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Kawasaki Steel has developed a hydrogen gas injection method at the RH degasser for promoting the decarburization reaction of the ultra-low carbon steel in the range of a carbon content of less than 20 ppm. Hydrogen gas is blown into the molten steel in the snorkel of 260-t RH at Chiba Works in the later period of decarburization treatment at a flow rate of up to 4 m³-norm/min. Part of the hydrogen gas is dissolved in the molten steel to raise the hydrogen concentration of the molten steel up to about 3 ppm, which promotes the evolution of gas bubbles in the molten steel in the vacuum vessel and increases the interfacial area between the gas and metal. The apparent rate constant of decarburization in the range of carbon content from 20 ppm to 10 ppm is increased from 0.05 min⁻¹ to 0.1 min⁻¹ by this method. The carbon content can be decreased to 7 ppm in average in 25 min of decarburization treatment. Ultra-low carbon steel of [C] ≤ 10 ppm can be obtained with certainty in 25 min of decarburization treatment.

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Development of Hydrogen Gas Injection Method for Promoting Decarburization of Ultra-low Carbon Steel in RH Degasser*



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Kawasaki Steel has developed a hydrogen gas injection method at the RH degasser for promoting the decarburization reaction of the ultra-low carbon steel in the range of a carbon content of less than 20 ppm. Hydrogen gas is blown into the molten steel in the snorkel of 260-t RH at Chiba Works in the later period of decarburization treatment at a flow rate of up to 4 m³-norm/min. Part of the hydrogen gas is dissolved in the molten steel to raise the hydrogen concentration of the molten steel up to about 3 ppm, which promotes the evolution of gas bubbles in the molten steel in the vacuum vessel and increases the interfacial area between the gas and metal. The apparent rate constant of decarburization in the range of carbon content from 20 ppm to 10 ppm is increased from 0.05 min⁻¹ to 0.1 min⁻¹ by this method. The carbon content can be decreased to 7 ppm in average in 25 min of decarburization treatment. Ultra-low carbon steel of [C] ≤ 10 ppm can be obtained with certainty in 25 min of decarburization treatment.

1 Introduction

Recent years have seen increasing demand for cold-rolled steel sheets with broadly improved elongation, deep drawability, and other workability characteristics in response to the trend toward integrated one-piece stamping of automotive outer panels and greater complexity in the configuration of parts. To manufacture this type of cold-rolled sheet with extra-deep drawability at a relatively low price, it is desirable in the steelmaking process to realize further reductions in the carbon content of ultra-low carbon steel from the [C] = 20 ppm level.¹⁾

Ultra-low carbon steel is generally produced from molten steel decarburized to approximately 200–500 ppm [C] in the converter, which is then refined to [C] < 30 ppm by vacuum decarburization using the RH degasser. It is well known that the decarburization reaction rate in the RH decreases sharply at [C] < 20 ppm, and the standardized mass production of ultra-low carbon steel with [C] ≤ 10 ppm has therefore been difficult.²⁾ For this reason, it is desirable to increase the rate of decarburization in the ultra-low carbon region of [C] < 20 ppm.

In the RH, the rate of decarburization is extremely high in the initial stage of decarburization because vigorous CO boiling spontaneously occurs under reduced pressure. However, CO boiling decreases sharply in the ultra-low carbon region of [C] < 20 ppm, and the decarburization rate drops.³⁾ Accordingly, dissolving a gaseous component other than CO in the melt in order to promote bubbling from the molten steel and thereby increase the gas-metal interfacial area is considered an effective method of increasing the rate of decarburization in the ultra-low carbon region.

An experiment was conducted at No. 3 RH in Chiba Works in order to study methods of dissolving hydrogen in the steel melt and utilizing boiling of such hydrogen gas in the vacuum chamber, and technology for consistently producing ultra-low carbon steel with [C] ≤ 10 ppm was developed.

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2 Study of Decarburization Behavior of Ultra-low Carbon Steel in RH and Techniques for Promoting Decarburization

The decarburization reaction ($C + O = CO$) in the ultra-low carbon region in the RH is considered to be mainly controlled by the mass transfer of carbon in the molten steel, and can therefore be appropriately described using a first-order equation for the reaction rate of carbon, as shown in Eq. (1).

$$\frac{d[C]}{dt} = -K_C[C] \dots \dots \dots (1)$$

where $[C]$ in equilibrium with the partial pressure of CO, P_{CO} , is disregarded as insignificant. The apparent reaction rate constant, K_C , can be expressed by Eq. (2) based on the analysis by Sumida *et al.*⁴⁾

$$K_C = \frac{ak \cdot Q}{V(Q + ak)} \dots \dots \dots (2)$$

- a : interfacial reaction area (m^2)
- k : mass transfer coefficient of carbon in metal phase (m/s)
- V : volume of molten steel (m^3)
- Q : circulation rate of molten steel (m^3/s)

