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Optimized Decarburization Process for Stainless Steel with Combination of Refining in Converter and RH Degasser

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Optimized Decarburization Process for Stainless Steel with Combination of Refining in Converter and RH Degasser*



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1 Introduction

The EF-VOD and EF-AOD methods are widely known refining processes for stainless steel and have in numerous cases been adopted by Japanese stainless steel makers as main refining processes.[1]

After the stainless steel department was consolidated at Kawasaki Steel's Chiba Works in 1981, stainless steel was produced using the 85-t top and bottom blowing converter (K-BOP) at No. 1 Steelmaking Shop.[2] The K-BOP-RH process using pretreated hot metal was adopted thereafter in place of the EF-K-BOP-RH route to take advantage of site conditions, namely, the location of the stainless steel shop in an integrated steel works.[3] The recent practice is Cr-ore smelting reduction via a K-BOP-K-BOP-RH using two K-BOP converters.[4]

In the decarburization converter in this process, the bottom blowing gas flow rate and number of tuyeres have been optimized[5] and efforts have been made to improve the quick dynamic tapping ratio[6] in order to reduce Cr oxidation loss during decarburization refining and decrease the consumption of FeSi ferroalloy used for reduction. A N_2/O_2 mixed gas blowing method which does not require expensive Ar gas has also been established. However, there are limits to the promotion of preferential decarburization without Cr oxidization in a process which depends entirely on the converter for decarburization refining.

Recent years have also seen increased need and greater demand for high purity in stainless steel, which includes ultra-low carbon and ultra-low nitrogen levels.

This background suggested the desirability of stainless steel decarburization using a secondary refining process with a decarburization function, which would make it possible to respond to the needs for more rational decarburization and high purity in the steel while maintaining a high level of productivity in the existing process. At Chiba Works No. 1 Steelmaking Shop, this led to the development in 1992 of a top lance oxygen top-blowing method (KTB process), applied in RH degassing during the refining of stainless steel, and then to the establishment of K-BOP-KTB process for stainless steel decarbuization, which combines mixed gas decarburization by bottom blowing in the decarburizing converter and oxygen blowing decarburization under a vacuum with the KTB.[7]

This report describes the decarburization behavior of stainless steel during secondary refining follwoing the

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introduction of this K-BOP-KTB process, together with measures for the effective use of the KTB.

2 Stainless Steel Production Process at Chiba Works

The flow of the stainless steel production process at Chiba Works No. 1 Steelmaking Shop is shown in **Fig. 1**. The Cr source in the main process of Cr-ore smelting reduction is prereduced Cr pellet, which is produced by reducing Cr ore to the 65-70% level using a rotary kiln. The refining process uses two K-BOPs, one as a smelting reduction furnace and the other as a decarburization converter. Secondary refining equipment includes an RH degasser equipped with a top lance for top oxygen blowing (KTB) and an SS-VOD (strongly stirred VOD), both with the function of decarburization by oxygen blowing under a vacuum. The choice of secondary refining processes depends on the steel grade: General grades of steainless steel such as SUS 430 are produced by the K-BOP-KTB route, while high-purity steels such as high-Cr, ultra-low carbon low nitrogen stainless steels are produced by the K-BOP-SS-VOD. The object steel grades of each process are summarized in **Table 1**.

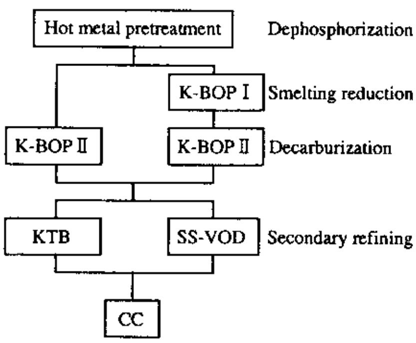

Fig. 1 Process for stainless steelmaking in Chiba Works

3 Necessity of Vacuum Oxygen-Blowing Decarburization Process in Production of Stainless Steel

An essential task in refining stainless steel is to promote decarburization while suppress Cr loss to oxidation. It is generally known that reducing the partial pressure of CO (P_{CO}) is useful for achieving this end.[1] For this reason, decarburization refining in the K-BOP-RH has conventionally been performed by mixed gas bottom-blowing in the K-BOP to reduce P_{CO}. However, as shown in **Figs. 2 and 3**, the amount of Cr oxidation loss increases precipitously in the low carbon region, indicating that there are limits to dilution decarburization at atmospheric pressure. On the other hand, if it is possible to tap the converter before reaching the low carbon region where Cr oxidation loss increases and then to decarburize down to the target carbon content under a vacuum, the amount of Cr oxidation shown in Figs. 2 and 3 can be reduced and decarburization oxygen efficiency improved, resulting in more rational decarburization refining.

