Acceleration of Nitrogen Removal in Stainless Steel under Reduced Pressure*

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Synopsis

New methods have been developed for accelerating the nitrogen removal in stainless steel under reduced pressure. In the first method, nitrogen can be removed effectively by reducing the ambient pressure at high carbon levels after interrupting oxygen top blowing in the VOD process. In the second method, the efficiency of nitrogen removal increased twice as much as that in the oxygen gas blowing by blowing the powdered oxidizer into the molten steel from a top lance under reduced pressure. In these methods, the favourable conditions for increase of nitrogen removal were satisfied, such as the increase of gas–metal interfacial area where the oxygen content is kept at low level and so on.

Key words: secondary steelmaking; refining in vacuum; stainless steel; nitrogen removal; VOD process; powdered oxidizer blowing.

I. Introduction

In recent years there has been an increased demand for stainless steels containing extremely low impurities.4~6 The ferritic stainless steel is relatively less expensive and has stronger resistance to stress corrosion cracking than the austenitic stainless steel. On the other hand, the ferritic stainless steel has several disadvantages—namely weak toughness and poor resistance to pitting corrosion at the heat affected zone of welding. However, it has been evident that such disadvantages can be solved by reducing carbon and nitrogen contents to extra-low level.5~6 Thus, the authors studied how to produce low nitrogen stainless steel.1~3

It is well known that the removal of nitrogen proceeds with the decarburization reaction in the VOD process,6~11) as shown in Fig. 1. It is also known that the nitrogen content can be lowered by increasing the initial carbon content.2~4 However, by this conventional method, the average nitrogen content can not be reduced lower than 85 ppm, even though it takes longer oxygen blowing period as shown in Fig. 2. Further, it would be more difficult to produce the low nitrogen stainless steel containing such high chromium as 30 %, shown in Fig. 3, because the activity coefficient of nitrogen in the high chromium steel is smaller.

In this paper, the behaviour of nitrogen removal are examined 1) by reducing the atmospheric pressure after interrupting oxygen top blowing and 2) by blowing of powdered oxidizer from the top lance at the high carbon levels in laboratory scale and production scale tests.

II. The First New Refining Method1~3)

(Acceleration of Nitrogen Removal without Improvement of the Equipment)

1. Experimental Method

Experiments were carried out in a 2.5 t laboratory scale vacuum induction furnace, shown in Fig. 4, by using 1.5 t of crude steel containing 19 % Cr and 0.8 % C. The argon gas flow rate for agitating the molten steel through the porous plugs was 2~7 N/min, and the oxygen gas flow rate through a top lance with a laval nozzle, 3 mm in diameter, was 0.45 m³N/(min·t). The bath temperature was kept at...
1600°C and the ambient pressure was held at 2.00 \times 10^4 \text{ Pa}, as in the actual VOD process. The first new refining operations for accelerating the nitrogen removal rate were tried twice at the high carbon contents of 0.8 and 0.4 % by reducing the ambient pressure down to (1.33-2.67) \times 10^2 \text{ Pa}, after interruption of oxygen gas blowing.

2. Experimental Results

The typical relationship between nitrogen content and carbon content by this new method is compared with that by the conventional method in Fig. 5. It is seen that the first new refining method is effective for removing nitrogen and that the final nitrogen content is lowered by about 50 ppm.

It was observed that smaller CO bubbles evolved uniformly from the surface of the molten steel by the reaction with the oxygen accumulated during the former oxygen blowing period at 2.00 \times 10^4 \text{ Pa}.

3. Application of the First New Refining Method to the Industrial VOD

Experiments were carried out by using a 50 t VOD in order to confirm the effect of this method. In the 50 t VOD, the ambient pressure was reduced to (1.33-2.67) \times 10^2 \text{ Pa} in the period of interruption of oxygen blowing for 5 to 10 min.

Figure 6 shows the typical relationship between nitrogen content and carbon content when the first new refining method is applied to the industrial VOD process. It is clear that the new method is also useful for accelerating nitrogen removal in the industrial VOD process. The new method can be applied repeatedly by interrupting oxygen gas blowing at high carbon content levels. Figure 7 shows the relationship between the final nitrogen content and the number of application of the new method. It is seen that the final nitrogen content can be lowered as the numbers of application of the new method increases. In fact the final nitrogen content can be lowered to 70 ppm in 26 % Cr steel by applying the new method three times. Thus ultra-low interstitial ferritic stainless steels can be easily produced by the first new refining method.
4. Discussion

The VOD process normally consists of three periods shown in Fig. 1: an oxygen gas blowing period, a vacuum decarburization period and a reduction period. The oxygen gas blowing period, in turn, is separated into two stages. In the first stage, the decarburization rate is kept at constant under the condition that the flow rate of oxygen gas is kept at constant. In the second, the decarburization rate decreases in proportion to the carbon content.

