# Kinetics of Decarburization of Iron-Chromium Melts in Highly Oxidizing Atmosphere

SUSHANTA KUMAR DEY AND DHIRENDRA NATH GHOSH

The kinetics of decarburization in Fe-Cr-C melts were studied to determine the rate controlling step for the process. The experiments were carried out under nitrogen-oxygen atmosphere in a resistance-heated vertical-tube furnace. The liquid melt was held in a freshly prepared magnesite crucible. Sampling and chemical analysis of the metal phase led to time-carbon concentration curves for the system. An iron oxide layer just below the impinging area and a general boil were observed. Results obtained by varying parameters such as temperature, partial pressure of oxygen, flowrate of the oxidizing gas and amount of melt determined the limiting reaction mechanism. The rate has been found to be almost independent of flow rate and partial pressure of oxygen (between 1.0 to 2.0 l/min. and 0.5 to 1.0 atm of oxygen). The amount of melt and temperature have a marked effect on the reaction rate. The apparent activation energy has been found to be 48.0 ± 5.4 K cal/mol. The carbon oxidation reaction has been proposed to occur predominantly at CO bubble/metal interface. On the basis of the experimental results and discussions reaction involving reduction of oxides by carbon has been proposed to be the rate controlling step.

DECARBURIZATION is one of the most important reactions and the progress of the steel making technique can be said as the history of decarburization reaction itself. Therefore, if the mechanism of decarburization process is more completely understood it should be possible to improve on the control and thereby the efficiency and economy of steel making.

The kinetics of decarburization of molten Fe-C melts have been studied by many investigators using various oxidizing agents and experimental procedures. Broadly, there are two schools of opinion. Fuji *et al*,[1] Mori *et al*,[2] Paderin and Philippov[3] See and Warner[4] *etc* have concluded that the rate is controlled by gaseous diffusion. On the contrary, Swisher and Turkdogan,[5] Ghosh and Sen,[6] Medvedevskikh *et al*[7] *etc* have suggested a chemical reaction controlled mechanism.

Recently there has been a major breakthrough in the manufacturing process of stainless steel by AOD (Argon-Oxygen-Decarburization) process. Stainless steel can now be produced without any addition of high cost low carbon Fe-Cr, from the cheap sources of chromium *i.e.* high carbon Fe-Cr and stainless steel scrap. In AOD process a high carbon Fe-Cr melt is preferentially decarburized to a very low carbon by argon-oxygen gas mixture. In this respect Fe-Cr-C system present an excellent system for the decarburization study.

In the present investigation, Fe-Cr-C melts have oxidized by oxygen-nitrogen gas mixtures. The effects of variables such as partial pressure of oxygen, flowrate of gas mixture, amount of melt and temperature were studied and a reaction mechanism has been proposed for the carbon oxidation reaction.

## EXPERIMENTAL SET-UP AND PROCEDURE

The experimental set up has been discussed in detail elsewhere.[6] In the present investigation 200 g of Fe-Cr-C melt were prepared in a freshly prepared magnesite crucible in the graphite resistance furnace, under argon atmosphere. The starting composition of the melt was approximately 10 pct chromium and 1.0 pct carbon. Sample were taken at 5 min interval. Carbon in the samples was analyzed by the combustion method.

## EXPERIMENTAL OBSERVATIONS

During the experiments, the melt surface was observed frequently to determine the effect of oxygen partial pressure. In the high flow rate region, when gas mixture of low partial pressure of oxygen, was blown on the melt surface, a bright spot at the impinging area was observed. The spot however vanished when the gas flow was stopped. With increasing partial pressure of oxygen the area over which the bright spot was observed increased and boiling could be observed. At 100 pct oxygen, the bright area covered almost the whole surface of the melt and appreciable boiling was seen.

## EXPERIMENTAL RESULTS

Results are shown in Figs. 1 through 12. Carbon concentration in metal shows a linear relationship with time under all experimental conditions, indicating a zero order reaction. The slopes of these curves represent the specific rate constants of the decarburization reaction. The experimental results, obtained under different conditions are given below.