On the basis of Eqs. (1) and (2), value of the volumetric coefficient of mass transfer, ak , which is the product of mass transfer coefficient, k , and the interfacial reaction area, a , were calculated from the decarburization data obtained at the 260-t RH at No. 3 Steelmaking Shop in Chiba Works. Figure 1 shows the relationship between $[C]$ and values obtained by dividing ak by the surface area in the vacuum degassing vessel, S (m^2); the figure also compares the results with an RH and a small-scale induction melting furnace of 20-kg melt.⁵⁾

In the decarburization experiment with the small-scale induction furnace, when the pressure of the atmosphere in the furnace was reduced, ak increased in the relatively high $[C]$ region of more than 20 ppm due to the CO gas boiling.⁵⁾ When gas boiling stopped at $[C] \leq 10$ ppm, the decarburization rate slowed to approximately the same level as in decarburization at normal atmospheric pressure, where the CO gas boiling was not observed.⁵⁾ The gas-metal interfacial area in the RH is much larger than that in the small-scale induction furnace because large amount of Ar gas is injected as circulation gas and therefore splashing in the degassing tank occurs in the RH. As a result, ak/S in the RH is approximately 10 times as large as that in the small-scale induction furnace, even in the vicinity of $[C] = 10$ ppm, where the effect of CO boiling is considered to be slight. In the relatively high $[C]$ region, the difference between ak/S in the RH and that in the small scale induction furnace becomes more significant, that is, the dependency of ak/S on $[C]$ in the RH is much larger than that in the small scale induction furnace. In the $[C]$

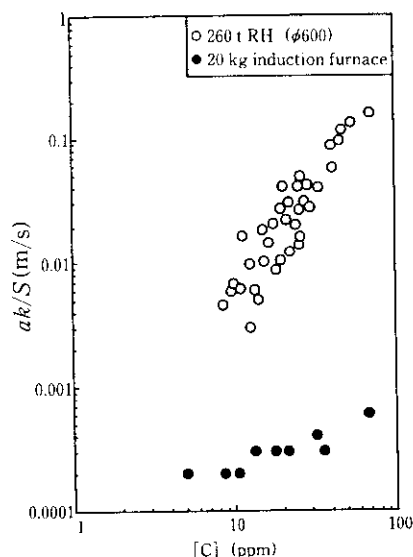


Fig. 1 Relation between apparent mass transfer coefficient, ak/S , and $[C]$

region of 20–30 ppm, therefore, there remains a large difference between ak/S in the RH and that in the furnace. These facts mean that the effect of CO boiling on the values of ak/S is much larger in the RH than that in the small scale induction furnace. This effect is valid even in the low $[C]$ region of 20–30 ppm.

In the region of $[C] = 20\text{--}30$ ppm, the rate of CO gas generation is 1–3 Nm^3/min , and the rate of Ar gas blowing for circulation is on the same order. In the low $[C]$ region of less than 10 ppm, the decarburization rate becomes quite small, as mentioned above, even though the same flow rate of Ar gas is injected through circulation pipes. This fact may suggest that the gas evolution from the molten steel is more effective than the inert gas injection in increasing the gas-metal interfacial area. If the soluble gas evolves from the molten steel in the degassing, we can expect a marked increase in the gas-metal interfacial area. Especially, in the carbon range of less than 10 ppm, where the decarburization rate decreases, it is expected that the use of soluble gas other than CO enhances the decarburization rate.

Considering CO, H_2 , and N_2 as gaseous components, Eq. (3) expresses the conditions for growth of bubbles due to gas dissolved in the molten steel.

$$P_t = P_{CO} + P_{H_2} + P_{N_2} > P_v + \rho gh + \frac{2\sigma}{r} \dots \dots (3)$$

- P_t : total pressure of gas in equilibrium with molten steel (Pa)
- P_{CO} : partial pressure of CO gas in equilibrium with molten steel (Pa)
- P_{H_2} : partial pressure of H_2 gas in equilibrium with molten steel (Pa)
- P_{N_2} : partial pressure of N_2 gas in equilibrium with molten steel (Pa)

P_V : pressure of vessel atmosphere
 ρ : density of molten steel (kg/m^3)
 g : acceleration of gravity (m/s^2)
 h : depth from liquid surface to bubbles (m)
 σ : surface tension (N/m)
 r : radius of bubbles (m)

