Decarburization of Iron Melt by an Immersed $\text{Al}_2\text{O}_3\text{--Fe}_2\text{O}_3$ Porous Tube

Mehdi AHMADI NAJAFABADI, Masahiro HIRASAWA¹⁾ and Masamichi SANO¹⁾

Graduate School, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi-ken, 464-01 Japan.

1) School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi-ken, 464-01 Japan.

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A porous $\text{Al}_2\text{O}_3\text{--Fe}_2\text{O}_3$ tube, the inside of which is evacuated, is used to decarburize molten iron. Effects of inside pressure and Fe_2O_3 content of the porous tube, initial carbon content of the melt and melt temperature on the decarburization rate are investigated. Evacuating the inside of the tube reduces the partial pressure of CO at the tube–melt interface and enhances the decarburization reaction. However, in the case of lower initial carbon content of the melt, liquid slag is formed at the surface of higher Fe_2O_3 content tube, and sucked into its pore. Penetration of the liquid slag into the tube reduces the thermal strength and leads to the tube deformation. As a result, the gas permeability of the tube is decreased, and the decarburization rate becomes lower. The apparent decarburization rate constant (apparent first-order rate constant) for the non-deformed tube increases with increasing Fe_2O_3 content and decreasing inside pressure of the tube. At higher carbon contents, the tube is not severely deformed, but the effect of evacuation on the decarburization rate is little due to formation of large amount of CO (or CO boiling). The apparent decarburization rate constant decreases with increasing initial carbon content, and hence the rate is presumed to be controlled mainly by oxygen supply from the tube. The apparent activation energy for the decarburization reaction is 72.5 kcal/mol.

KEY WORDS: molten iron; decarburization; Fe_2O_3 ; porous tube; vacuum suction degassing; gas permeability; steelmaking; secondary refining.

1. Introduction

Recently, many studies have been made on decarburization of molten iron in a very low carbon range under reduced pressures.^{1–5)}

The decarburization rate depends on the mode of oxygen supply to the melt. Shinme and Matsuo¹⁾ injected solid oxides into the melt and found that the carbon content rapidly lowers to a few ppm. Sano *et al.*⁵⁾ developed a new degassing method (Vacuum Suction Degassing (VSD) method) with immersing a porous oxide tube into the melt and reducing its inside pressure. The tube supplies oxygen to the melt by dissociation of the solid oxide, and the pressure at the tube–melt interface is kept very low. Under these conditions, the carbon content decreases to a few ppm, while the oxygen content is kept at a low value. They showed that the decrease in the pressure at the interface greatly enhances the decarburization and its rate is affected by the dissociation rate of the solid oxide.⁵⁾

In the present study, the VSD method is applied to decarburization of molten iron with using an $\text{Al}_2\text{O}_3\text{--Fe}_2\text{O}_3$ porous tube. Since the dissociation of Fe_2O_3 is easier than that of SiO_2 , the oxygen supply is assumed to be larger than that with using an $\text{Al}_2\text{O}_3\text{--SiO}_2$ porous tube.⁵⁾ Effects of Fe_2O_3 content of the porous tube, initial carbon content of the melt and inside pressure of the

tube are examined.

2. Experimental

Figure 1 shows the experimental apparatus. A high frequency induction furnace (15 kW, 100 kHz) was used to melt electrolytic iron in a magnesia crucible (38 mm in I.D., 100 mm in height and 20% in porosity). After melting the iron, a mixture of Ar and H_2 was blown onto the melt surface through an alumina lance (4 mm in I.D.) located 10 mm above the melt surface to de-oxidize the melt. Then, the blowing gas was changed to argon (gas-flow rate = 1 000 Ncm^3/min). An appropriate amount of carbon was added to the melt to control the initial carbon content. A porous tube (14 mm in O.D., 6 mm in I.D. and 20–50 mm in length) was immersed into the melt, and the inside of the tube was evacuated by means of a rotary vacuum pump. The first sample of the melt was taken after about 3 min from immersing the tube, which corresponds to time 0. The period of 3 min was required to adjust the inside pressure of the tube, P_{in} , at a desired level. The porous tube was composed of Al_2O_3 and Fe_2O_3 . The tube was sintered at an appropriate temperature (1 723°K) and with air flowing so that the Fe_2O_3 particles were not melted. The characteristics of the porous tube are summarized in Table 1. In the table, P_{min} in air is the minimum pressure in the

Fig. 1. Experimental apparatus.

