treatment time. The model was based on Nabeshima's model(3) and can explained as follows.

The rates of [N] absorption in the RH vessel and ladle are calculated using equations [1] and [2] when perfect mixing in molten steel is assumed, and the reaction sites of [N] are the 4 sites shown in Fig. 5.

$$\frac{d[N]_V}{dt} = -\frac{Q}{V_V}([N]_V - [N]_L) + R_S + R_{Ar} + R_{N_2}$$

[1]

$$\frac{d[N]_L}{dt} = -\frac{Q}{V_L}([N]_V - [N]_L) + R_{leak}$$

[2]

where
$[N]_L$: [N] of molten steel in ladle (%)
$[N]_V$: [N] of molten steel in the RH vessel (%)
V_L : volume of molten steel in ladle (m³)
V_V : volume of molten steel in the RH vessel (m³)
t : reaction time (min)
R_S : the rate of [N] absorption at surface of molten steel in the RH vessel (%/min)
RAr : the rate of [N] absorption at interface of circulation Ar gas (%/min)
R_{N2} : the rate of [N] absorption of interface at circulation N_2 gas (%/min)
R_{leak} : the rate of [N] absorption of air leak from snorkel (%/min)

Q (m³/min) is the circulatiing quantity of molten steel and is calculated using equation [3] proposed by Kuwabara et al.(4).)

$$Q = 11.4 Q_g^{\frac{1}{3}} D^{\frac{4}{3}} \left\{ \ln\left(\frac{P_0}{P_V}\right) \right\}^{\frac{1}{3}} / \rho_{Fe}$$

[3]

where
Q_g : circulation gas flow rate (Nm3/min)
D : diameter of snorkel (m)
P_0 : pressure at height of nozzle of circulation gas (atm)
P_V : pressure in the RH vessel (atm)
ρFe : density of molten steel (ton/m³)

R_S and R_{Ar} are calculated using equation [4] when rate-determining steps are both transferring [N] to the surface of the molten steel and the chemical reaction of N on the surface of the molten steel.

$$R_n = -\frac{A_n}{V_V} k_m ([N]_V - [N]_{i,n}) = -\frac{A_n}{V_V} k_r ([N]_{i,n}^2 - [N]_{e,n}^2)$$

[4]

where
n : S or Ar of subscript
A_n : reaction interfacial area of surface of molten steel or inter-
face between Ar gas bubbles and molten steel (m2)
$[N]_{i,n}$: initial [N] of surface of molten steel or interface between
Ar gas bubbles and molten steel (%)
$[N]_{e,n}$: equilibrium [N] of surface of molten steel or interface
between Ar gas bubbles and molten steel (%)
k_m : mass transfer coefficient of [N] of molten steel (m/min)
k_r : chemical reaction rate constant of [N] (m/(min/%))

R_S and R_{Ar} are calculated using equation [5] when $[N]_{i,n}$ from equation [4] was deleted.

$$R_n = -\frac{A_n}{V_V} \left\{ k_m [N]_V - k_m \left(\frac{-k_m + \sqrt{k_m^2 + 4k_m k_r [N]_V + 4k_f^2 [N]_{e,n}^2}}{2k_r} \right) \right\}$$

[5]

R_{N2} is calculated using equation [6] taking into consideration that N2 partial pressure in gas bubbles is different between the height of the snorkel nozzle and the surface of molten steel.

$$R_{N_2} = -\int_0^h \frac{A_{N_2}(x)}{V_V}\left\{k_m[N]_V - k_m\left(\frac{-k_m + \sqrt{k_m^2 + 4k_m k_r[N]_V + 4k_r^2[N]_{e,N_2}^2(x)}}{2k_r}\right)\right\}dx \qquad [6]$$

where
h : height between nozzle of snorkel and surface of molten steel (m)
A_{N2} : reaction interfacial area of interface between N2 gas bubbles and molten steel (m)
$[N]_{e,N2}$: equilibrium [N] of interface between N2 gas bubbles and molten steel (%)

$[N]_{e,n}$ and $[N]_{e,N2}$ are calculated using equations [7] and [8].

$$[N]_{e,n} = \frac{\sqrt{P_{N2,n}}}{f_N} \exp\left(-\frac{9916 + 20.17T}{RT}\right) \qquad [7]$$

$$[N]_{e,N_2} = \frac{\sqrt{P_{b,N2}(x)}}{f_N} \exp\left(-\frac{9916 + 20.17T}{RT}\right) \qquad [8]$$

where
$P_{N2,n}$: N2 partial pressure in the RH vessel or Ar gas bubbles (atm)
$P_{b,N2}$: N2 partial pressure in N2 gas bubbles (atm)
f_N : activity coefficient of [N]
R : gas constant (J/(mol•K)

$P_{b,N2}(x)$ is N_2 partial pressure in N_2 bubbles and is calculated using equation [9].

$$P_{b,N2}(x) = P_V + \frac{\rho_{Fe}g(h-x)}{1.013 \times 10^5} \qquad [9]$$

where
g: acceleration of gravity (m/s2)
kr is expressed as equation [10] estimated by Harashima et al.(1).

$$k_r = \frac{0.15f_N^2}{(1 + 161a_O + 63.4a_S)^2} \times 60 \qquad [10]$$

where
a_O : activity of [O]
a_S : activity of [S]

A_{Ar} and A_{N2} are considered to be proportional to geometrically 2/3 square of quantity of circulation gas in molten steel and they are calculated using equation [11].

$$A_m = \alpha_m \frac{(Q_g t_b)^{\frac{2}{3}}}{h}$$

where   [11]
m : Ar or N2 of subscript
α_m : coefficient of A_m
t_b : bubbles residence time (min)

R_{leak} is calculated using equation [12].

$$R_{leak} = \frac{0.80 Q_{leak} M_{N_2}}{0.0224 V_L \rho_{Fe}} \times 10^{-1}$$

[12]

where
Q_{leak} : 0.17 Nm3/min(4)
M_{N2} : molecular weight of N2

Parameters fitting

Unknown parameter values in the model are k_m, AS, α_{Ar} and α_{N2}. They were estimated by fitting calculated changes in [N] to actual measured data under a vacuum of 30 Torr and 0.5 Torr in the RH vessel.