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## EFFECT OF FLOW RATE OF THE GAS

Rates of decarburization were studied using different flow rate of the gas mixture. The temperature was maintained constant at 1600°C. For 100 pct oxygen as the oxydent the reaction was studied under the flow rates of 0.5, 1.0, 1.5 and 2.0 l/min whereas for 50 pct $O_2$-50 pct $N_2$ gas mixture, the experiment was carried out at 0.5, 1.0 and 1.5 l/min. The change of carbon concentration with time at different flow rates is shown in Fig. 1. The rate of decarburization was then plotted against flow rate as shown in Fig. 2. In both the curves a nonlinear relationship was obtained with a gradual decrease of influence of gas flow rate on the decarburization rate. For pure oxygen the rate was found to become independent of flow rate between 1.0 to 2.0 l/min. For 50 pct $O_2$-50 pct $N_2$ the rate increase with the increase of gas flow rate, but at higher flow rates it becomes almost independent of flow rate.

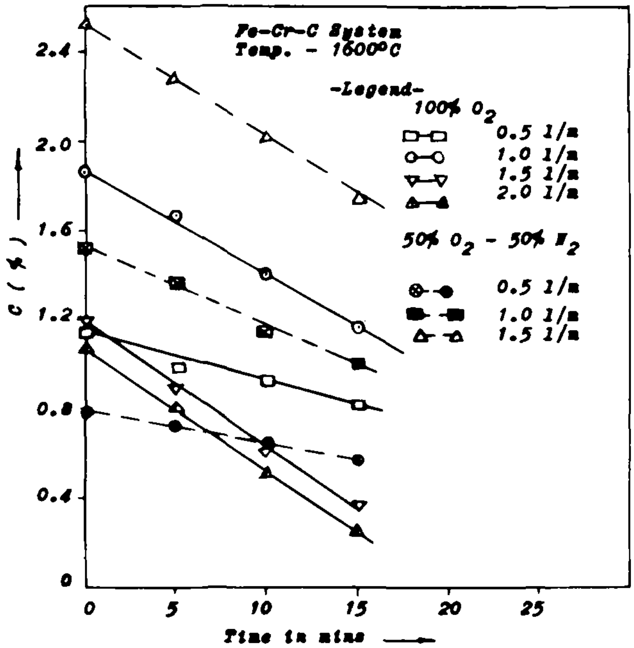

Fig. 1—Change of carbon concentration of bath with time for different flow rates of gas mixture.

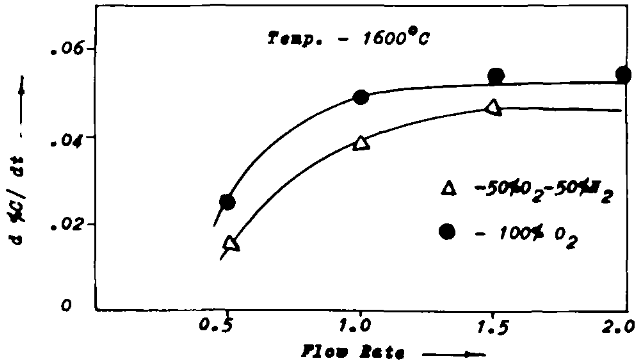

Fig. 2—Relation between the flow rate of gas and the rate of decarburization.

## EFFECT OF AMBIENT OXYGEN PRESSURE

The experiment was carried out at partial pressure 0.1, 0.25, 0.50, 1.0 of oxygen with the flow rates of 1.0 l/min and 1.5 l/min at temperature 1600°C. The plot of carbon percentage with time at different partial pressures is shown in Fig. 3. The variation of decarburization rate with partial pressure is illustrated in Fig. 4. At both the flow rates the variation shows a nonlinear relationship with the partial pressure with progressively decreasing influence of partial pressure. The rate is independent of partial pressure of oxygen after 0.5 atm of oxygen for 1.5 l/min of flow rate.

