Decarburization of Molten Iron with Oxidizing Gases and Oxidation of Coexisting Metallic Elements*

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Synopsis

The rates of decarburization were measured on molten Fe-C and Fe-C-Me alloys with H₂O-Ar and CO₂-Ar mixtures. The oxidation rates of coexisting metallic elements were also measured. Before an oxide phase appears on the surface of melt, rates of decarburization were proportional to the partial pressure of oxidant gas component. The alloying elements did not affect the rate of decarburization. Apparent activation energies of these reactions were found to be 5.5 ± 3 and 6 ± 2 kcal for H₂O-Ar and CO₂-Ar mixtures, respectively. Accordingly, the reaction in the high-carbon content range seems to be controlled by the rate of transfer of the oxidant component from bulk of gas to the surface of melt. The carbon concentration where oxide appears on the surface of melt, $[C]_f$, is proportional to the partial pressure of oxidant gas component, and varied with the species of the gas and the alloying elements. The rate of decarburization for carbon concentration above $[C]_f$ was analyzed by the rate equation which was derived from the rate of diffusion of the oxidant gas component. The variations of $[C]_f$ can be explained by an equation which was derived from the rate of transfer of gas component and those of carbon and oxygen in the melt. An explanation was tried thermodynamically on the difference between the values of $[C]_f$ in the present work and in the converter steelmaking.

I. Introduction

In connection with the steelmaking reactions, there have been many works on the kinetics of decarburizations of molten iron with gases. Most of them were carried out by using oxygen gas diluted with argon, nitrogen, or other inert gases as the oxidizing gas. Various models were proposed on the reaction mechanism for the decarburization without slag. These models suggested that the rate determining step is to be mass transfers in gas phase for the carbon content greater than a critical value and changes to carbon transfer in the melt for carbon contents less than the critical value. The activation energy of reaction was found to be 13 to 35 kcal/mole,^{1,2)} but these values are thought to be too large for the mass transfer process.

The authors had studied previously the decarburization of molten iron using H₂O-Ar mixtures in order to clarify its mechanism more accurately by making use of the extremely weak oxidizability of H₂O. The activation energy obtained was 5.5 ± 3 kcal/mole.³⁾ In the same paper, the authors had proposed a model of the reaction with successful explanation of the experimental results. Thereafter, the activation energies of reactions of this type have been reported in several papers as a few kilocalories.⁴⁾ There are still many discrepancies among the models of the mechanism, but the differences of experimental results may be due to each measurement condition. The authors also studied on the relations between decarburization with CO₂-Ar mixtures and oxidation of coexisting metallic

elements during the decarburization in order to confirm the validity of the previous postulations. In this paper, the authors will summarize the major points of their previous papers.

II. Experimental

1. Apparatus

A schematic diagram of the apparatus used is shown in Fig. 1. It consisted of two parts, one being a combination of equipments for purification of H₂, CO₂, and Ar, and of a water vapor saturater, and the other the reaction furnace. The saturater consisted of a water-filled bottle as a preliminary saturater and an accurate saturater dipped in the constant-temperature water bath. A 40 mm ID and 50 mm depth recrystallized magnesia or electro-fused zirconia crucible containing 300 g of electrolytic iron was placed in a 80 mm ID quartz reaction tube surrounded by an induction coil. A 430 kC H.F. generator was used as the power source. Reacting gases were passed through a 9 mm ID alumina preheating tube (about 1200°C) which was fixed below the water-cooled brass cap, and blown into the reaction crucible. The lower end of the preheating tube was kept apart from the metal surface by about 7 mm, in order that the gas stream upon the surface of melt would be always constant.

2. Operation

In a typical experiment, 300 g of electrolytic iron was melted in a pure argon atmosphere and was re-

Fig. 1. Schema of experimental apparatus

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duced at 1600°C sufficiently with H₂-Ar (1 : 1) mixture for 1.5 hr. Again atmosphere was replaced by pure argon in order to remove the dissolved hydrogen, and then carbon and some alloying element were added to the molten iron to make an alloy of desired composition. Holding the molten iron at the constant temperature, the decarburization reaction started by replacing the atmosphere by the oxidizing gas mixture. During the reaction, every 5 to 7 g of iron were pumped out several times with suitable intervals by 3 mm ID quartz tube and cooled quickly for analysis. Analysis of each component was done respectively according to the JIS methods. (JIS means Japanese Industrial Standard.) Temperature of molten iron was measured with an optical pyrometer calibrated by Pt5Rh/Pt20Rh thermocouple.