Kawasaki Steel uses SS-VOD equipment as secondary

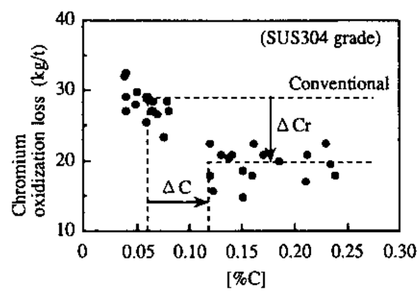

Fig. 2 Effect of tapping carbon content on chromium oxidization loss in K-BOP (SUS 304 grade)

Table 1 Process application for stainless steel grades

Process	Stainless steel grades
K-BOP I -K-BOP II -KTB (or K-BOP II -KTB)	Normal stainless steel: SUS 304(L), SUS 316(L), SUS 321, SUS 410, SUS 420, SUS 430, SUS 434, SUS 436 L SUS 409, etc.
K-BOP I -K-BOP II -SS-VOD (or K-BOP II -SS-VOD)	Ultra low carbon and low nitrogen stainless steel: SUS 447 J1, SUS 444, 20%Cr-5%Al steel, etc.

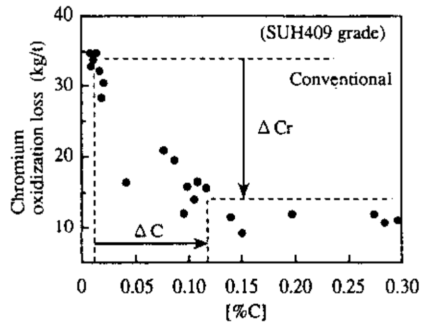

Fig. 3 Effect of tapping carbon content on chromium oxidization loss in K-BOP (SUH 409 grade)

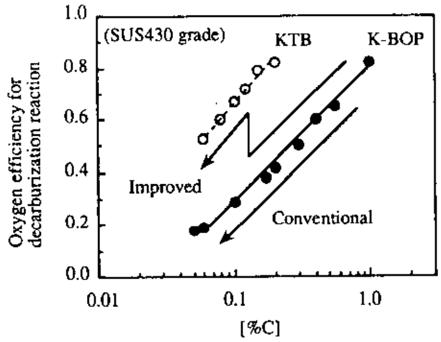

Fig. 5 Relation between carbon content in molten steel and oxygen efficiency for decarburization reaction (SUS 430 grade)

refining equipment with the function of oxygen-blowing vacuum decarburization, but from the viewpoint of maintaining high-efficiency productivity, it was considered desirable to equip the RH degasser with an oxygen-blowing vacuum decarburization function in order to respond to increasing demand and need for high-purity stainless steel while avoiding a negative effect of the RH on productivity.

4 Outline of Stainless Steel Refining Process Using K-BOP-KTB

As described above, the K-BOP-KTB was developed at Chiba Works No. 1 Steelmaking Shop by combining mixed gas bottom-blowing in the decarburizing converter and oxygen-blowing vacuum decarburization by the top-lance oxygen top-blowing method (KTB process) in the RH degasser with the aim of rationalizing the refining process and simultaneously achieving stable, high-efficiency refining of stainless steel.

A schematic diagram and the main specifications of the KTB equipment at No. 1 RH are shown in **Fig. 4**. Because oxygen-blowing decarburization depended entirely on the K-BOP in the conventional process, decarburization oxygen efficiency dropped markedly in the

Oxygen flow rate	5-25 m3-norm. / min
Lance height	2.1 - 3.6 m
Lance	Water cooled
Lance tip profile	Single laval nozzle

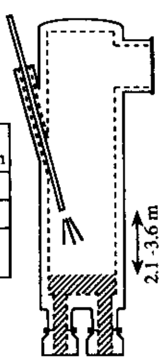

Fig. 4 Schematic illustration of KTB

low carbon region, as shown in **Fig. 5**. However, the development of the K-BOP-KTB process, incorporating oxygen-blowing vacuum decarburization by the KTB in the production route, made it possible to improve total decarburizatrion oxygen efficiency and realize a rational process for decarburizing stainless steel by separating the decarburization refining function.