Table 1. Composition and gas permeability of porous tube.

Tube	$P_{\min}$ in air (kPa)	Composition			Size	
		Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	SiO ₂ (%)	Length (mm)	O.D. (mm)
AS7	20–21	93	—	7	45	14
AF2	6.8–7.8	98	2	—	46	14
AF5	7.2–15.9	95	5	—	50	14
AF7	11.9–23.2	93	7	—	48	14
AF10	81.5–111	90	10	—	50	13
AF10(S)	50–61.8	90	10	—	20	13
AF10(N)	111.5–147.5	90	10	—	45	19
AF20	89.5–111.5	80	20	—	48	13
AF20(S)	53–80	80	20	—	20	13
AF20(N)	108–145	80	20	—	50	19
AF30	83–94	70	30	—	49	13

tube when it is evacuated in the air, and this minimum pressure is used as an index of permeability of gas to the tube.

During the experiment Ar was blown into the tube (100 Ncm³/min) to reduce the partial pressure of CO in the gas phase of the inside of the tube. The melt temperature was controlled at 1580 ± 5°C. In some experiments, the temperature was changed to investigate the temperature dependence of the decarburization rate. Sampling of the metal was made by a silica tube (2 mm in I.D.), and the metal sample was supplied for analyzing carbon and oxygen contents. The combustion-infrared absorptiometry method was used to analyze carbon and oxygen. The accuracy of the carbon analysis was ± 2 ppm in the range of carbon content below 5 ppm.

3. Experimental Results and Discussion

3.1. Comparison of Decarburization Rates for Al₂O₃–SiO₂ and Al₂O₃–Fe₂O₃ Tubes

Figure 2 shows an effect of composition of the porous tube on the decarburization. The Al₂O₃–5%Fe₂O₃ tube gives a higher decarburization rate than the Al₂O₃–7% SiO₂ tube. The dissociation rate of Al₂O₃ is very slow as compared with that of SiO₂ or Fe₂O₃. Hence, the total mole of oxygen of SiO₂ is compared with that of

Fig. 2. Effect of composition of porous tube on the decarburization.

Fig. 3. Changes in carbon and oxygen contents with time.

Fe₂O₃. By taking the tube weight into account, the mole of oxygen of the Al₂O₃–5%Fe₂O₃ tube is estimated to be almost equal to that of the Al₂O₃–7%SiO₂ tube. The decarburization rate is higher for the Al₂O₃–5%Fe₂O₃ tube, which is thought to be related to a higher oxygen supply rate. Under the present experimental conditions, oxygen dissolved in the melt and supplied by the tube is consumed by CO reaction at the early stage of the experiment. At the later stage, the oxygen content of the melt increases due to the excess oxygen supply.

3.2. Kinetic Equation

The present experimental result is arranged according to the first-order rate equation, Eq. (1).

$$-\frac{d[C]}{dt} = k_C \left(\frac{A}{V} \right) [C] \quad \text{.....(1)}$$

where k_C is the apparent decarburization rate constant (cm/s), $[C]$ is the carbon content of the melt (ppm), A is the total area of reaction interfaces (cm²), V is the metal volume (cm³), and t is the time (s). Here, since the final carbon content is less than 10 ppm, the equilibrium carbon content, which should be smaller than the final carbon content, is neglected in Eq. (1).

Figure 3 shows the first-order plot of the typical result of the experiment with Al_2O_3 -20% Fe_2O_3 tube. The average of internal pressure of the tube during the experiment, $P_{\text{in,av}}$, is about 40.2 kPa. It is seen that $\log[C]$ changes almost linearly with time for $[C] \geq \sim 10$ ppm. Hence, Eq. (1) can be applied in the carbon concentration range of $[C] > \sim 10$ ppm. Deviation of plots from the straight line for $[C] < 10$ ppm is due to the carbon content approaching to an equilibrium level.⁸⁾ As seen in Fig. 3, the oxygen content in the melt increases initially, but remains almost constant at the later stage of the experiment.