III. Experimental Results

At the temperatures of 1560°, 1600°, and 1660°C, molten iron-carbon alloys were decarburized with various H₂O-Ar mixtures. Gas mixtures were prepared by blowing argon at constant flow rate, 1700 cm³/min, into the water vapor saturator. Some of the results are shown in Fig. 2, in which carbon concentration decreased linearly in each case until carbon concentration reached to a critical value. Let this value designate [C]_f. There, oxide film began to cover the surface of the melt, and thereafter decarburization curves seemed to behave as the first order with respect to the carbon concentration.

Fig. 2. Decarburization curves at 1600°C by argon gas with various P_{H_2O}

Decarburization curves of Fe-C alloy with various CO₂-Ar mixtures were obtained at 1300° to 1600°C. Flow rate of gases was taken constant as total 1700 cm³/min. The rates of the reaction were similar to that of decarburization with H₂O-Ar mixtures as a whole. However, values of [C]_f were far lower than those with H₂O-Ar mixtures.

Next measurements were done on the decarburization of molten alloys containing deoxidizing metallic elements with various H₂O-Ar mixtures at 1600° to 1610°C.⁵⁾ The results are shown in Fig. 3. Decarburization curves of Fe-C-Cr alloys had a similar tendency with those of Fe-C alloys under the present experimental condition. The values of [C]_f seemed to be almost same or a little higher comparing with

Fig. 3. Effects of alloying elements on the decarburization of iron with various H₂O-Ar mixtures at 1600° to 1610°C

those in Fe-C alloys. Consequently, it is supposed that the decarburization rate was not affected with the existence of chromium. Oxide on the surface of the melt was solid and a rigid film. However, the oxide film disappeared gradually in spite of the very low-carbon concentration, when the supply of H₂O was stopped.

In case of Fe-C-Si alloys, the rates of decarburization were also same as those in Fe-C alloy until oxide appeared on the surface. The oxide was a liquid film flowing on the surface of the melt, and appeared at a considerably high-carbon concentration comparing with those in Fe-C alloys. After the appearance of oxide films, the rates of decarburization decreased a little but the oxide films vanished away quickly if the supply of H₂O was stopped. From these observations, it may be concluded that the oxide plays a carrier of oxygen atoms on the metal surface for carbon concentrations less than [C]_f.

In case of Fe-C-Mn alloys, decarburizations were carried out as well as those above mentioned, but the values of [C]_f were devoid of reproducibility. At high-carbon concentration, oxide particles began to flow on the surface of the melt, but these particles were manganese oxide formed by the gaseous reaction between CO₂ and manganese evaporated from the melt. Consequently, carbon concentration in which the oxide particles appeared, varied widely in accordance with the initial carbon concentration, and the true value of [C]_f could not be pointed out. Furthermore, in these alloys, smokes of manganese evaporated from the melt were so dense that it could not be observed whether the oxide films were solid or liquid.

Decarburization curves of Fe-C-Al alloys were very different from those of the other alloys above-mentioned. For aluminum concentration above about

0.1%, a solid film of the oxide covered the surface of alloys as soon as the decarburization started, and prevented the further progress of reaction. The surface of metal which the oxidation continued after the oxide appeared, was covered with a grey film, and some of white powder was there. The powder was thought to be mainly Al_2O_3 , but it may contain iron oxide also since it sometimes turned grey. There were many holes on the oxide film. If the supply of water vapor was stopped after the oxide began to appear, 30 to 50 min were required for the disappearance of oxide layers. For aluminum concentration below 0.1%, oxide did not cover the metal surface, and decarburization curves were almost the same as those of the other alloys. This might be caused by the lack of oxide, since the amount of aluminum in the melt was too little for the amount of oxide to cover the surface.