## EFFECT OF TEMPERATURE

Attempts were made to determine the effect of temperature on the decarburization rate at 0.5 atm oxygen partial pressure. The flow rate was maintained at 1.0 l/min. The experiments were carried out at 1600, 1625 and 1650°C. The plot of carbon variation with

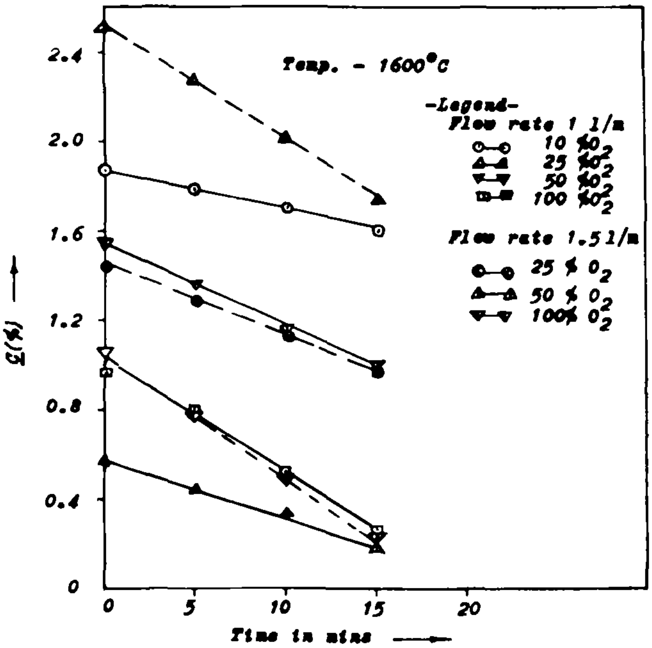

Fig. 3—Change of carbon concentration of bath with time for different partial pressure ($O_2$) of gas mixture.

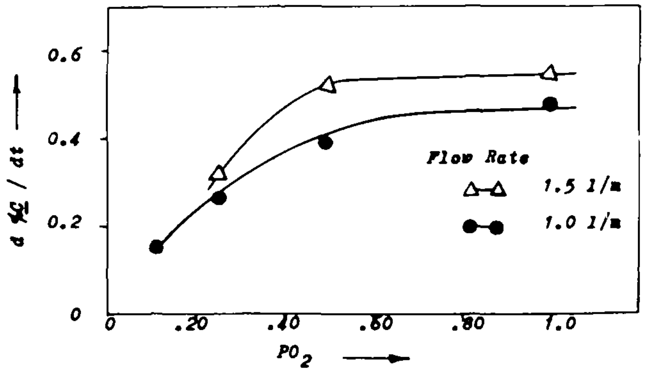

Fig. 4—Relation between oxygen partial pressure of gas and the rate of decarburization.

time at different temperatures is shown in Fig. 5. The log of decarburization rate was then plotted against the reciprocal of absolute temperature (Fig. 6). The activation energy, calculated from the graph was 48.0 Kcal/mole.

## EFFECT OF THE AMOUNT OF MELT

In an attempt to find out the effect of amount of melt on the decarburization reaction rate the experiments were performed with 200 and 500 gms of melt keeping the area of free surface on the melt constant. The corresponding metal depths were 29.8 mm and 74.5 mm respectively. The study was made at two different oxygen partial pressure 0.5 atms and 1.0 atms. The flow rate of the gas mixture was maintained at 1.0 l/min in both cases. The variation of carbon in gms with time is shown in Fig. 7. The rate of decarburization versus amount of melt is plotted in Fig. 8.

In this figure the rate of carbon removal was expressed in gms/min rather than in percent per minute (pct C/min), because gms/min is an absolute rate suitable for comparison of carbon removal from melts of different weight. The plot clearly indicates that the rate of decarburization increases with the increase in the amount of melt.

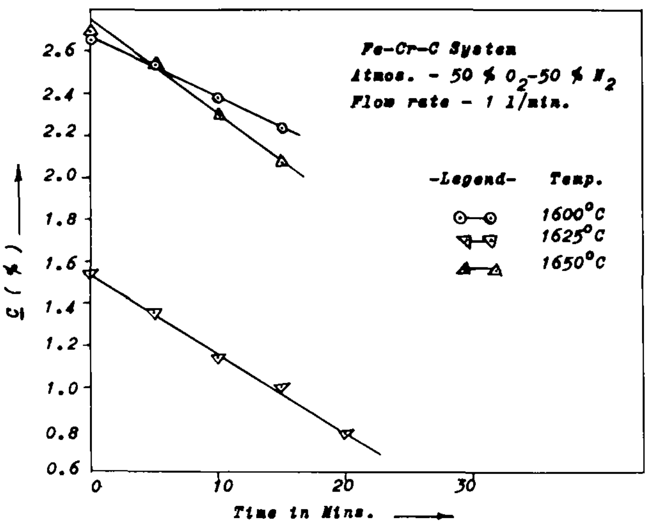

Fig. 5—Change of carbon concentration of bath with time for different temperature.