3.3. Effect of Fe_2O_3 Content of Porous Tube

Figure 4 shows the effect of Fe_2O_3 content of the porous tube on the decarburization rate at the initial carbon content $[C]_0 = 100$ ppm. The overall apparent rate constant, $k_c(A/V)$, obtained by using Eq. (1) is also shown in the figure. The rate increases with increasing Fe_2O_3 content up to 20%.

It should be mentioned that the melting point of Fe_2O_3 (1565°C) is lower than the experimental temperature. When the tube temperature rises and approaches the melt temperature, the Fe_2O_3 particles of the tube may fuse. As a result, the thermal strength of Al_2O_3 - Fe_2O_3 tube decreases to cause deformation of the tube under the external forces exerted by the melt. Increasing the Fe_2O_3 content of tube promotes the deformation. Generally, the deformed zone of the tube was localized at the part near the melt free surface. This phenomenon was not observed in the case of the Al_2O_3 - SiO_2 tube.

The tube deformation alters the tube-melt interfacial area and the porosity of the tube. These changes affect

Fig. 4. Changes in carbon and oxygen contents with time.

the oxygen supply by the tube and the CO removal rate from the tube-melt interface. In Fig. 4 the slope of the curve in the case of the 30% Fe_2O_3 tube is smaller than those of the other tubes ($\text{Fe}_2\text{O}_3 < 30\%$) due to the distinctive deformation of the 30% Fe_2O_3 tube.

It is seen in Fig. 4 that in the experiment with 2% Fe_2O_3 tube, the oxygen content in the melt decreases at the early stage ($[C] > 45$ ppm). For 20 and 30% Fe_2O_3 content tubes, the oxygen content of the melt increases in the same period. This shows that the oxygen content is determined by a balance between the rates of oxygen supply by the porous tube and oxygen consumption by the reaction with carbon in the melt. However, at the later stage of the experiment, the oxygen supply even from higher Fe_2O_3 content tubes decreases and the oxygen content of the melt tends to become constant.

Figure 5 shows the results obtained by using 20 and 30% Fe_2O_3 tubes and under the conditions of $[C]_0 = 500$ and normal internal pressure. As shown later, in a higher initial carbon content range, the tubes were not severely deformed. It is seen that the apparent decarburization rate constant is larger for the 30% Fe_2O_3 tube. This indicates that the oxygen supply by the tube has an influence on the decarburization rate. However, the oxygen content of the melt is higher in the case of 30% Fe_2O_3 tube, and the higher oxygen content may also enhance the decarburization at the melt free surface to some extent.

3.4. Effect of Initial Carbon Content

The results obtained with the 20% Fe_2O_3 tube for different initial carbon contents, $[C]_0$ (ppm), are shown in Fig. 6. It is seen in the figure that the slope of the linear line, which gives $k_c(A/V)$, decreases with the increase in $[C]_0$.

The oxygen content initially increases for $[C]_0 = 50$ and 150 ppm. For $[C]_0 = 300$ ppm, the oxygen content remains almost constant, while for $[C]_0 = 500$ ppm, it decreases after 240 s from the beginning of the experiment. This indicates that the oxygen consumption rate in the case of the higher initial carbon content is larger than the oxygen supply rate.

Fig. 5. Effect of Fe_2O_3 content of tube on decarburization.

Fig. 6. Changes in carbon and oxygen contents with time.

The mole of oxygen supplied by the tube, $[molO]_{supply}$, and consumed by the decarburization reaction, $[molO]_{cons.}$, can be calculated from Eqs. (2) and (3).

$$[molO]_{supply} = [molO]_{cons.} + \frac{10^{-6}w}{n_O}([O] - [O]_0) \quad \text{.....(2)}$$

$$[molO]_{cons.} = \frac{10^{-6}w}{n_C}([C]_0 - [C]) \quad \text{.....(3)}$$

where $[C]$ and $[O]$ are the carbon and oxygen contents of the melt (ppm), w is the metal mass (g), n_O and n_C are the atomic masses of oxygen and carbon (g/mol), and subscript 0 denotes the initial condition.