More detailed measurements were done on the decarburization of Fe-C-Si alloys using H_2O -Ar and CO_2 -Ar mixtures at 1600°C .^{6,7)} Variations of each component in alloys during the reaction are shown in Figs. 4 and 5. Carbon concentration decreased at a constant rate until oxides began to appear on the metal surface, whereas silicon concentration did not decrease at all and oxygen concentration did hardly increase. After oxide covered the metal surface, silicon concentration began to decrease noticeably and oxygen concentration began to increase rapidly. Values of $[\text{C}]_f$ were affected with the species and amounts of added element and with the composition of oxidizing gas mixtures as shown in Figs. 6 and 7. On the contrary, the decarburization rate for carbon concentration above $[\text{C}]_f$, $-d[\%C]/dt$, which were estimated from

Fig. 4. Decarburization curves by various CO_2 -Ar mixtures at 1600°C and variations of silicon and oxygen contents

the slopes of reaction curves in their linear ranges, were almost independent of the alloying elements and species of oxidant gas component but those were proportional to the partial pressures of oxidant gas component as shown in Fig. 8. It is supposed from the results in Fig. 8 that the rate determining step in the initial period was principally the transfer of oxidant gas molecules in the gaseous boundary layer on the metal surface.

In each experiment above-mentioned, when the oxidation stopped at the carbon concentration above $[\text{C}]_f$, the evolution of CO bubbles was not observed at all. However, after oxide appeared, many small bubbles evolved from the surface and small iron

Fig. 5. Decarburization curves by various H_2O -Ar mixtures at 1600°C and variations of silicon and oxygen contents

Fig. 6. Relationship between $[\text{C}]_f$ and $P_{\text{H}_2\text{O}}$ and P_{CO_2}

Fig. 7. Relationship between $[C]_f$ and amount of added element (Si)

Fig. 8. Relationship between $-dc/dt$ and P_{CO_2} (P_{H_2O})

droplets attached on the top of preheating tube and upper part of the crucible. If oxidation was further continued, the evolution of a few large bubbles was observed.

IV. Consideration

From the temperature dependence of decarburization rate with H_2O -Ar mixtures for carbon concentration above $[C]_f$, the apparent activation energy of the reaction was estimated to be 5.5 ± 3 kcal/mole. Further, from those with CO_2 -Ar mixtures in wider temperature range, the activation energy was found to be 6 ± 2 kcal. These small values seem to suggest that the reactions were controlled by diffusion processes. The authors had found previously that the oxidation reaction of liquid iron with H_2O -Ar mixtures was a boundary reaction between gas and melt.⁽⁸⁾ Accordingly, it is also possible that the decarburizations of molten iron with gases are the boundary reactions between gas and melt before oxide phase appeared on the metal surface. On the basis of these facts and

observations during and after reactions, the authors had postulated the following model as the mechanism of decarburization with gas. The decarburization with H_2O -Ar mixtures will be considered as examples.

The overall reaction of the decarburization of molten iron with atmosphere is thought to proceed always in several steps. At first, the oxidant molecules, H_2O , is transferred from the bulk of the blown gas mixture to the gas/melt boundary. Assuming that the transfer is caused by diffusion only in the gaseous boundary layer, the rate is expressed by

$$\frac{dn_{H_2O}}{dt} = \frac{D_G}{\delta_G} (P_{H_2O} - P_{H_2O}^i) \quad \dots\dots\dots (1)$$

where D_G is the diffusion coefficient of H_2O , δ_G thickness of the gas boundary layer, and P_{H_2O} and $P_{H_2O}^i$ the partial pressure of H_2O in bulk of gas and at the boundary, respectively. In the initial period of reaction, where carbon concentration is sufficiently high, the rate of carbon transfer through the boundary layer of melt from bulk of melt to the phase boundary is far larger than that of H_2O transfer to the phase boundary. Consequently, the reaction interface is the gas/melt phase boundary, and only the reaction