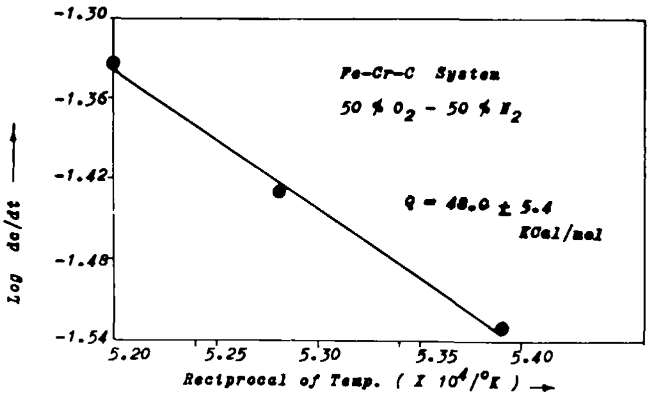

Fig. 6—Log *dc*/*dt* as function of reciprocal of temperature.

## EFFECT OF OXYGEN PARTIAL PRESSURE ON CRITICAL CARBON CONCENTRATION

The critical carbon concentration at which the crust of oxide forms and rate becomes dependent on carbon concentration has been determined at 0.25, 0.5 and 1.0 atm of oxygen. The result is shown in Fig. 11. The critical carbon concentration was then plotted against oxygen partial pressure in Fig. 12. It has been observed that oxygen partial pressure has no effect on the critical carbon concentration e.i. on the chromium/carbon ratio.

## DEGREE OF UTILIZATION OF OXYGEN

The oxygen efficiency was calculated for different flow rates and partial pressures of oxygen. The efficiency as a function of flow rate at 0.5 and 1.0 atms partial pressures of oxygen is shown in Fig. 9. In both cases the efficiency increases initially and then decreases with flow rates higher than 1.0 l/min. The plot of the oxygen efficiency with its partial pressure is shown in Fig. 10. It is clearly indicated that the efficiency falls linearly with increasing partial pressure of oxygen.

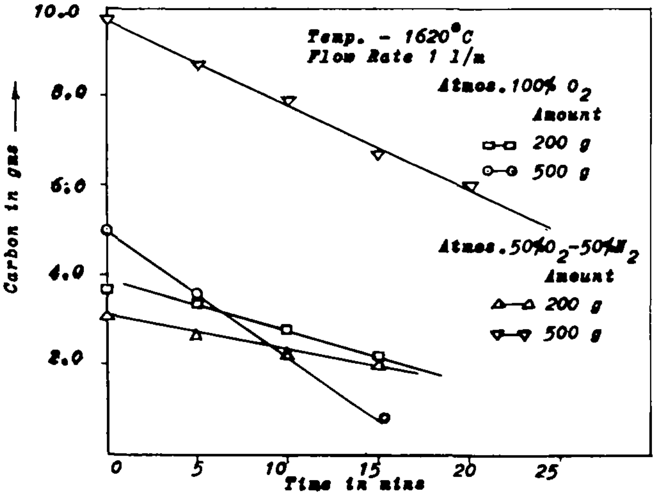

Fig. 7—Carbon concentration of the bath with time for different amount of melt.

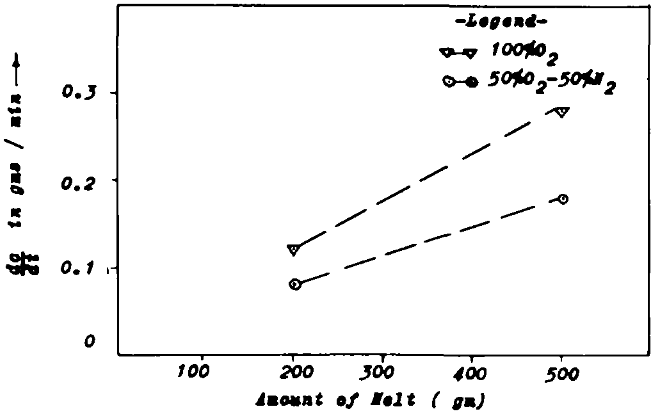

Fig. 8—Relation between the amount of metal and the rate of decarburization.