5 Decarburization Behavior in Oxygen Blowing under Vacuum

5.1 Estimation of Cr Oxidation in Oxygen-Blowing Vacuum Decarburization

In deciding the treatment pattern in oxygen-blowing vacuum decarburization with the KTB, we studied the decarburization reaction under a vacuum and the Cr reduction reaction. The decarburization reaction attributable to [O] in the steel is expressed by Eq. (1), and the Cr oxidation reaction by Eq. (2).[8] From Eqs. (1) and (2), assuming the operating temperature in the RH is 1 620°C (1 893 K), the [Cr] in the steel bath in equilibrium with [C] under given vacuum conditions can be expressed by Eq. (3).

$$\underline{C} + \underline{O} = CO$$
$$\log (P_{CO}/a_C \cdot a_O) = 1\ 160/T + 2.03 \cdots\cdots (1)$$

$$Cr_2O_3 = 2\underline{Cr} + 3\underline{O}$$
$$\log a_{Cr}^2 \cdot a_O^3 = -44\ 040/T + 19.42 \cdots\cdots (2)$$

$$[T = 1\ 893\ \mathrm{K}]$$
$$2 \log a_{Cr} - 3 \log a_C = 3.994 - 3 \log P_{CO} \cdots (3)$$

Figure 6 shows the equilibrium relationship of [C] and [Cr] as calculated from Eq. (3) at in-vessel degrees of vacuum ranging from 10 to 100 Torr (1.33 – 13.33 kPa). The figure also shows simultaneously the predicted behavior when 11% Cr ultra-low carbon steel (SUH 409), SUS 304, and SUS 430 are decarburized by oxygen blowing under a vacuum. It can be estimated that

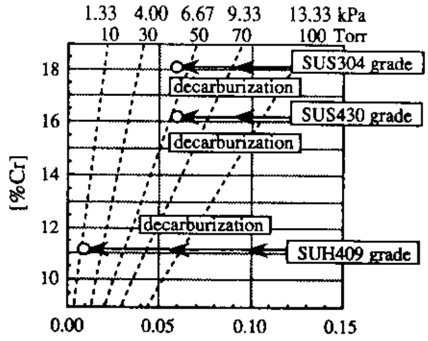

Fig. 6 Relation between [%C] and [%Cr] in equilibrium

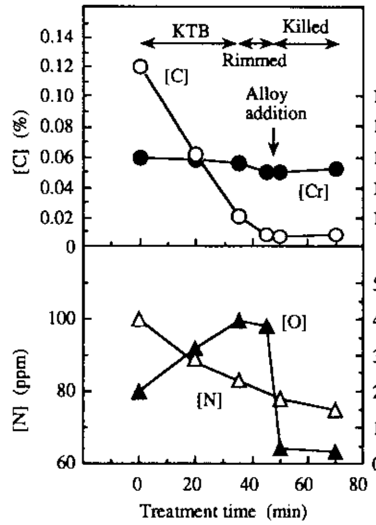

Fig. 7 Change in chemical composition during RH treatment (SUH 409 grade)

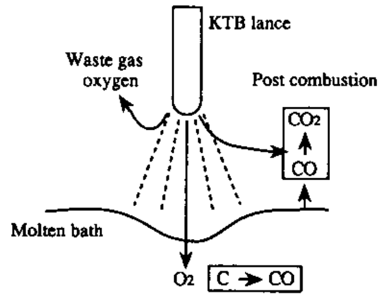

Fig. 8 Schematic illustration of the decarburization mechanism of the KTB method

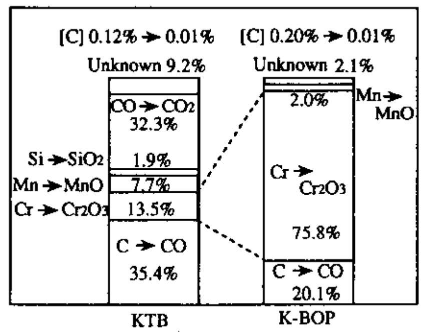

Fig. 9 Comparison of oxygen balance between KTB and K-BOP (SUH 409 grade)

decarburization of SUS 304 and SUS 430 is possible without Cr oxidation if decarburization can be performed at 50 Torr (6.67 kPa) or under, and that SUH 409 can be decarburized to a melt [C] of 0.02% at 30 Torr (4.00 kPa) without Cr oxidation. The oxygen-blowing vacuum decarburization patterns of the respective steel grades were decided from these estimated results.