must be taken into account. In accordance with the decrease of carbon concentration, the concentration gradient of carbon in boundary layer becomes small. Therefore, the rate of carbon transfer to the phase boundary decreases step by step, whereas it is readily estimated from the equilibrium constant of reaction (2) that the rate of transfer of H_2O in gaseous boundary layer remains almost constant. When the rate of carbon transfer decreases to a value smaller than the rate of H_2O transfer, the reaction interface moves from the phase boundary into the boundary layer of melt. At the same time, the oxygen concentration at the phase boundary begins to increase and at last reaches to its saturation value. As the result, oxide appears on the surface of melt. For some time after oxide layer formed itself, the surface still seemed to be calm. Accordingly in this period of reaction, carbon and oxygen atoms move to the reaction interface respectively through the diffusion layer at each side of the interface, and CO molecules are formed there. Even if the CO molecules are removed through the surface of melt to gas phase, it is probable that those cannot grow up to large bubbles because the distance between the reaction interface and phase boundary is very small. As the carbon concentration in melt decreases further, the rate of carbon transfer to the reaction interface becomes so small that oxygen atoms begin entering into iron bulk, and so the reaction interface or region vanishes away. Carbon and oxygen atoms in melt flock by diffusion to active sites at the melt/crucible boundary, where the formation of CO bubbles proceeds. Thus formed CO bubbles may reach to the free surface of melt after having some sufficiently large volumes, and be removed off to gas phase. As a result, the surface of oxide layer seems to be foamed

and the larger iron droplet were found on the upper parts of crucible wall. After oxide appears on the surface of melt, the reaction must take place in two steps as follows:

On the basis of these postulations on the mechanisms of decarburization, the rate of reaction can be considered. The rate of reaction for carbon concentrations above $[\text{C}]_f$, must be controlled by the rate of gaseous diffusion of H_2O and be expressed by Eq. (1) as mentioned above. In this period of reaction, however, it is seen from the equilibrium constant of reaction (2) that the partial pressure of H_2O at the phase boundary, $P_{\text{H}_2\text{O}}^i$, is always negligibly small. Consequently, changing the variables, Eq. (1) is rewritten as follows:

$$-\frac{d[\% \text{C}]}{dt} = \frac{D_G}{\delta_G \rho} \frac{1}{V} 200F P_{\text{H}_2\text{O}} \dots\dots\dots(5)$$

where ρ is density of iron melt, V the volume of melt, and F the area of gas/melt boundary. This equation is in good agreement with the relation between the rate of reaction and partial pressure of H_2O , given in Fig. 8. The linear velocity of gas stream is different according to localities of the surface of melt. Accordingly the value of so-called δ_G must be different in various localities also. The experiments on the variation of δ_G with experimental conditions will be given elsewhere. Here, the hydrodynamic factors remain constant and so the values of δ_G is simply a mean value at the phase boundary. It is also readily supposed from Eq. (5) that the rate of decarburization is almost independent of the species of oxidant gas component.

Carbon concentration in which oxide appears on the surface of melt, $[\text{C}]_f$, will be estimated on the basis of the present model. A schematic pattern of concentrations in the vicinity of phase boundary where a little before oxide appears is shown in Fig. 9. Then assuming that the increase of oxygen concentration at phase boundary can be neglected, and equating the rate at each process to each other, the following relation can be derived: when oxide appears:

$$\begin{aligned} -\frac{d[\text{C}]}{dt} &= \frac{D_G F}{\delta_G V} (P_{\text{H}_2\text{O}} - P_{\text{H}_2\text{O}}^i) \\ &= \frac{D_O F}{l_1 V} ([\text{O}]_{\text{sat}} - [\text{O}]_e) \\ &= \frac{D_C F}{l_2 V} ([\text{C}]_e - [\text{C}]_f) \dots\dots\dots(6) \end{aligned}$$

where D_C and D_O is respectively the diffusion coefficient of $\underline{\text{C}}$ and $\underline{\text{O}}$, and $[\text{C}]_e$ and $[\text{O}]_e$ is respectively concentration of $\underline{\text{C}}$ and $\underline{\text{O}}$ at the reaction interface. At the phase boundary, assuming that the carbon concentration is equal to zero and that the reaction (3) attains the equilibrium state, the following relation is given:

$$\frac{P_{\text{H}_2\text{O}}^i}{P_{\text{H}_2}^i} = \frac{[\text{O}]_{\text{sat}}}{K} = k_f$$