## REACTION MECHANISM

Many investigators have studied the mechanism of decarburization.[1-11] Their experimental conditions and gas aerodynamics do not differ much from the present experimental conditions. Most of them suggested that the gas-metal interface was the only reaction site.

Under the present experimental conditions with a constant gas-metal interface area it has been found that the rate of decarburization depends on the amount of alloy (Fig. 8). This observation contradicts that the gas/metal interface is the only reaction site. Iron oxide was observed just below the impinging area along with carbon boil. The critical carbon concentration at which a crust of oxide is formed and the decarburization rate becomes dependent of carbon concentration was found to be independent of partial pressure of oxygen (Fig. 12). If the reaction occurred at gas/metal interface only, the increasing oxygen partial pressure would form an oxide layer at relatively higher carbon concentration, which is not true (Fig. 12). All these observations suggest that the mechanism of decarburization under the present experimental conditions must therefore, be different.

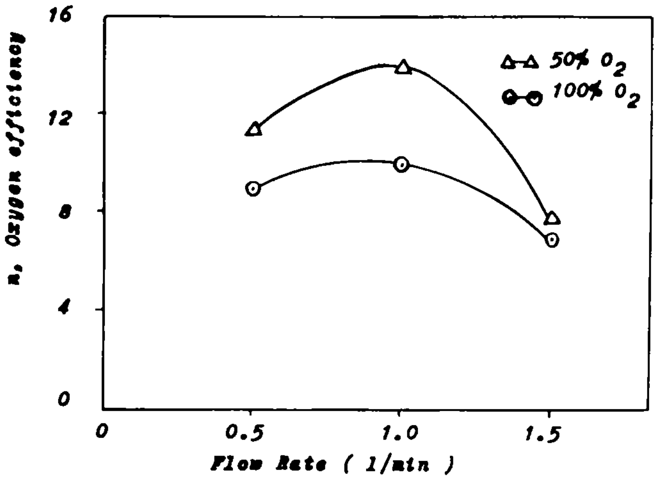

Fig. 9—Change of oxygen effective with oxygen partial pressure.

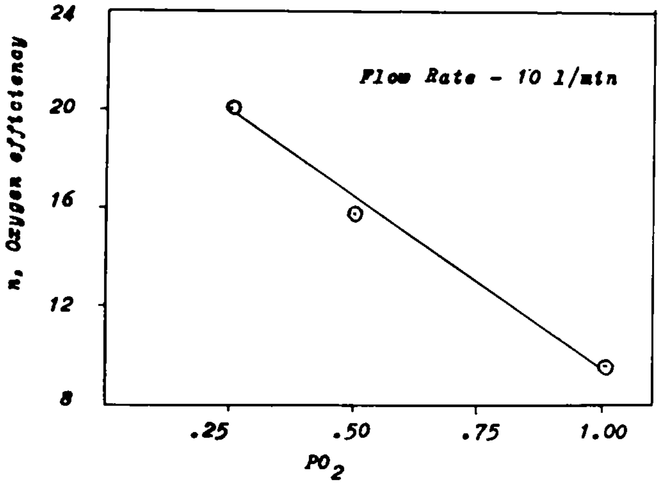

Fig. 10—Change of oxygen effective with oxygen partial pressure.

The experimental set-up with top blowing is considered basically simulating the BOF process. It is of interest, therefore, to consider whether or not the experimental results may be explained on the basis what actually may occur in the BOF process. The first question to be answered, and a very important one is, "What is the mechanism by which oxygen is received by the metal bath?" It seems most likely that at low partial pressure of oxygen, the step in the reaction of gaseous oxygen with liquid steel is chemisorption, $O_2$ molecules get attached to the metal surface probably by dissociation in the process. At high partial pressure of oxygen, due to local enrichment, the iron becomes saturated. The adsorbed oxygen reacts with the metals to form liquid oxides. The oxides may be swept across the metal surface, to dissolve at some other point where the melt is not saturated with oxygen. Hence, oxides act as a carrier for oxygen transfer.