The first new refining method was applied in the first stage of the oxygen gas blowing period. In the first stage, the decarburization rate is kept at constant against the refining time, as is represented in Eq. (1). The decarburization rate constant value, $k_\alpha$, increases in proportion to the oxygen gas flow rate.\(^1\)\(^2\) The oxygen content increases slightly from 20 to 100 ppm with the decarburization reaction. Therefore the chromium is not oxidized in this stage.

$$\frac{-d[\%C]}{dt} = k_\alpha \tag{1}$$
$$\frac{-d[\%N]}{dt} = k_N[\%N]^2 \tag{2}$$
$$\frac{d(1/[\%N])}{dt} = k_N \tag{2'}$$

The nitrogen removal reaction proceeds with the decarburization reaction.

According to the results of the fundamental research,\(^1\)\(^3\) the nitrogen removal rate is represented in Eq. (2) or (2'),\(^1\)\(^3\) assuming that the rate determining process is a chemical reaction on the gas-metal interfacial area.有利条件 for the removal of nitrogen are as follows:

1. Increasing the gas-metal interfacial area,
2. Decreasing the oxygen content at the gas-metal reaction interface, and
3. Decreasing the N\(_2\) gas partial pressure.

In order to get further removal of nitrogen in the VOD, the above three conditions need to be satisfied at the same time.

During the first stage of the oxygen gas blowing period, all the conditions for effective nitrogen removal are clearly satisfied:

1) The formation of a large number of CO gas bubbles,
2) the low oxygen content because of high carbon contents, and
3) the dilution of the N\(_2\) gas partial pressure by the aid of large amounts of CO gas under reduced pressure.

In addition to these conditions, the activity of nitrogen becomes high because the activity coefficient of nitrogen increases with increase of carbon content. Activity of nitrogen in 1 % C steel is about 1.3 times as that in 0.1 % C steel.

In order to compare the effect of nitrogen removal by the new method with the conventional method, the index of nitrogen removal against decarburization is defined\(^1\)\(^2\)\(^3\)\(^4\) as $\alpha$, represented in Eq. (3), which is derived by eliminating the time term, $t$, from Eqs. (1) and (2').

$$\alpha = \frac{-d(1/[\%N])}{dt[\%C]} = \frac{k_N}{k_\alpha} \tag{3}$$

In other words, $\alpha$ is defined as the proportion of the change of the absolute value of the term, 1/[\%C], to that of [\%N], given in Eq. (3').

$$\alpha = \frac{d(1/[\%N])}{dt[\%C]} \tag{3'}$$

The value of $\alpha$ was estimated as about 200 in the conventional process, whereas it was 600 when the first new refining method is applied. The effect of the first new refining method on the nitrogen removal is, therefore, three times as large as that of the conventional method.

The first new refining method is based on the assumption that further removal of nitrogen would proceed effectively by reducing the ambient pressure after interrupting oxygen gas blowing at high carbon levels. There are three reasons why the first new refining method is highly effective in accelerating the nitrogen removal rate. One is the high nitrogen activity in the high carbon content, another is the low oxygen content which would be lowered by the carbon deoxidation reaction and the other is the formation of a large number of fine CO bubbles which would evolve uniformly from the surface of the molten steel. The lower the ambient pressure of the carbon deoxidation treatment in the interrupting oxygen gas blowing becomes, the more effectively the nitrogen removal proceeds. This is because the CO bubbles were formed more rapidly and more finely.

III. The Second New Refining Method

(Acceleration of Nitrogen Removal by Blowing the Powdered Oxidizer)

In order to produce the ultra low nitrogen stainless steel, it is very effective to apply the first new refining method. However, the number of application of the new method had to be increased with the increase of chromium content in molten steel. Then, the more effective method in order to reduce the nitrogen content in the molten steel containing high chromium content was required.

