Decarburization Reaction of Molten Iron of Low Carbon Concentration with Vacuum Suction Degassing Method

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A kinetic study has been made on decarburization reaction of molten iron of low carbon and oxygen concentrations with solid oxides. A new degassing method, namely Vacuum Suction Degassing (VSD) method, was applied to decarburize molten iron to an ultra-low carbon concentration. A porous oxide tube, the inside of which was evacuated, was immersed into molten iron. The initial carbon concentration was varied between 30 and 110 ppm. The initial oxygen concentration was below 50 ppm. The experiments were performed under Ar atmosphere (1.01×10^5 Pa). The experimental temperature was 1853 K.

The VSD method can greatly increase the rate of decarburization of molten iron and the carbon concentration decreases to a very low value of a few ppm. The rate of decarburization with an Al_2O_3 - SiO_2 tube is higher than that with an Al_2O_3 tube. Increase in gas permeability of a porous tube enhances the decarburization reaction. The apparent rate constant of decarburization at the porous tube–molten iron interface with evacuation in the porous tube is about 10 times larger than that without evacuation.

KEY WORDS: vacuum degassing; porous tube; gas permeability; solid oxide; decarburization; molten iron; ultra low carbon steel.

1. Introduction

Conventionally, production of ultra-low carbon steel is made by the reaction between carbon and oxygen in molten iron under reduced pressures, such as in the RH vacuum degassing method. Shinme and Matsuo¹⁾ have shown that the carbon concentration of molten iron can be decreased to a very low value by injecting iron oxide powder under a reduced pressure. In these processes, the decarburization of molten iron proceeds at a considerably high oxygen concentration of several hundreds ppm.

In a previous paper,²⁾ the present authors made a kinetic study on the decarburization of molten iron by the reaction between carbon in molten iron and solid oxide (MgO , Al_2O_3 and CaO). The experiment was made at an oxygen concentration lower than 50 ppm. It was shown that even at such a low oxygen concentration, the carbon concentration decreases lower than 10 ppm. However, the decarburization rate was quite low, as compared with those for the RH degassing method and injection of iron oxide powder.

The present study proposes a new method of decarburization by solid oxide (vacuum suction degassing method), by which the decarburization rate is greatly enhanced. This method is applied to the decarburization of molten iron in the ranges of low carbon and oxygen

concentrations. In the experiment, a porous oxide tube, the inside of which is evacuated, is immersed into molten iron. The decarburization proceeds by the reaction between carbon in molten iron and oxide at the molten iron–oxide interface, and the gaseous reaction product (CO) is sucked into the pore of the porous oxide at a reduced pressure and easily removed from the interface. By applying this method, the molten iron can be decarburized to a very low carbon concentration of a few ppm. Effects of oxide composition and porosity (gas permeability) of the porous material and the initial carbon concentration on the decarburization rate are examined.

2. Principle and Characteristics of Vacuum Suction Degassing Method

Figure 1 is a schematic view showing a principle of the present method. Molten iron to be decarburized is separated from the outer space by porous oxide material, which is permeable to gas, but impermeable to molten iron. The outer space is made vacuous. In this case, at the metal–porous material interface the pressure changes abruptly from static pressure of the melt to very low pressure in the porous material. Then, CO gas will nucleate easily at the interface and be removed through

Fig. 1. Illustration of principle of vacuum suction degassing method.

the porous material.

The general equation of decarburization is given by Eq. (1).

Various oxides can be used for the porous material, such as Al_2O_3 , MgO , CaO , SiO_2 , MnO , TiO_2 , Fe_2O_3 , Cr_2O_3 , etc.

As shown in the previous paper, stable refractory oxides (MgO , Al_2O_3 , CaO , etc.) can be used as components of the porous material. However, in order to increase the decarburization rate, such a material as Fe_2O_3 , MnO , SiO_2 , etc., which can dissociate more easily, should be mixed as an agent for oxidizing carbon in molten iron.