Under a given flow rate the area over which the oxide formed, was found to be very small at 0.1 atm of oxygen, which increased and ultimately covered almost the whole metal surface with 1.0 atms of oxygen. This observation supports the above statement. Since little work has been done at low partial pressure and low flow rate (*i.e.* below 0.5 atm and 1.0 l/min), henceforth the discussion will be confined only to the high

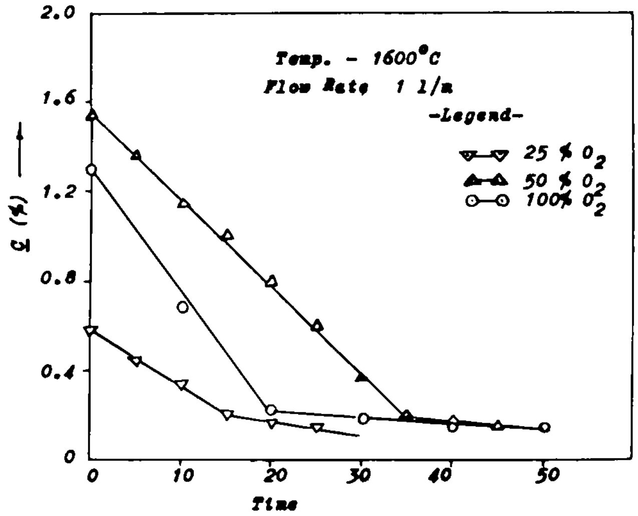

Fig. 11—Change of carbon concentration of bath with time for different partial pressure of oxygen.

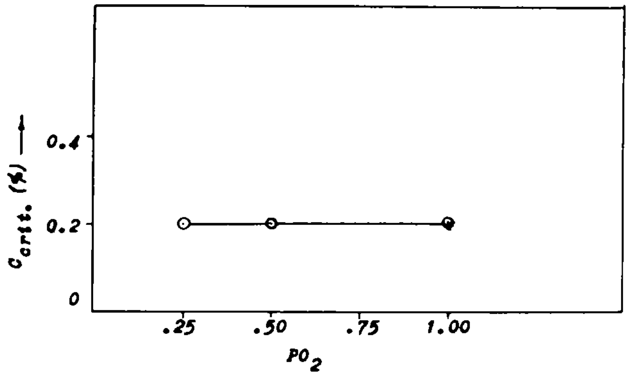

Fig. 12—Relation between the critical carbon and the partial pressure of oxygen.

partial pressure and high flow rate (*i.e.* 0.5 to 1.0 atm and 1.0 to 2.0 l/min).

The reaction may occur at Fe/FeO interface, CO bubble/metal interface or crucible-metal interface. This mechanism explains satisfactorily the observations of boiling and oxide formation.

The rate of decarburization increases with the increase in amount of melt which indicates that the rate decreases with increasing apparent specific surface area ($cm^2$/gram). This clearly indicates that the gas-metal and crucible-metal interface areas do not play the predominant role as the reaction sites for the decarburization reaction, although it is understood that the increase in total metal-crucible interface area gives rise to more probable nucleation sites. If it is assumed that the reaction occurs predominantly at the CO bubble/metal interface, the actual specific surface area in the case of larger amount of melt will be higher due to the increased resident time of bubbles inside the melt. This leads to the increased rate increased rate of decarburization with larger amount of melt (Fig. 8) and also explain the constant Cr/C ratio at all partial pressure of oxygen (Fig. 12). It may be noted here that the depth of the melt is 8 cms in case of 500 gms against 3.2 cms in case of 200 gms of melt.

Having found a satisfactory reaction mechanism the results are evaluated in effort to determine the rate controlling step.

## DIFFUSION OF OXYGEN IN THE GASEOUS PHASE

This step does not appears to be rate determining, under the present experimental conditions on the following counts.

1) The apparent activation energy of 48 ± 5.4 K cal/mol is much higher than the activation energy of 1 to 4 K cal/mol. for gaseous diffusion controlled process.

2) The rate is independent of oxygen partial pressure (Fig. 4) and flow rate (Fig. 2) which contradicts the oxygen diffusion controlled process.

3) If the reaction would have been controlled by the gaseous diffusion the amount of melt would not have any effect but in the present case it has (Fig. 8). So the possibility of gaseous diffusion control is discounted.