From Eq. (3), we can see that the increase in the value of P_t enables bubbles to be evolved at a position deeper in the bath. In addition to the effect, the increase in the value of P_t allows smaller bubbles to be evolved at positions. These two effects increase the gas-metal interfacial area. Therefore, if, in the carbon range of less than 20 ppm, P_t can be kept at the same level as that at higher carbon range by increasing the partial pressure of nitrogen or hydrogen, we can expect that the decarburization rate can be kept at the same level as that at higher carbon content. Because the customer requirements for nitrogen content for ultra-low carbon steel is quite low, we can not increase the partial pressure of nitrogen. Hence, we decided to use hydrogen gas for enhancing the decarburization rate. As the partial pressure of nitrogen, P_{N_2} , is quite low, from now on we disregard P_{N_2} . Figure 2 shows the relation of [C] and the hydrogen content, [H], with P_{CO} , P_{H_2} and P_t . In these calculations, we assume [O] = 350 ppm and a molten temperature of 1 873 K, and the equilibrium values recommended by the Japan Society for the Promotion of Science (JSPS)⁶⁾ were used.

In the RH, the decarburization rate decreases rapidly in the [C] range of less than 20 ppm. This means that the effect of CO boiling deteriorates in the [C] range of less than 20 ppm. This fact may also suggest that in order to improve the decarburization rate in the [C] range of less than 20 ppm, P_t should be kept at a level of $P_t = 3 \times 10^3$ Pa or over, which corresponds the value of P_t at [C] = 20 ppm. To realize this condition even in the carbon range of less than 10 ppm, we need to keep the [H] content 4 ppm over as shown in Fig. 2. But, the [H] content of 3 ppm over may be enough to keep $P_t = 3 \times 10^3$ Pa or over in the [C] range of more than 10 ppm. That is, if the target is to decarburize only down to [C] = 10 ppm, we need to keep [H] content of more than 3 ppm.

Assuming the rate constant of hydrogen removal of approximately 0.1 min^{-1} , the rate of hydrogen dissolution required in a 260-t RH should be on the order of $1.2 \text{ m}^3\text{-norm/min}$ or higher to maintain the hydrogen content of more than 4 ppm. This resolution rate should be $0.9 \text{ m}^3\text{-norm/min}$ or above to keep [H] of more than 3 ppm, considering the balance with the rate of dehydrogenation. Therefore, for effectively promoting decarburization in the ultra-low carbon region, we need to increase the rate of hydrogen dissolution and thus maintain a high [H] in the melt. This will be discussed in the following chapter.

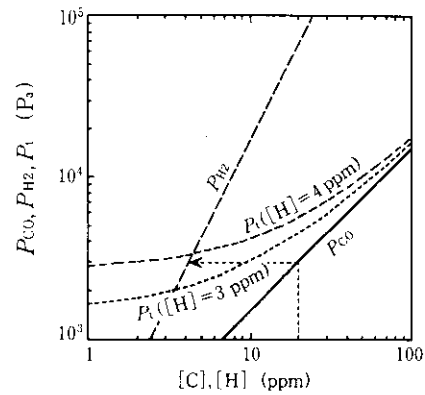


Fig. 2 Relation between concentrations of gas species in molten steel and partial pressures in equilibrium

3 Promoting Decarburization by Hydrogen Injection Method in RH

3.1 Experimental Method

Experiments were conducted using No. 3 RH degasser (capacity, 260 t; inner diameter of snorkel, 0.6 m) at Chiba Works. A schematic diagram of the equipment is shown in Fig. 3. Hydrogen mixed with Ar was injected through the circulation tuyere at the side of the RH snorkel. This method was adapted because a high volume of hydrogen, which is over $4 \text{ m}^3\text{-norm/min}$, can be injected without any trouble, while injection of more than $1 \text{ m}^3\text{-norm/min}$ into the ladle makes troubles in the operation. However, the injection method through the circulation tuyere has a disadvantage: the rate of hydrogen dissolution may be lower than that in the injection method into the ladle due to the short distance for flotation.