Table 3 shows estimated parameter values. The value of k_m is assumed to be 10,000 m/min assuming that nitrogen transfers so rapid in molten steel and it doesn't become mass transfer rate-determining step. The apparent reaction surface area of molten steel using circulating N_2 gas is about 4 times larger than the sectional area of the lower vessel under a vacuum of 30 Torr and about 10 times larger under 0.5 Torr. We assume that the surface area of molten steel in the RH vessel is large because [N] desorption is increased under a high degree of vacuum.

**Tab. 3** – Estimated unknown parameter values

	Degree of vacuum	
	0.5 Torr	**30 Torr**
Km	10,000 m/min	
A_s using Ar gas	43 m^2	17 m^2
A_s using N$_2$ gas	74 m^2	16 m^2
α_{Ar}	38.5	36.5
α_{N2}	33.7	32.0

RESULTS OF NITOROGEN ADJUSTMENT IN RH

This model was used as guidance for the operators of RH to control [N] onsite. Both static control which determined RH treatment conditions before starting the treatment and dynamic control in which changing RH treatment conditions on the way to treatment end according to actual analysis of [N] composition were used to adjust [N]. Figure 6 shows the results of [N] control and Figure 7 shows the accuracy of [N] adjustment. [N] was controlled with a high degree of accuracy and an accuracy of 6.3 ppm was achieved for [N] adjustment. Case-hardening steel having various [N] specifications was successfully manufactured using RH with only N2 gas flow. In addition, the consumption of nitride alloys was greatly reduced compared to ASEA-SKF.
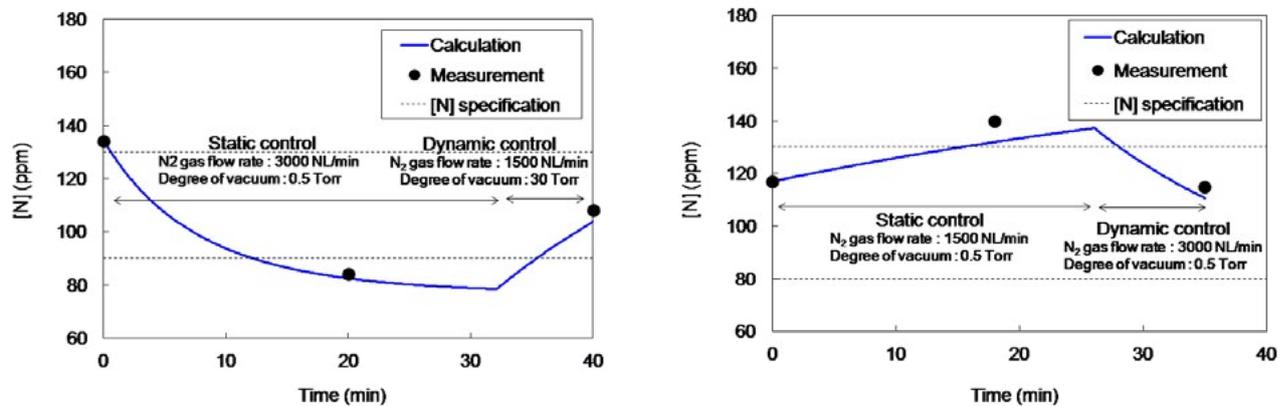
a) – [N] absorption control under dynamic control

b) – [N] desorption control under dynamic control
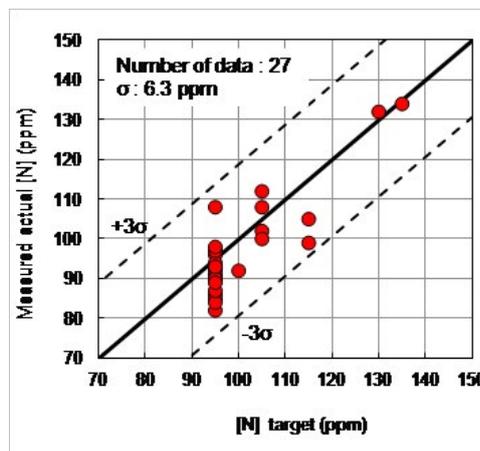
Fig. 6 – Results of [N] adjustment

Fig. 7 – Accuracy of [N] adjustment

CONCLUSIONS

• [N] behaviors were investigated under various RH treatment conditions. Apparent equilibrium [N] in molten steel increased with an increase in circulating N2 gas flow rate, a decrease of degree of vacuum in the RH vessel and an increase of [S]. Rates of [N] desorption and absorption both decreased with an increase in [S].

• To determine appropriate RH treatment conditions according to the various [N] specifications, prediction model of [N] in RH was adopted and unknown parameter values in the model were estimated by fitting calculated changes in [N] to actual measured data.

• This model is used for guidance to control [N] onsite. As a result, [N] adjustment could be achieved with high accuracy and case-hardening steel having the various [N] specifications was successfully manufactured in Kakogawa Works using RH with only N2 gas flow.

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