It is usual in investigations of this type to calculate the absolute value of the rate based on an assumed theoretical kinetic model and to compare this result with the observed rate. The equation[5] for decarburization rate, assuming a gaseous dissusion control process is given by

$$\frac{d\,\text{pct C}}{dt} = -\frac{2000}{L\rho}\cdot\frac{1}{RT}\,\frac{D}{\delta}\,\ln(1 + PO_2)$$

where $\rho$ is the density of the metal and $L$ is the depth of the bath. The plot of rate of decarburization as a function of ln $(1 + PO_2)$ is linear as shown in Fig. 13. The slope of the curve was found to be $1.8 \times 10^{-3}$ pct C/s for a bath depth of 2.98 cms. The mass transfer coefficient $D/\delta$ is equal to 1.01 cm/s. From the kinetic theory of gases, the $N_2$-$O_2$ interdiffusivity at atmospheric pressure and at 1600°C[12,14] is $D_{N_2}{:}O_2 = 2.297\ cm^2/s$. Then the values of $\delta$ will be 2.28 cm. This value appears to be most unrealistic under the present experimental conditions, were the gas stream impinges on the surface of the melt a linear velocity of 140 cms/s.

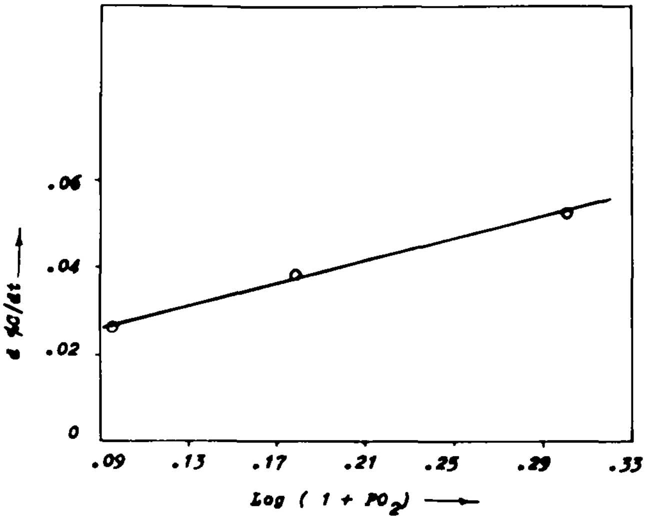

Fig. 13—Rate of decarburization as a function of log $(1+ PO_2)$ in accordance with the gas transport rate equation.

Therefore, the decarburization reaction rate does not appears to be determined by gas diffusion under the present experimental conditions.

## TRANSPORT IN THE METAL

In the present investigation all the kinetic curves were found to be independent of carbon contents (Figs. 1, 3, 5, 7), indicating a zero order reaction kinetics. The apparent activation energy 48.0 ± 5.4 K cal/mole obtained in the present investigation is much higher than 10 to 17 K cal/mole which has been reported[13] for the diffusion of carbon in iron melts. It may also be regarded that the agitation created in the present case during the escape of CO bubbles from the melt, makes carbon transport in the melt much faster a process than what would be expected in still baths.

If the rate controlling mechanism was the diffusion of oxygen in the melt then the rate of decarburization would have been directly proportional to the partial pressure of oxygen which has not been confirmed (Fig. 4). The activation energy for the diffusion of oxygen in melten Iron has been reported[15] to be 10 to 12 Kcal/mol which is much lower than the observed activation energy of 48.0 ± 5.4 Kcal/mol reported here (Fig. 6). Further, independence of decarburization rate on the flow rate of the oxidizing gas also contradicts oxygen diffusion control process.

These observations, therefore, rule out the possibility of transport of reactants in the molten metal phase as the rate determining step.

## CHEMICAL REACTION CONTROLLED PROCESS

Since all other steps involved in decarburization process have been ruled out, it appears that some chemical reaction controls the overall reaction rate. The following experimental observations also support the above statement.

1) The apparent activation energy was found to be 48.0 ± 5.4 K cal/mol
2) The rate was independent of oxygen partial pressure (Fig. 4)
3) The rate was independent of flow rate (Fig. 2)
4) The oxygen efficiency decreased with increasing flow rate (Fig. 9) and oxygen partial pressure (Fig. 10)

It has been found that the rate of decarburization in Fe-Cr-C melt is much lower than Fe-C melt[16,17] under the same experimental conditions. The activation energy of 48.0 ± 54 K cal/mol reported here, is much higher than the activation energy of 18 to 29 K cals/mol reported[16,17] in Fe-C melts. Therefore, it may be considered that reduction of oxides by carbon appears to be the rate controlling step.