1. Experimental Method

Experiments were carried out in a 2.5 t laboratory scale vacuum induction furnace using 1.5 t of crude
steels containing 26 % Cr and 0.8 % C. The powdered oxidizer were blown through the central nozzle of a top lance with the argon gas, 0.27 m³N/(min•t), for carrying the powder. Argon gas jet was blown, 0.4 m³N/(min•t), through the three nozzles around the central nozzle for accelerating the powder speed. The argon gas jet speed was estimated to have a combined speed of mach 3.8. The height of the top lance was 400 mm over the molten steel surface. Argon gas was injected, 35 5 lN/ (min • t), through the porous plugs for agitating the molten steel. The bath temperature was kept at 1 650°C and the ambient pressure was held at 2.67 × 10² Pa.

The powdered oxidizers were Cr–Oxide and Fe–Ore, and were finer than 0.1 mm in diameter. The feeding rate of the oxidizers was 0.2 kg/(min • t).

Figure 8 shows the schematic profile of powdered oxidizer blowing method.

2. Experimental Results

The typical behaviour of [C] and [N] during Fe–Ore powder blowing is shown in Fig. 9. In the case of Cr–Oxide powder blowing, the behaviours of [C] and [N] were the same as that in the case of Fe–Ore. The chromium content decreased at the speed of 7.5 × 10⁻³ % • min⁻¹ during Fe–Ore powder blowing and increased at the speed of 7.5 × 10⁻³ % • min⁻¹ during Cr–Oxide powder blowing. Then the behaviour of nitrogen was mainly discussed by using the experimental results of Fe–Ore powder blowing. It was found that nitrogen removal proceeds with decarburization and neither generation of fume dust nor powder splash was observed through the port.

Figure 10 shows the behaviour of [N] during the powdered oxidizer blowing compared with that during the oxygen gas blowing. It is found that the behaviour of [N] is represented by Eq. (2) or (2'). And the value of $a$ in the second new refining method was calculated to be 250 as shown in Fig. 11.

In the application of the second new refining method to the industrial VOD process, however, there is limitation on the supply of the powdered oxidizer, because of the temperature drop of the molten steel. Therefore, the second new refining method is quite effective in the application of the process which has a heating-equipment, such as ASEA-SKF or VAD process.

3. Discussion

1. Effect of the Second New Refining Method

In the case of oxygen gas blowing method, the value of $a$ was about 200 in 19 % Cr steel and was about 55 in 30 % Cr steel.¹

Assuming that the value of $a$ is the inverse proportion of the chromium content, $a$ was calculated to be 100 in 26 % Cr steel during oxygen gas blowing period. It was found, therefore, that the nitrogen removal efficiency in the powdered oxidizer blowing method becomes about twice or three times as much as that in the oxygen gas blowing method.

2. Characteristics of Powdered Oxidizer Blowing

In this method, it was found that the nitrogen removal reaction proceeded effectively with decarburization reaction in high carbon contents.

![Fig. 8. Schematic profile of powdered oxidizer blowing method.](image)

![Fig. 9. Behaviours of [C] and [N] during Fe–Ore powder blowing in a 2.5 t VIF.](image)

![Fig. 10. Behaviour of 1/[N] during Fe–Ore powder blowing in a 2.5 t VIF.](image)

![Fig. 11. Relationship between 1/[N] and [C] during Fe–Ore powder blowing in a 2.5 t VIF.](image)
The characteristics of the powdered oxidizer particles on decarburization are summarized into following three points:

1. The particles themselves become the source of oxygen for decarburization.
2. The particles penetrate deeply and are dispersed uniformly in molten steel to act as fine nuclei for the CO bubble formation.
3. The particles increase the oxidizer efficiency for decarburization as a result of the above two features.

These characteristics on decarburization are expected to build up the following two favourable conditions for removing nitrogen in the molten steel:

i) An increase of the gas–metal interfacial area by the formation of many fine CO bubbles.
ii) A decrease of the oxygen content by the higher oxidizer efficiency for decarburization.

3. Penetration Distance of Oxidizer Particles

The total penetration distance of oxidizer particles below the free surface of molten steel is calculated as above 70 mm in depth just under the lance by measuring the dynamic pressure of top blowing gas and by using E. Kimura’s experimental equation\(^{16}\) on the powder-penetration.