Fig. 9. Schematic pattern of concentrations in the reaction a little before oxide appears on the surface of melt

Further assuming that the total pressure of atmosphere remains constant everywhere, there is following relation between the partial pressures of H_2O and H_2 at the phase boundary,

$$P_{\text{H}_2\text{O}}^i + P_{\text{H}_2}^i = P_{\text{H}_2\text{O}}$$

Although oxygen and carbon concentrations at the reaction interface are unknown, these are assumed here to be negligible respectively against $[\text{O}]_{\text{sat}}$ and $[\text{C}]_f$. Combining these relations, the following expression is derived:

$$\frac{D_G/\delta_G \cdot 1}{D_C/l_2} \cdot \frac{200/\rho}{1+k_f} P_{\text{H}_2\text{O}} = [\% \text{C}]_f \dots\dots\dots(7)$$

It is clear from the reaction model mentioned above that the value of l_2 must be varied with the change of $[\text{C}]_f$. From the range of variation of $[\text{C}]_f$ obtained in present experiments, it is thought to be possible that the range of variation of l_2 is so small that it is assumed to be constant. Accordingly, two fractions in left of Eq. (7) is assumed to be constant at a given temperature and denoted as k . So the following relation is derived:

$$k P_{\text{H}_2\text{O}} = [\% \text{C}]_f \dots\dots\dots(8)$$

By means of this equation, the linear relation between $P_{\text{H}_2\text{O}}$ and $[\text{C}]_f$ shown in Fig. 6 is explained. A similar relation is obtained in the cases of decarburization with CO_2 -Ar mixtures. If the present reaction model is applied to the cases of decarburization with oxygen containing gases, the partial pressure of oxygen at the phase boundary is very small, i.e., of the order of 10^{-8} atm. Therefore, by similar approximations, the following relation is derived:

$$\frac{D_G/\delta_G}{D_C/l_2} P_{\text{O}_2} = [\text{C}]_f$$

In this case also, it is clear that the value of $[\text{C}]_f$ is proportional to the partial pressure of oxygen in atmosphere. Substituting some reasonable values

given in other papers to the rate constants and equilibrium constants in Eq. (7), the following relation is derived at 1 600°C.

$$0.30 P_{\text{H}_2\text{O}} = [\% \text{C}]_f$$

From the results given in Fig. 6, it is obtained that $k=0.6$. It may be supposed that this agreement is in a better extent from the validities of numerical values used in above estimation. Since Eq. (7) contains δ_G and l_2 , it is clear that the values of $[\text{C}]_f$ are affected by hydrodynamic factors such as the linear velocity of gas stream and stirring of molten iron.

If a deoxidizable metallic element is added to Fe-C alloys, the saturation value of $\underline{\text{O}}$, $[\text{O}]_{\text{sat}}$, decreases and then k_f decreases. Accordingly, assuming the other numerical values in Eq. (7) remain constant, k increases. Then it is obviously supposed that the stronger the deoxidizability of an added element becomes, the higher $[\text{C}]_f$ becomes.

In converter operations, the oxidation of silicon and other metallic elements proceed as soon as the decarburization starts, whereas in present works, the decrease of silicon concentration started until carbon concentration decreased to considerably low values as shown in Fig. 7. Taking silicon as an example of alloying elements, this discrepancy shall be considered thermodynamically. The equilibrium constant K_1 of the decarburization of molten iron with silica slag :

can be evaluated from those of the reactions :

and $(\text{SiO}_2)_{\text{sat}} = \underline{\text{Si}} + 2\underline{\text{O}} ; \log K = -30\,720/T + 11.76$. Thus K_1 is found as follows :

$$K_1 = P_{\text{CO}}^2 \cdot a_{\text{Si}} / a_{\text{C}}^2 ; \log K_1 = -28\,400/T + 15.77$$