The resistance to mass transfer of CO through the pore of the porous material is required to be small. Therefore, it is preferable that its porosity is as large as possible, provided that molten iron does not penetrate into the pore. This necessary condition can be satisfied only by using a material which does not get wet with molten iron.

The characteristics of the vacuum suction degassing method are as follows:

- (1) A space under a reduced pressure can be locally created in molten iron, and gas forming impurities is removed into the space through a porous material.
- (2) The porous material–molten iron interfacial area and the decarburization rate can be arbitrarily made large.
- (3) Since only gaseous reaction products are sucked and removed, the load on the vacuum pump for exhausting the products is very small.
- (4) Argon injection into the melt in large quantity is unnecessary, splash of molten iron is not formed, lowering of the melt temperature is small, and hence a large vacuum chamber is not needed.
- (5) Continuous operation of the decarburization is possible.
- (6) The present method is very simple, and can be applied to decarburize molten iron held in a ladle.

3. Experimental

Figure 2 is a schematic diagram of the experimental apparatus. A high frequency induction furnace (15 kW, 100 kHz) was used to melt electrolytic iron in a magnesia crucible of 38 mm in I.D., 100 mm in height, and 20 %

Fig. 2. Experimental apparatus.

Table 1. Composition of porous immersion tube and minimum pressures in tube.

	$P_{\min}$ in air (Pa)	$P_{\min}$ in melt (Pa)	Al_2O_3 (%)	SiO_2 (%)
VSD-(A)	$(6.3-7.5) \times 10^2$	$(0.8-1.1) \times 10^2$	~70	~30
VSD-(B)	$(1.3-2.0) \times 10^4$	$(2.7-4.0) \times 10^2$	~84	~16
VSD-(C)	$(0.9-1.3) \times 10^4$	$(1.6-2.0) \times 10^2$	>98.5	0.4-0.8
VSD-(D)	6.0×10^3	$(1.2-2.0) \times 10^2$	>98.5	0.4-0.8
VSD-(E)	7.5×10^2	1.1×10^2	0.15	99.72

in porosity. Argon was blown onto the melt surface through an alumina lance of 4.2 mm in I.D. and 6.2 mm in O.D. The distance between the lance tip and the melt surface was 10 mm. The argon gas was deoxidized and its oxygen partial pressure, which was measured continuously with an oxygen sensor in the gas supply train, was lower than 1.01×10^{-8} Pa. The pressure of atmosphere in the furnace was 1.01×10^5 Pa.

Various devices can be adopted for sucking gaseous reaction products through a porous material. In the present experiment, a refractory oxide tube, which was connected with a vacuum pump, was immersed into the melt and its inside was evacuated. The tube was porous and 6 mm in I.D., 14 mm in O.D. and 60 mm in length. The tube was composed of Al_2O_3 and SiO_2 . The composition of the tube is summarized in Table 1. $P_{\min}$ in air and $P_{\min}$ in melt were the minimum pressures in the tube when it was evacuated in the air and in the melt, respectively. A rotary vacuum pump was used. Its exhaust rate was 60 l/min and the minimum pressure was 6.7×10^{-2} Pa.

After melting the iron, a mixture of Ar and H_2 was blown onto the surface to deoxidize the melt. Then, a porous tube was immersed into the melt, and the gas mixture was further blown onto the surface. After deoxidizing the melt, the blowing gas was changed to argon (gas-flow rate = 1 000 Ncm^3/min), and the melt temperature was maintained at 1 853 K. Then, the inside of the tube was evacuated. When the inside pressure reached a steady state, an appropriate amount of carbon was added to control the initial carbon content of the melt and to initiate the kinetic experiment. In some experiments, the inside of the tube was not evacuated and

argon was blown into the tube. Sampling of the metal was made by using a silica tube of 2 mm in I.D. Carbon and oxygen concentrations of the sample were measured by using automatic coulometric titration methods.