4. Measurement of the CO Bubbles Size

The mean size of CO bubbles on the free surface of molten steel was measured through the port by photographs and video television recorder (VTR) during the decarburization reaction. As a result, the mean size measured was approximately 30~50 mm in diameter in the case of the oxygen gas blowing. On the other hand, the bubble size was about 10~15 mm in diameter in the case of the powdered oxidizer blowing. From these measurements, the interfacial area of bubbles in the powdered oxidizer blowing was calculated to be twice or five times as large as that in the oxygen gas blowing. It seems to explain the experimental result that the \(k_N\) value in the powdered oxidizer blowing, which was represented in Eqs. (2) and (2)', was almost twice as much as that in the oxygen gas blowing.

However, in order to study nitrogen removal in details, it should be considered the oxygen content in molten steel or on the gas–metal interfacial area, because it is well known that oxygen is a surface-active element and prevents nitrogen from removing on the gas–metal interfacial area.

5. Behaviour of the Oxygen Content in Molten Steel

The relationship between [C] and [O] in molten steel during the powdered oxidizer blowing is shown in Fig. 12, comparing the results of the oxygen gas blowing.

It was found that the oxygen content during the powdered oxidizer blowing was kept about 30~40 ppm lower than that during the oxygen gas blowing, at high carbon level ([C]=0.6~0.8%). The increasing tendency of oxygen content during decarburization was shown on a [C]–[O] equilibrium line with \(P_{CO}=0.01\ atm\), approximately 1.01 \times 10^4 Pa. Here, as for the oxygen content, the lower values were taken because the obtained samples may include some oxidizer particles.

As mentioned above, it can be concluded that the nitrogen removal reaction was accelerated under such favourable conditions as lower oxygen level in molten steel and larger gas–metal interfacial areas, by blowing the powdered oxidizer into molten steel.

By the way, it is well known that the oxygen content has a direct influence on \(k_N\), as represented by Eq. (4),\(^{17}\) in other words, that the \(k_N\) value must be decreased with increase of the oxygen content by Eq. (4).

\[
k_N = 60 \times \frac{A}{V} \times \frac{0.974f_N^{2}}{1 + 28.4[O] + 5.34[S]^2} \quad \cdots \cdots \cdots (4)
\]

\[
\log f_N = -0.04[Cr] + \sum_{i \neq \text{Cr}} \varepsilon_i [i] \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdOTSISIJ,Vol. 28, 1988 (301)
decarburization reaction proceeds at the oxidizer particles where oxygen content was extremely high, and the nitrogen removal reaction proceeds on the CO gas–metal interfacial area where oxygen content was relatively low.

Figure 13(b) shows the model in the oxygen gas blowing. This model presents that both the decarburization and the nitrogen removal reactions occur simultaneously at any point on CO bubble’s surface.

As for the nuclei of CO gas formation, there are some points; free surface of molten steel where the oxygen gas was blown, the surface of refractory, the surface of argon gas which was injected through the porous plugs and the surface of CO gas bubbles.

As the supply-point of the oxygen source was only at the free surface of molten steel where the oxygen gas was blown, the oxygen content must distribute uniformly on the gas–metal interfacial area where the nitrogen removal reaction proceeds.

By using these models, it was explained that the decarburization reaction during the powdered oxidizer blowing was accelerated even if the oxygen content in molten steel was relatively low. It was also explained that a large number of fine CO bubbles were formed in the molten steel.

7. Top Blowing of SiO2 Powder Particles

If the powdered oxidizer has rather weak oxidizing power, the nitrogen removal would be accelerated, because the oxygen potential on the gas–metal interfacial area, around the oxidizer particles, was reduced to low level. In other words, if the decarburization reaction can be proceeded by using the rather weak oxidizer, such as SiO2, as shown in Fig. 14, the nitrogen removal would proceed more effectively than that in the strong oxidizer blowing, such as Fe–Ore.

Figure 15 shows the behaviours of [C], [N] and [Si] during SiO2 powder blowing. The nitrogen content decreased and the silicon content increased during decarburization. The recovery of silicon was approximately 70%.

The behaviour of the nitrogen content is shown in Fig. 16. The value of $k_N$ was about 1.42(%)$^{-1}$.min$^{-1}$, taking the analytical scattering into account, and $\alpha$ was, nearly 526(%)$^{-1}$, twice as much as that of the Fe–Ore powder blowing, as shown in Fig. 17.