5.2 Refining of 11% Cr Ultra-low Carbon Steel

The KTB process was used to refine 11% Cr ultra-low carbon steel. The compositional behavior during RH treatment is shown in **Fig. 7**. The oxygen-blowing decarburization treatment was conducted under a vacuum of 30 Torr (4.00 kPa) until [C] = 0.05%, and thereafter, at 10 Torr (1.33 kPa). Oxygen enrichment of the melt increased with oxygen blowing by the KTB, promoting decarburization. On the other hand, the [Cr] content of the melt showed virtually no oxidation at [C] levels down to 0.02%, and only slight oxidation in the vicinity of 0.01%. In the thermodynamic calculations, at a pressure of 10 Torr (1.33 kPa), no chromium oxidation occurs in the range where [C] > 0.01%. In the actual RH, however, the decarburization rate is controlled by the mass transfer of carbon in the low carbon region. Therefore, a part of oxygen gas supplied to the steel may oxidize chromium in the steel. The [O] content of the melt decreases due to vacuum decarburization following the completion of oxygen blowing decarburization and deoxidation treatment with ferroalloys. Nitrogen removal is promoted by CO bubbling during decarburization.

Next, the oxygen balance was studied. **Figure 8** shows a conceptual diagram of KTB oxygen blowing. Because oxygen is blown from a top lance, the total oxygen balance comprises not only the oxygen which actually reaches the bath and is utilized in decarburization, but also oxygen which is consumed in the post combustion of CO evolved from the molten steel, and oxygen which fails to react and is exhausted as-is from the system. **Figure 9** shows a comparison of the oxygen balance with the KTB and the K-BOP at melt [C] contents down to 0.01%. With the KTB process, 35% of the oxy-

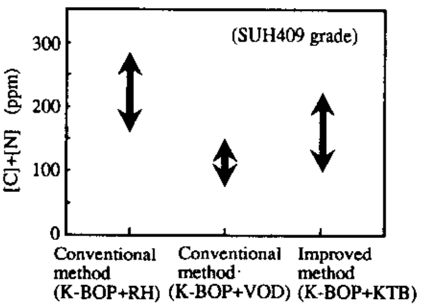

Fig. 10 Comparison of final [C] + [N] level between experimental and conventional method (SUH 409 grade)

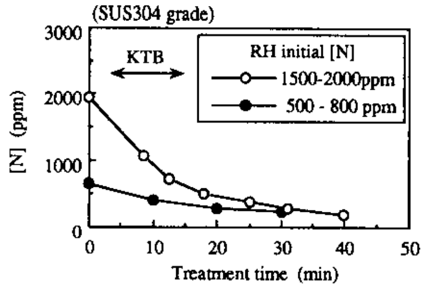

Fig. 11 Change in nitrogen content during RH treatment (SUS 304 grade)

gen is consumed by decarburization. The oxidations of Cr, Mn, and Si use 13.5%, 7.7%, and 1.9% respectively. Thirty-two percent of the supplied oxygen is used in post combustion, and approximately 9.2% does not react. In the K-BOP, on the other hand, 100% of the supplied oxygen reaches the molten steel bath because bottom blowing is employed. However, only about 20% of this amount is used in decarburization, while 76% is consumed by Cr oxidation. Thus, the KTB process causes less Cr oxidation than the K-BOP and offers better decarburization efficiency.

As described above, high-efficiency decarburization is possible with the RH degasser when the KTB process is used to refine ultra-low carbon steels, and the nitrogen removal is promoted by the CO bubbles generated by the decarburization reaction. In this connection , **Fig. 10** shows that the KTB process route is capable of achieving product C + N levels comparable to those possible with the K-BOP-VOD.