The mass of the melt was 400 g. The initial carbon concentration was varied below about 100 ppm. The initial oxygen concentration was lower than 50 ppm. The immersion depth of the tube was 45 mm. The minimum pressures in the tube are listed in Table 1. The experimental temperature was 1853 K.

4. Experimental Results and Discussion

4.1. Decarburization Rate without Evacuating the Inside of the Porous Tube

The experimental result of decarburization with immersing a porous Al_2O_3 tube and replacing the inside gas by argon is shown in Fig. 3 and compared with that obtained without immersing a porous tube in the previous paper.²⁾ It is seen that the decarburization rate with immersing the tube is a little larger than that without immersing it. This is because the oxide-molten iron interfacial area was increased by immersing the porous tube. In both experiments, the oxygen concentration was kept constant.

Figure 4 shows experimental results with changing the composition of the porous tube. The decarburization rate increases in the order of $\text{Al}_2\text{O}_3\sim 16\%\text{SiO}_2$,

Fig. 3. Changes in carbon and oxygen concentrations with time.
(Immersion tube: Al_2O_3)

Fig. 4. Changes in carbon and oxygen concentrations with time.
(Immersion tube: $\text{Al}_2\text{O}_3\text{-SiO}_2$, SiO_2)

$\text{Al}_2\text{O}_3\sim 30\%\text{SiO}_2$ and SiO_2 . While the oxygen concentration was almost constant in the experiments with using $\text{Al}_2\text{O}_3\sim 16\%\text{SiO}_2$, $\text{Al}_2\text{O}_3\sim 30\%\text{SiO}_2$ tubes, it increased considerably in the experiment with using a SiO_2 tube. From this it follows that SiO_2 dissociates rapidly, and supplies oxygen for the decarburization of molten iron. In the case of the SiO_2 tube, it was observed that after the experiment its surface became glassy.

4.2. Decarburization Rate with Evacuating the Inside of the Porous Tube

4.2.1. Behavior of Gas Permeation through the Pore of the Porous Tube

Figure 5 shows the change in the pressure in the tube immersed into the melt with time. An increase in the pressure inside the tube before the experiment is observed in the figure. This increase is caused by the addition of carbon to the melt, namely by sucking CO gas formed by the reaction between C and O at the porous tube-molten iron interface. The increase in the pressure inside the tube for the experiment ② is larger, since the melt was not deoxidized and the oxygen concentration was higher ($[\text{ppm O}] \approx 300$). In the other experiments with deoxidizing the melt before the carbon addition ($[\text{ppm C}] < 100$), the pressure increase due to the carbon addition is small. Sampling was made at the time indi-

Fig. 5. Changes in pressure in immersion tube with time.

Fig. 6. Illustration of inner surface of immersion tube after experiment.

cated by the arrow. The level of the melt surface was lowered by the sampling, and the surface area of the porous tube exposed to the atmosphere was increased. As the result, the pressure in the tube increased discontinuously. The lower $P_{\min}$ in air and hence the worse the gas permeability is, the smaller is the increase in the pressure in the tube due to the sampling.

Figure 6 shows the appearance of the inner surface of the immersed tube after the decarburization experiment. When the tube inside was evacuated, the inner surface of the tube above the level of the melt surface became black. The reason is that the CO gas sucked into the tube decomposed into C and CO_2 by the lowering of the gas temperature. On the other hand, in the experiment without evacuation, the inner surface of the tube remained white. From Fig. 6 it is clear that the evacuation of the tube inside is quite effective in enhancing the decarburization of molten iron.

4.2.2. Effect of Evacuation of the Tube Inside on Decarburization of Molten Iron

In Fig. 7, comparison is made between the experimental results obtained with and without evacuation of the inside of the porous Al_2O_3 tube (VSD-(C)). It is seen that the evacuation of the tube inside slightly increased the decarburization rate. The oxygen concentration remained constant during the experiment.