With respect to the oxygen potential which the oxidizer has in itself, it is found that the lower the oxygen potential of the oxidizer is, the more effective the nitrogen removal proceeds under the condition that the decarburization reaction can be proceeded by blowing the oxidizer. As results of these experiments, the relationship between $k_s$ and $k_N$ is shown in Fig. 18.

Fig. 13. Comparison of reaction mechanism between powdered oxidizer blowing and oxygen gas blowing.

(a) Fe–Ore powder blowing

(b) Oxygen gas blowing

Fig. 15. Behaviour of [C], [N] and [Si] during SiO$_2$ powder blowing in a 2.5 t VIF.
8. Comparison between the First Refining Method and the Second Refining Method

The index of nitrogen removal ($\alpha$) in the first refining method is about 600, larger than that in the second method 250. It is also easy to apply the first method to industrial VOD process, because no improvement of the equipment is required. In the second method, further improvement of the equipment is necessary such as the strong endurance of lance nozzle material, setting up the equipment for the powder supply and so on.

The first refining method has, however, some inconvenient points. There are limitations in the amount of decarburization and nitrogen removal in every application of the first method, because the decarburization reaction proceeds by consuming the oxygen in the molten steel which is supplied in the oxygen gas blowing period. In other words, the first refining method can be applied not only continuously but also alternately with oxygen gas blowing method. When the amount of decarburization in 26% Cr steel is about 1%, the number of the application of the first method is no more than 3~4, and the final nitrogen content becomes about 50~60 ppm as shown in Fig. 7. There are no special nuclei for CO bubble formation in the first method such as powder particles in the second method.

The second refining method can be continuously got the decarburization and nitrogen removal reactions, because the oxygen for decarburization reaction is supplied by blowing the powdered oxidizer. When the amount of decarburization in 26% Cr steel is about 1%, the final nitrogen content is about 30 ppm on calculation. It is desirable to apply the second refining method to the vacuum equipments with heat source such as VAD process and VIM process, because the temperature of the molten steel will decrease by blowing the powdered oxidizer.

We must decide which method is useful for producing the ultra-low nitrogen stainless steels, after the production cost and the steel grades are considered.

IV. Conclusion

(1) The first new refining method (Acceleration of nitrogen removal in stainless steels) can accelerate the nitrogen removal with a decrease in oxygen content on the gas–metal interfacial area by applying carbon deoxidation with an interruption of oxygen blowing during the high carbon period.

The index of nitrogen removal against decarburization was three times that of the conventional method, and the final nitrogen content was reduced to half of that obtained by the conventional method.

(2) The second new refining method can accelerate the nitrogen removal with the formation of many fine CO bubbles by blowing powdered oxidizer under reduced pressure. The index of nitrogen removal against decarburization increases twice or three times as much as that of oxygen gas blowing method, even in the case of refining of high chromium steels.

The reasons, why the satisfactory nitrogen removal was obtained by using these two new refining methods, are summarized as follows;

(i) An increase of the gas–metal interfacial area by the formation of quite many fine CO bubbles: In the first method, by the reaction of carbon deoxidation in the molten steel and in the second method, by the decarburization reaction just around the oxidizer particles blown and penetrated into the molten steel.

(ii) A decrease of the oxygen content on the gas–metal interfacial area by the higher oxidizer efficiency for decarburization: In the first method, by the decrease of oxygen content with proceeding of carbon deoxidation reaction, and in the second method, effect of the oxidizer particles on the nuclei of the decarburization reaction.
Nomenclature

[C]: the carbon content in molten steel (%)
[Cr]: the chromium content in molten steel (%)
[N]: the nitrogen content in molten steel (%)
[O]: the oxygen content in molten steel (%)
[S]: the sulphur content in molten steel (%)
A: the gas–metal interfacial area (cm²)
V: the volume of molten steel (cm³)
\( A \): the activity coefficient of nitrogen
\( k_r \): the rate constant of decarburization (%•min⁻¹)
\( k_N \): the apparent rate constant of nitrogen removal (%•min⁻¹)
t: the time (min)
\( \Delta [C] \): the absolute variation of [C] (%)
\( \Delta (1/[N]) \): the absolute variation of 1/[N] (%⁻¹)
\( \alpha \): the nitrogen removal efficiency against the decarburization (%⁻²)
\( \epsilon_i \): the interaction parameter of the element i against nitrogen

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