In Fig. 7, the total mole of oxygen supplied by the 20% Fe_2O_3 tube is compared with the total mole of oxygen consumed during the experiment. It is seen that both the total amounts of oxygen supply and oxygen consumption, at the end of the experiment, increase with increasing $[C]_0$. When $[C]_0 = 50$ ppm, the oxygen supply is larger than the oxygen consumption. In the cases of $[C]_0 = 150$ and 500 ppm, the oxygen supply is nearly equal to the oxygen consumption. This suggests that the oxygen supply from the tube can be a rate controlling step at the higher initial carbon content.

After the experiment, the tube was cut along its axis to examine the inside of the tube. It is found that most of the tubes used for $[C]_0 = 50$ ppm were filled with slag, while those used for $[C]_0 = 500$ ppm were not. This indicates that the liquid slag is formed at the tube-melt interface. The mechanism of slag formation at the tube-melt interface is thought to be as follows.

In the lower initial carbon content range the oxygen

Fig. 7. Comparison between oxygen supply and oxygen consumption.

Fig. 8. Changes in carbon and oxygen contents with time.

content of the melt at the tube-melt interface increases and the liquid iron oxide can be formed at the interface. The melting point of $FeO-3\%Al_2O_3$ is about 1350°C. Under the present experimental conditions, evacuation of the porous tube can cause the molten FeO to be sucked into the tube pores and reduces the permeability of the CO gas to the tube. This may result in the increase in P_{CO} at the reaction interface and may decrease the decarburization rate.

In the case of higher initial carbon contents, the consumption rate of the oxygen at the tube-melt interface is fast and the liquid slag does not form at the interface. Moreover, endothermic reduction of Fe_2O_3 of the tube with carbon of the melt (Reaction (4)) does not favor formation of liquid slag near the tube surface. Consequently, the decarburization reaction proceeds without the interference of the slag.

3.5. Effect of Inside Pressure of the Tube

The results obtained under the conditions of $[C]_0 = 500$ ppm and the various inside pressures of the tube are shown in Fig. 8. It is seen that $k_c(A/V)$ is not appreciably changed with the inside pressure of the porous tube. At

the higher initial carbon content, the decarburization is accompanied by CO boiling. Although the tube is evacuated, the removal of CO is not sufficient to reduce P_{CO} at the tube-melt interface due to limited permeability of the gas to the tube.

The results obtained under the conditions of $[C]_0 = 100$ ppm with and without evacuating the porous tube are shown in Fig. 9. Apparently, $k_c(A/V)$ of the experiment under the reduced inside pressure is 1.4 times as large as that of the experiment under the normal inside pressure. This indicates that at a lower initial carbon content and without severe tube deformation, evacuation of the porous tube enhances the decarburization.

Comparing the experimental results obtained for $[C]_0 = 100$ and 500 ppm (Figs. 8 and 9) shows that evacuating the porous tube, which is an effective means to increase the decarburization rate in the lower carbon content range, loses its effect in the higher carbon content range.

3.6. Effect of Temperature

The effect of temperature was investigated experimentally by using a 5% Fe_2O_3 tube. The experimental results obtained at three different temperatures are shown in Fig. 10. The apparent decarburization rate constant as

Fig. 9. Changes in carbon and oxygen contents with time.

Fig. 10. Influence of temperature on decarburization.

well as the oxygen contents in the melt are considerably increased with increasing melt temperature. The rate data in Fig. 11 are plotted in terms of the Arrhenius relation in Fig. 11. The apparent activation energy for the reaction is 72.5 kcal/mol. This value is much larger than that of activation energy for the mass transfer of carbon 8.98 kcal/mol⁽¹⁰⁾ or that of oxygen 11.6 kcal/mol⁽¹¹⁾ in the iron melt. Thus, the increase in the melt temperature favors the oxygen supply by the tube or the dissociation of the tube oxide, and enhances the decarburization.

3.7. Estimation of the Apparent Rate Constant for the Reaction at the Tube-Melt Interface

Contributions of the tube-melt and the crucible-melt (including the bath surface) interfaces to the decarburization can be separated according to Eq. (5).

$$k_c \left(\frac{A}{V} \right) = k_{c,t} \left(\frac{A_t}{V} \right) + k_{c,c} \left(\frac{A_c}{V} \right) \quad \text{.....(5)}$$

where $k_{c,t}$ and $k_{c,c}$ are the decarburization rate constants at the tube-melt and the MgO crucible-melt (including the bath surface) interfaces, and A_t and A_c are the respective interfacial areas.