The experimental result obtained with immersing the $\text{Al}_2\text{O}_3\sim 16\%\text{SiO}_2$ tube (VSD-(B)) is plotted in Fig. 8.

Fig. 7. Effect of pressure in immersion tube on decarburization rate.
(Immersion tube: Al_2O_3)

Fig. 8. Effect of pressure in immersion tube on decarburization rate.
(Immersion tube: $\text{Al}_2\text{O}_3\sim\text{SiO}_2$)

While in the evacuated case, the carbon decreased from 97 to 8 ppm in 30 min, in the non-evacuated case it merely decreased from 126 to 32 ppm in 60 min. It is shown that the decarburization rate greatly increased by the evacuation of the inside of the $\text{Al}_2\text{O}_3\sim 16\%\text{SiO}_2$ tube. The experimental result for the initial carbon concentration of 32 ppm is also plotted in Fig. 8. The carbon concentration decreased from 32 to 3 ppm in 45 min. It is to be noted that the decarburization of molten iron proceeds to a very low carbon concentration.

4.2.3. Effect of the Composition of Porous Immersion Tube

Figure 9 shows comparison between decarburization rates for Al_2O_3 and $\text{Al}_2\text{O}_3\sim 16\%\text{SiO}_2$ tubes. The rate for the latter tube is much larger than that for the former tube. It is considered that when the immersion tube contains an oxide, which easily is dissociated, its dissociation rate and hence the decarburization rate is accelerated by the removal of CO into the evacuated porous tube.

4.2.4. Effect of Gas Permeability of Porous Immersion Tube

Figure 10 shows the experimental results obtained by using the VSD-(A) tube ($\text{Al}_2\text{O}_3\sim 30\%\text{SiO}_2$) and the VSD-(B) tube ($\text{Al}_2\text{O}_3\sim 16\%\text{SiO}_2$). Although the SiO_2 content of the former tube is larger, the decarburization rate is a little smaller. This is due to the fact that as

Fig. 9. Effect of composition of immersion tube on decarburization rate.
(Immersion tube: Al_2O_3 and $\text{Al}_2\text{O}_3\sim\text{SiO}_2$)

Fig. 10. Effect of gas permeability through immersion tube on decarburization rate.
(Immersion tube: $\text{Al}_2\text{O}_3\sim\text{SiO}_2$)

indicated in Table 1, both $P_{\min}$ in air and $P_{\min}$ in melt of the VSD-(A) tube are very low and CO gas permeation through its pore is not so good as that of the VSD-(B) tube.

The present experimental results clearly indicate that in order to decarburize molten iron quickly to a very low carbon concentration, the porous immersion tube should be highly gas permeable and contain a dissociative oxide.

4.3. Apparent First-order Rate Constant

The experimental result is rearranged according to the first-order rate equation. Since the carbon concentration could be decreased to a few ppm, the following equation is used to obtain the apparent first-order rate constant k .

$$-\ln([\text{ppm C}]/[\text{ppm C}]_0) = k(A/V)t \quad \text{.....(2)}$$

where A is the area of reaction interface, V is the volume of molten iron, t is the time, and the subscript 0 denotes the initial condition. It is to be noted that A includes all reaction interfaces, such as the porous tube-molten iron, crucible-molten iron interfaces and the melt free surface, and k is the overall rate constant for those reaction interfaces.

The experimental results for the Al_2O_3 tube with and without evacuation are rearranged according to Eq. (2) and plotted in Fig. 11. It is seen that $k(A/V)$ increased by approximately 50% by evacuating the tube. One previous experimental result²⁾ obtained without immersing a porous tube is also plotted in the figure. Comparison between the results of the present and the previous studies reveals that $k(A/V)$ of the present experiment without evacuation is only a little larger than that of the previous experiment and hence evacuation of the porous tube is by all means necessary for enhancing the decarburization.