Because the rate of hydrogen removal is high in the

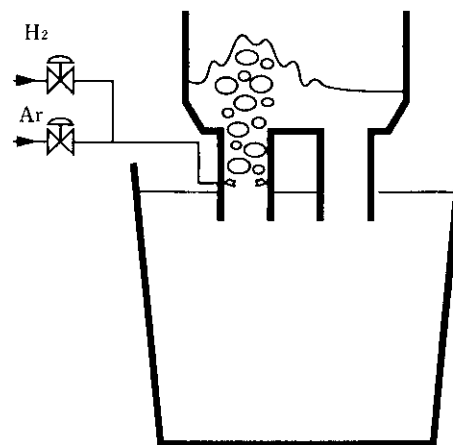


Fig. 3 Schematic diagram of experimental apparatus

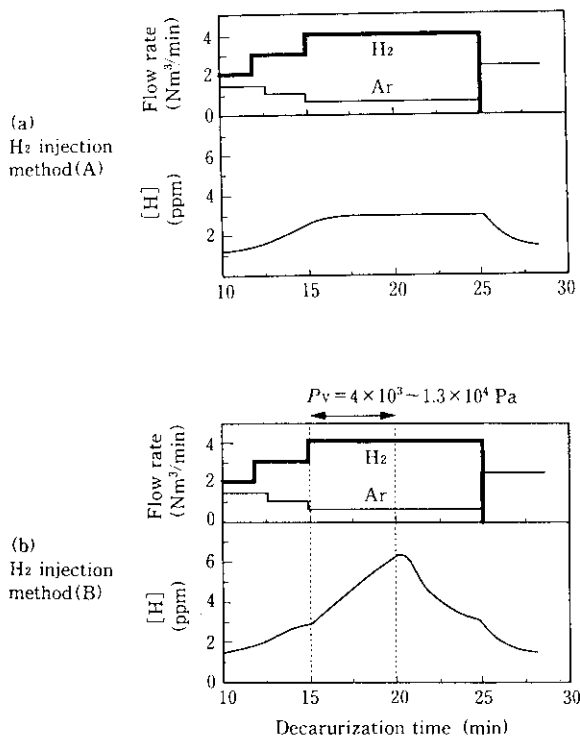


Fig. 4 Typical pattern of gas flow rates and typical change in hydrogen content of molten steel

initial stage of decarburization treatment, and consequently [H] does not increase, hydrogen injection was begun about 10 min after the start of decarburization. The hydrogen was injected for 10–20 min in the experiment. After hydrogen injection began, [H] increased to about 3 ppm after approximately 6 min and then remained constant. After the completion of decarburization, aluminum was added and the deoxidation treatment was conducted by circulating using Ar gas. During the deoxidation operation, [H] decreased to under 2 ppm. A typical gas injection pattern and changes in [H] are shown in Fig. 4 (a).

Treatment under low vacuum conditions was attempted with the aim of achieving a further increase in [H]. In this experiment, the pressure in the degassing chamber was increased to $4 \times 10^3 - 1.3 \times 10^4$ Pa to suppress hydrogen removal during the hydrogen injection. It was possible to raise [H] to over 5 ppm after about 5 min of treatment under low vacuum, but during this period, the decarburization rate was quite low. When the pressure in the chamber is then reduced to approximately 2×10^2 Pa by reactivating the booster, dehydrogenation will progress in tandem with decarburization, and [H] will reach a constant value of about 3 ppm in approximately 5 min. With this method, only an extremely limited period of time is available for obtaining significantly improved decarburization at $[H] > 3$ ppm, and it is therefore necessary to increase [C] concentration in order to obtain an ultra-low

carbon content of $[C] \leq 10$ ppm. For this reason, a pattern was adopted in which low-vacuum treatment was started at the point when [C] had been reduced to under 20 ppm, about 15 min into the decarburization period, and after adding hydrogen during low-vacuum treatment for about 5 min, decarburization was carried out for approximately 5 min under high vacuum. To distinguish this method from the method of injecting hydrogen during decarburization under high vacuum, discussed previously, the high-vacuum H₂ injection method is termed method A, and the low-vacuum method, method B. Fig. 4 (b) shows a typical gas injection pattern and changes in [H] in Method B. In the conventional method, with which the above methods were compared, the circulation gas is Ar, which is supplied at a uniform rate of 2.5 m³-norm/min.

3.2 Experimental Results

Figures 5 and 6 show the relationship between decarburization treatment time and final [C] with hydrogen injection methods A and B, respectively, in comparison with the conventional method.

Variations were great with the conventional method, but from Fig. 5 we can see that the decarburization reaction can be expressed by a first-order reaction and the rate constant in the conventional method is about 0.05 min^{-1} .

In contrast, with method A, decarburization proceeded rapidly even at $[C] < 20$ ppm, and it was possible to decarburize to the level of $[C] = 10$ ppm in 20 min of decarburization treatment time. The decarburization rate constant during this period was approximately 0.1 min^{-1} , which represents an increase of about two times over that of the conventional method.