Experiments were performed with different tube

Fig. 11. Temperature dependence of the apparent rate constant.

Fig. 12. Changes in carbon and oxygen contents with time.

lengths to evaluate the contribution of the tube–melt interface to the reaction. The results obtained under the conditions of $[C]_0 = 130$ ppm and $P_{in,av} = 40.2$ kPa are shown in Fig. 12.

To estimate $k_{C,t}$ and $k_{C,e}$, the overall apparent decarburization rate constant, $k_C(A/V)$, is plotted against (A/V) in Fig. 13 for 10% and 20% Fe_2O_3 tubes. The average value of $k_C(A/V)$ obtained by regression analysis is shown by a solid line in the figure.

The approximate values of $k_{C,t}$ and $k_{C,e}$ are obtained from the slope of the line and the extrapolated value of $k_C(A/V)$ at $A/V = 0$, respectively and summarized in Table 2.

As seen in Table 2, $k_{C,t}$ increases with Fe_2O_3 content of the porous tube. This shows that even at the relatively low initial carbon content in the melt (130 ppm) the oxygen supply from the tube has a large influence on the decarburization reaction. The values of $k_{C,t}$ obtained in the present experiment are smaller than those with using $Al_2O_3-SiO_2$.⁵⁾ The reasons may be explained as follows.

(1) The $Al_2O_3-Fe_2O_3$ porous tube used in the present experiment is deformed due to the lower melting point of Fe_2O_3 compared with SiO_2 .

Fig. 13. Relation between $k_C(A/V)$ and A/V .

Table 2. Estimation of $k_{C,t}$ and $k_{C,e}$ for 10% and 20% Fe_2O_3 tubes. ($P_{in,av} = 40.2$ kPa, $[C]_0 = 130$ ppm)

Fe_2O_3 content of the tube (%)	$k_{C,t}$ ($\times 10^4$) (cm/s)	$k_{C,e}$ ($\times 10^4$) (cm/s)
10	19.45	9.71
20	23.4	9.41

(2) The slag formed at the tube–melt interface is sucked into the tube and reduces the permeability of the CO gas to the porous tube.

(3) The internal pressure of the tube is controlled at higher levels to prevent severe deformation of the tube.

(4) The Al_2O_3 of the tube is combined with FeO at the tube surface to form hercynite. This decreases the total amount of oxygen supplied by the tube.

As seen in the Fig. 4, the oxygen content of the melt increases considerably during the experiment. Since controlling the oxygen content of the melt in a narrow range is very difficult under the present experimental conditions, the value of $k_{C,t}$ shown in Table 2 is only approximate.

The value of $k_{C,e}$ obtained in the present study is larger than that obtained from the experiment without immersing the porous tube.⁷⁾ This may be due to the higher oxygen content in the present experiment.

4. Conclusion

The decarburization of iron melt with immersing porous $Al_2O_3-Fe_2O_3$ tube is performed by applying VSD method. The following conclusions are obtained.

(1) Evacuating the inside of the tube enhances the decarburization reaction under the conditions of higher initial carbon content in the melt and lower Fe_2O_3 content of the porous tube.

(2) In the lower initial carbon content of the melt, liquid slag is formed at the surface of higher Fe_2O_3 content tube.

(3) Under the conditions of liquid slag formation at the tube surface, evacuating the inside of the tube causes the liquid slag to be sucked into the tube. Consequently, the gas permeability of the tube is decreased and the decarburization rate becomes slower.

(4) The apparent decarburization rate constant increases with increasing Fe_2O_3 content and decreasing inside pressure of the non-deformed tube.

(5) In higher carbon content range a large amount of CO is formed and the effect of evacuation on the decarburization rate is decreased.

(6) The apparent decarburization rate constant decreases with increasing initial carbon content, and hence the rate is presumed to be controlled mainly by oxygen supply from the tube.

(7) The decarburization rate increases with increasing the melt temperature, and the activation energy for the decarburization reaction is 72.5 kcal/mol.

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