At 1 600°C, $K_1=4$. It is clear from the form of K_1 that when reaction (9) attains the equilibrium state, the carbon concentration is proportional to P_{CO} . In converter operations, P_{CO} at the phase boundary must be above 2 atm in calculations because the oxygen pressure adding its hydrodynamic pressure is 1.4 to 2 atm. On the other hand in present works, P_{CO} at the phase boundary may be 0.1 to 0.5 atm because oxidation is carried out by using H_2O or CO_2 diluted with Ar. Consequently it is reasonable that in present works, oxide did not appear until carbon concentration decreased to a sufficiently low value. Relations between $[\text{C}]_f$ and silicon concentration are shown in Fig. 10, where the observed points distributed in the region of equilibrium of reaction (9) corresponding to $P_{\text{CO}}=0.3$ to 0.9 atm. However, these values of carbon concentrations are those in iron bulk, and strictly speaking, the values at the phase boundary must be used. It is probable by calculations that the carbon concentrations at the phase boundary are smaller than those in bulk of melt by 0.12 to 0.25%.

It was supposed previously that oxidation of molten steel with air in the ingot practice might be a cause of the formation of non-metallic inclusions.⁹⁾ It was re-

Fig. 10. Relations between silicon and carbon contents when oxide appears. Solid lines express the equilibrium state of reaction (9).

ported that in casting in the air, oxygen concentrations increased in cases of low-carbon 18-8 stainless steel and that large inclusions formed in cases of the steels added by aluminum.¹⁰⁾ On the other hand, it was found that oxidation with air did not affect much on the quality in cases of middle carbon chromium steel.¹¹⁾ It is readily seen that these phenomena can be reasonably explained by the model and the rate equations mentioned above. If all the values of rate constants and equilibrium constants were known, it should be possible to estimate the necessity of controlling the atmosphere for a given molten steel to cast.

V. Conclusions

The rates of decarburization were measured on molten Fe-C and Fe-C-Me alloys with H_2O -Ar and CO_2 -Ar mixtures and on the oxidations of coexisting metallic elements. Results are as follows:

(1) Before oxide appears on the surface of melt, the rate of decarburization is proportional to the partial pressure of oxidant gas component, and independent almost of its species and the alloying elements. Accordingly, the reaction seems to be controlled principally by the rate of transfer of the oxidant component from gas bulk to the surface of melt, and is expressed by Eq. (5). Apparent activation energies of these reactions are found to be 5.5 ± 3 and 6 ± 2 kcal, respectively.

(2) Carbon concentration where oxide appears on the surface of melt, $[\text{C}]_f$, is almost proportional to the partial pressure of oxidant gas component, varied with its species and the amount of added element, and increases according to the deoxidizability of added element. These relations were explained by Eq. (7) which was derived from the model shown in Fig. 9. It was explained thermodynamically that the values of $[\text{C}]_f$ obtained in the present works are very low in comparison with those observed in converter steelmaking.

(3) With respect to the possibility of formation of nonmetallic inclusions, the effects of oxidation of mol-

ten steels with air in casting was estimated by the present results.

REFERENCES

- 1) K. Niwa, Y. Watanabe, Y. Itō, S. Maekawa, and Y. Nakagawa: *Jap. Soc. Prom. Sci.*, 19C-4791, (1957, Dec.).
- 2) T. Fujii: *Tetsu-to-Hagané*, **46** (1960), 12.
- 3) K. Itō and K. Sano: *Tetsu-to-Hagané*, **50** (1964), 873.
- 4) Y. Gunji, Y. Katase, and Y. Aoki: *Tetsu-to-Hagané*, **50** (1964), 1828.
- 5) K. Itō and K. Sano: *Tetsu-to-Hagané*, **51** (1965), 1252.
- 6) K. Sano, K. Itō, and S. Arino: *Tetsu-to-Hagané*, **53** (1967), 777.
- 7) K. Sano, K. Itō, S. Arino, and T. Takenouchi: *Tetsu-to-Hagané*, **53** (1967), 1193.
- 8) K. Itō and K. Sano: *Tetsu-to-Hagané*, **49** (1963), 1652.
- 9) Z. Takao, K. Narita, K. Kanda, and A. Miyamoto: *Tetsu-to-Hagané*, **47** (1961), 1156.
- 10) T. Sugiyama and G. Katō: *Elec. Steelmaking*, **33** (1962), 129.
- 11) S. Oda, H. Hori, K. Mori, and T. Katō: *Tetsu-to-Hagané*, **50** (1964), 1841.