The same rearrangement of the result for the Al_2O_3 - SiO_2 tube is made and shown in Fig. 12. Again the increase in $k(A/V)$ for the experiment without evacuation is only a little, as compared with the result of the previous decarburization experiment. The value of $k(A/V)$ for the experiment with evacuation is about four times larger than that without evacuation. It is made clear that the effect of evacuation of the porous tube is remarkable. Also, the slope of the linear line for the evacuated case is independent of the initial carbon

Fig. 11. Relation between $\ln([\text{ppm C}]/[\text{ppm C}]_0)$ and time. (Immersion tube: Al_2O_3)

concentration ($[\text{ppm C}]_0 = 97$ and 32). The deviation of the rate data from the linear relation at $t > 1200$ s, results from the decrease in the carbon concentration to below 10 ppm (6 ppm for $[\text{ppm C}]_0 = 32$). In this range of carbon concentration, the equilibrium carbon concentration can not be neglected, and Eq. (2) is inapplicable.

The contributions of the porous tube-molten iron interface and the MgO crucible-molten iron interface (including the bath surface) to the decarburization rate are separated by using the decarburization rate at the MgO crucible-molten iron interface (including the bath surface) obtained by the previous study.²⁾ The apparent first-order rate constants for the two reaction interfaces are denoted by k_t and k_c , the interfacial areas by A_t and A_c , respectively. Then, k is given by Eq. (3) approximately.

$$k(A/V) = k_t(A_t/V) + k_c(A_c/V) \quad \text{.....(3)}$$

The result of the previous paper is applied to the second term of the right side of Eq. (3).

Table 2 summarizes the values of $k(A/V)$, $k_c(A_c/V)$, $k_t(A_t/V)$ and k_t obtained from the experimental results shown in Figs. 11 and 12.

Both in the cases of Al_2O_3 and Al_2O_3 - SiO_2 tubes, the value of k_t for the experiment with evacuation is about one order larger than that without evacuation. Moreover, k_t of the Al_2O_3 - SiO_2 tube is much larger than that of the Al_2O_3 tube.

4.4. Mechanism of Decarburization Reaction

The overall reaction of decarburization of molten iron

Fig. 12. Relation between $\ln([\text{ppm C}]/[\text{ppm C}]_0)$ and time. (Immersion tube: Al_2O_3 - SiO_2)

Table 2. Rate constants for various immersion tubes.

Tube	$P_{\min}$ in melt (Pa)	$k(A/V)$ ($\times 10^4$) (s^{-1})	$k_c(A_c/V)$ ($\times 10^4$) (s^{-1})	$k_t(A_t/V)$ ($\times 10^4$) (s^{-1})	k_t ($\times 10^4$) (cm/s)
VSD-(C)	1.01×10^5	3.54	3.30	0.240	0.71
	2.0×10^2	5.22	3.35	1.870	5.40
VSD-(B)	1.01×10^5	3.99	3.34	0.650	1.84
VSD-(B)	3.0×10^2	17.95	3.30	14.65	42.4
	3.0×10^2	16.70	3.33	13.40	38.6

by solid oxide (M_xO_y) is given by Eq. (1). This overall reaction is consisted of the following elementary processes.

- (a) The dissociation reaction of oxide at the solid oxide–molten iron interface.

- (b) Mass transfer of $\bar{M}$ and $\bar{O}$ into molten iron.
 (c) Mass transfer of $\bar{C}$ to the solid oxide–molten iron interface.
 (d) CO formation at the interface.

- (e) Mass transfer of CO from the interface.
 The symbol “*” denotes the oxide–molten iron interface.

In the previous paper,²⁾ a kinetic study was made on the decarburization of molten iron by the refractory oxide, such as MgO, Al_2O_3 and CaO. In this case, the metal-phase mass transfer does not control the decarburization rate, since the rate is very low. And it is presumed that in the range of $[ppm C] > 100$ the rate is controlled by the process (a), and in the range of $[ppm C] < 100$ by the processes (a), (b), (d) and (e). In the previous study, however, the effect of mass transfer of CO on the rate could not be examined.