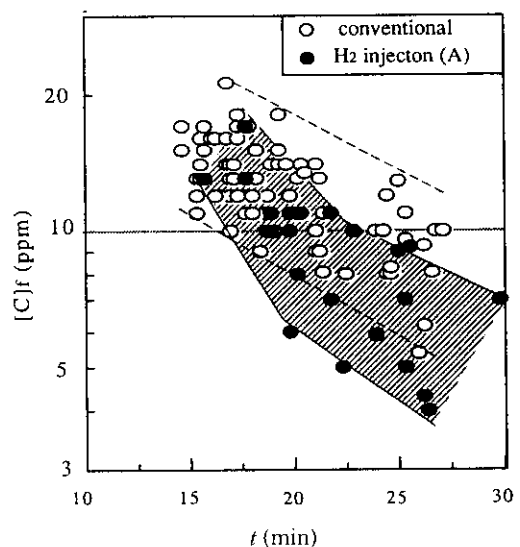


Fig. 5 Relation between final [C] and decarburization treatment time in H₂ injection method A and conventional method

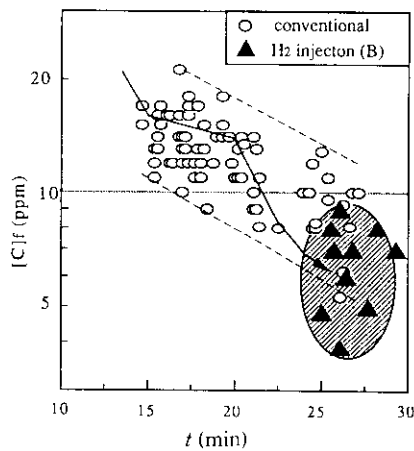


Fig. 6 Relation between final [C] and decarburization treatment time in H₂ injection method B and conventional method

With method B, in spite of the large decrease in the decarburization rate during low-vacuum treatment, which was performed about 15–20 min after the start of decarburization treatment, decarburization proceeded to [C] < 10 ppm in about 25 min of decarburization treatment time, and the same level of decarburization as in method A was ultimately obtained. It may be inferred from this result that the decarburization rate under the high [H] condition after low-vacuum treatment is extremely high.

Figure 7 shows the average values and standard deviation of final [C] values obtained with each of the methods after decarburization treatment times of 20 and 25 min. Figure 8 summarizes the success ratio for [C] ≤ 10 ppm.

With the hydrogen injection method, it was possible to decarburize to an average of approximately 10 ppm in 20 min of decarburization treatment time, and to about 7 ppm in 25 min. The success ratios for [C] ≤ 10 ppm were 100% with both method A and method B in 25 min of decarburization treatment time.

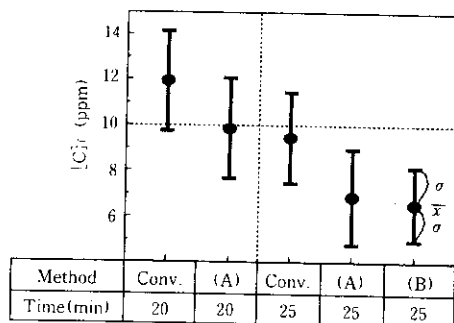


Fig. 7 Comparison of final [C] obtained by H₂ injection methods A and B with those by conventional method

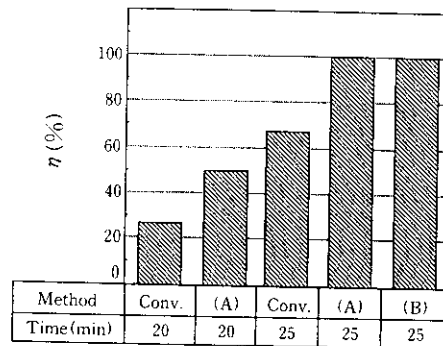


Fig. 8 Effect of H₂ injection method on decarburization of ultra-low carbon steel with carbon content of less than 10 ppm

4 Conclusions

- (1) Stable, high-speed dissolution of hydrogen was achieved by injecting hydrogen gas through the snorkel tuyere, making it possible to raise [H] during the decarburization to approximately 3 ppm.
- (2) It was possible to increase [H] to 5 ppm during a 5 min hydrogen injection period by raising the pressure in the degassing chamber to $4 \times 10^3 - 1.3 \times 10^4$ Pa while continuing hydrogen injection.
- (3) The decarburization rate constant during the 15–20 min decarburization period increased from 0.05 min^{-1} in the conventional method to 0.1 min^{-1} by hydrogen injection.
- (4) With the hydrogen injection method, it was possible to obtain an average final [C] value of 10 ppm in 20 min of decarburization treatment time, and 7 ppm in 25 min.
- (5) It was possible to consistently produce ultra-low carbon steel with [C] ≤ 10 ppm in 25 min of decarburization treatment time using either of the newly developed methods.

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