5.3 Establishment of Denitrification/ Decarburization Technique

With steel grades such as SUS 304, which have relatively high [N] specification, N_2/O_2 mixed gas decarburization is applied without the use of Ar in the decarburizing converter. The [N] content of the melt at the start of RH treatment reaches 1 500–2 000 ppm with N_2 dilution, in contrast with 500–800 ppm with Ar dilution decarburization. **Figure 11** shows the trend in the [N] content when Ar is used as the dilution gas in the decarburization converter, and when N_2 is used. When the [N] content is high at the start of RH treatment, a rapid denitrification reaction proceeds in tandem with the decarburization reaction which occurs during KTB oxygen-blowing decarburization in the initial period of the RH degassing treatment, and as a result, the phenomenon of steel foaming in the vessel can be observed. When the [N] content is high at the start of treatment, the decarburization oxygen efficiency of the KTB process is approximately 10% higher than when the [N] content is low, as illustrated in **Fig. 12**.

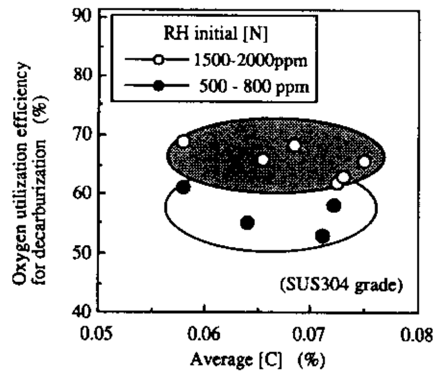

Fig. 12 Comparison of oxygen utilization efficiency for decarburization during RH treatment (SUS 304 grade)

To investigate decarburization behavior under the violent foaming conditions described above, operation was conducted at varying lance heights and oxygen blowing rates. As shown in **Fig. 13**, decarburization oxygen efficiency improves when soft blowing conditions are applied. This improvement in decarburization oxygen efficiency is attributed to the fact that the bulk of the CO generation region in the vessel increases due to the bath foaming which accompanies the decarburization and denitrification reactions in the initial period of treatment, while soft top blowing prevents oxidation of metal components and loss of unreacted oxygen. This phenomenon is shown schematically in **Fig. 14**.

Based on the foregoing, soft-blow oxygen blowing decarburization is practiced with steel grades which are decarburized by N_2/O_2 mixed gas in the decarburization converter, by lowering the oxygen injection velocity and/or raising the height of the lance in the range of operating conditions where the rate of decarburization will not be decreased. As a result, it has been possible to raise the tap [C] of SUS 304, as shown in **Fig. 15**, and

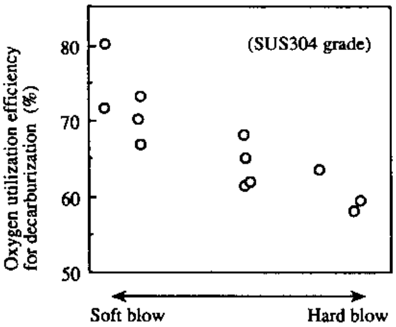

Fig. 13 Effect of blowing condition on oxygen utilization efficiency for decarburization (SUS 304 grade)

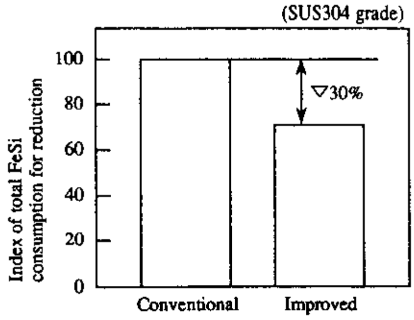

Fig. 16 Comparison of total FeSi consumption for reduction between conventional and improved process (SUS 304 grade)

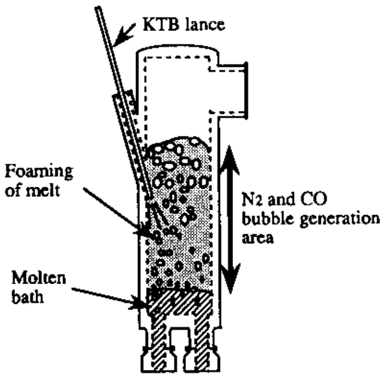

Fig. 14 Schematic illustration of decarburization mechanism when molten metal is foamed by N_2 and CO bubble generation

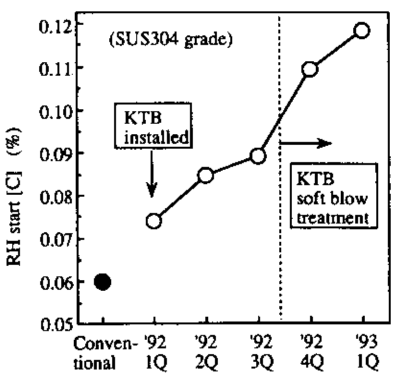

Fig. 15 Trend of [C] content at the start of RH treatment (SUS 304 grade)

to decrease the consumption of the FeSi ferroalloy used for reduction in the K-BOP by approximately 30% from the levels of the past, as shown in **Fig. 16**.