The mechanism of decarburization of molten iron by the vacuum suction degassing method is discussed in the following. The decarburization rate in the present experiment is strongly dependent on the composition of the porous tube. Therefore, the dissociation reaction of the oxide is thought to be one of the rate controlling steps.* The evacuation of the porous tube greatly enhances the decarburization or the CO formation. This increase originates in the decrease in the CO pressure at the immersion tube–molten iron interface by the suction of the CO gas into the tube. It follows that the small decarburization rate in the experiment without evacuation is attributable to existence of gas-phase mass transfer resistance. In addition, since the decarburization rate of molten iron by the present method is considerably large, the metal-phase transfer may be one of the rate controlling steps.

At our present state of understanding, it is difficult to eliminate any of the five processes ((a)–(e)) from the rate controlling steps.

4.5. Problems to be Solved in Applying the Vacuum Suction Degassing Method

The maximum value of the apparent first-order rate constant, k_t , is 0.00424 cm/s, which is obtained by using the VSD-(B) tube (Al_2O_3 –~16% SiO_2). The metal-phase mass transfer coefficient for an inductively stirred iron melt is about 0.02–0.04 cm/s,³⁾ so that the present value of k_t is about one-fifth or one-tenth of that obtainable under a metal-phase mass transfer control.

Therefore, more efficient decarburization of molten iron seems possible by approaching its rate to that of a metal-phase mass transfer control. This can be achieved

by using a porous material, which contains an easily dissociative oxide and also by using a high gas permeable porous material. Only SiO_2 was added to Al_2O_3 in the present experiment. It is thought that the decarburization rate or k_t may increase by adding MnO, Cr_2O_3 , Fe_2O_3 , NiO, etc. to the porous material. Since the porous material should be impermeable to molten iron, there is a limit to its gas permeability. The critical condition of the penetration of molten iron into the pore must be investigated to determine the optimum porosity and pore size.

Simultaneous decarburization, dehydrogenation and denitrogenation are possible by using the present method. Since the partial pressure of each gaseous product at the porous material–molten iron interface may decrease by the existence of the other gases, the decarburization can be enhanced by dehydrogenation and denitrogenation. However, the behavior of simultaneous degassings is quite complex and a further experimental study is needed to evaluate the increase in the decarburization rate.

5. Conclusion

A new degassing method (Vacuum Suction Degassing method) has been proposed to enhance decarburization of molten iron by solid oxide in low carbon and oxygen concentrations. On the basis of the kinetic experiments with and without evacuating the inside of the porous oxide tube immersed into the melt, the following conclusions are obtained.

(1) The decarburization of molten iron proceeds by the reaction between carbon and solid oxide. The CO gas formed by the reaction permeates the porous tube wall and is sucked into the tube, and hence the decarburization rate greatly increases.

(2) The decarburization rate increases with improving the gas permeability of the porous tube.

(3) The decarburization rate for the Al_2O_3 – SiO_2 tube is much larger than that for the Al_2O_3 tube. The rate is strongly dependent on the composition of the porous material.

(4) In the case of the Al_2O_3 –~16% SiO_2 tube, the carbon concentration decreased with time to 10–6 ppm, obeying the first-order rate equation (the equilibrium carbon concentration $[ppm C]_e = 0$). When the initial carbon concentration was 32 ppm, the concentration decreased to 3 ppm in 45 min.

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REFERENCES

- 1) K. Shinme and T. Matsuo: *Tetsu-to-Hagane*, **73** (1987), 313.
- 2) M. Sano, Han Yetao, T. Sawada and M. Kato: *ISIJ Int.*, **34** (1994), 649.
- 3) H. Nomura and K. Mori: *Tetsu-to-Hagane*, **55** (1969), 1134.

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* Since the oxygen concentration of the melt hardly changed with time, its effect on the decarburization rate is thought to be small.