6 Deskulling in the Vacuum Vessel Using KTB

In conventional RH degassers, skull frequently adheres to the interior of the vacuum vessel as a result of splashing metal. heating with an electrode has conventionally been used for deskulling, but this practice results in various problems such as compositional nonconformities due to skull falling into the melt and electrodes breaking. In more serious cases, the vacuum vessel may become clogged due to accumulated skull.

With the introduction of the KTB process, skull in the vessel has been sharply reduced due to the post combustion which occurs when top oxygen blowing decarburization begins. Moreover, when it is necessary to reduce the amount of skull adhering to the interior of the vessel, oxygen is blown at the lance holding position after the completion of oxygen blowing decarburization during vacuum treatment, melting the skull near the lance hole. This deskulling operation for the upper part of the vessel has been adopted as a standard procedure during RH treatment, using a special purpose jig. The interior of the RH vessel is now kept substantially free of skull, the practice of heating with electrodes has been completely abandoned, and operational problems attributable to skull are virtually nonexistent.

7 Improved Quality in SUS 304

With the establishment of the K-BOP-KTB process, oxygen reaction efficiency during the decarburization of stainless steel has been improved and the oxidation of metal has been suppressed. Moreover, the deskulling operation has brought about a broad reduction in oxide-type skull in the RH vessel. Following these improvements, heats with exceptionally high total oxygen (T.O.) levels have been virtually eliminated and deviations have been reduced. The average value of T.O. has improved from 49.5 ppm in the past to 42.8 ppm. The result has been a dramatic improvement in quality, as can be seen in **Fig. 17**, which shows that the scab defect detection ratio of SUS 304 has been reduced to approximately

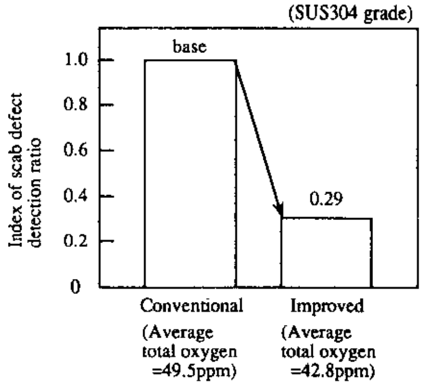

Fig. 17 Comparison of the scab defect detection ratio of coil between conventional and improved process (SUS 304 grade)

30% of the past level.

8 Conclusions

With the aim of rationalizing the decarburization of stainless steel, the K-BOP-KTB process was established by combining decarburization by mixed gas bottom blowing in the decarburization converter and a top lance oxygen top-blowing process (KTB process) introduced at the RH degasser. The results obtained with this process are described below.

(1) In contrast to the conventional K-BOP-RH route, the decarburization refining function is separated in the K-BOP and KTB in the K-BOP-KTB process.

(2) In refining ultra-low carbon steels, product C + N values comparable to those with the K-BOP-VOD can be achieved with the K-BOP-KTB.

(3) SUS 304 and other steel grades with relatively high ranges of refining target [N] are processed by N_2 dilution in the decarburizing converter to the point where [N] in the melt at the start of RH treatment is near the saturation concentration under $P_{N_2} =$ 1 atm. Foaming of the molten steel bath in the vacuum steel vessel can be observed due to the rapid denitrification reaction which accompanies decarburization at the start of RH treatment.

(4) Under these conditions, soft-blow KTB oxygen blowing improves decarburization oxygen efficiency.

(5) Following the introduction of the KTB process, problems related to skull adhering to the interior of the vacuum vessel have been eliminated by standardizing deskulling practices using the KTB lance.

(6) The optimization of KTB operating conditions and standardization of deskulling practices has reduced the total oxygen content of the molten steel, resulting in a dramatic improvement in product quality.

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