## POSSIBILITY OF MIXED CONTROL

The conclusion was drawn in this study based on the assumption that one step in the reaction was slower than the rest and thus controls the overall rate of reaction. However, the slight influence of the flow rate and partial pressure (between 0.5 and 1.0 l/min of the gas) on the rate of decarburization and transition of oxygen utilization efficiency at 1 liter/min flow rate (Fig. 9) shows the possibility of the existance of a mixed control mechanism. As discussed previously the mechanism of oxygen absorption by bath change from the dissociative adsorption of oxygen to the oxygen transfer via oxides, it also indicates some possible existance of a mixed control mechanism at the transition point.

Further work in this respect is clearly indicated, particularly at low partial pressure and low flow rate.

## CRITICAL CARBON CONCENTRATION

The carbon concentration at which chromium oxidized preferentially to carbon and rate of decarburization becomes very small and dependent on carbon concentration was found to be independent of oxygen partial pressure (Fig. 12). This observation contradicts the thermodynamics consideration on which argon-oxygen stainless steel making process is based, where a greater ratio of Cr/C was obtained with decreasing partial pressure of oxygen. This is due to the different experimental condition and mechanism of decarburization. Since in the present investigations a very soft blow is used and the decarburization reaction occurs mainly at the CO bubble/metal interface inside the metal bath, the partial pressure of CO remains constant and perhaps at 1.0 atm irrespective of the partial pressure of oxygen above the bath. The constant value of CO pressure gives rise to a constant value of Cr/C ratio at all partial pressures of oxygen. This also perhaps explains the initial failure of AOD process when the argon-oxygen was blown from the top of the furnace.

In actual Ar-$O_2$ reaction vessel the condition is somewhat different. The argon-oxygen mixture is blown from the bottom. Therefore, the partial pressure changes also at the reaction surface and thereby the greater Cr/C ratio.

## CONCLUSIONS

The following conclusions are drawn on the basis of the experimental results and discussion which have been made.

1) The rate of decarburization is independent of flow rate and partial pressure of oxygen (between 0.5 to 1.0 atm of oxygen and 1.0 and 2.0 l/min of flow rate).
2) The activation energy has been found to be 48.0 ± 5.4 K cal/mol
3) Critical carbon concentration is independent of partial pressure of oxygen.
4) Decarburization reaction occurs predominantly at CO bubble/metal interface.
5) The mechanism of decarburization of iron-carbon-chromium melts appear to be controlled by reduction reaction of oxides by carbon.

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## REFERENCES

1. T. Fuji and T. Arki: *Tetsu To Hagane,* 1965, vol. 5, no. 4, pp. 290-95.
2. K. Mori and H. Nomura: *Tetsu To Hagane,* 1971, vol. 9, pp. 1468-73.
3. S. N. Paderin and S. I. Phillippov: *Izv. Vyssh. Ucheb. Zaved., Chern. Met.,* 1965, vol. 5, pp. 10-14.
4. J. B. See and N. A. Warner: *J. Iron Steel Inst.,* 1973, vol. 211, pp. 53-58.
5. J. H. Swisher and E. T. Turkdogan: *Trans. TMS-AIME,* 1967, vol. 245, pp. 602-09.
6. D. N. Ghosh and P. K. Sen: *J. Iron Steel Inst.,* 1970, Oct., pp. 911-17.
7. Ya. G. Medvedevskikh: *Russ. Met.,* 1968, vol. 4, pp. 16-21.
8. K. Ito and K. Sano: *Trans. Iron Steel Inst. Jap.,* 1968, vol. 8, no. 3, pp. 165-69.
9. K. Goto, M. Kawakami, and M. Somenv: *Trans. TMS-AIME,* 1969, vol. 245, pp. 293-98.
10. S. G. Whiteway and A. H. Hayer: *Can. Met. Quart.,* 1968, vol. 7, pp. 211-15.
11. Water Loscher: *Stahl. Eisen,* 1970, vol. 90, pp. 1516-19.
12. O. A. Hougen: *Chem. Proc. Principles,* 2nd ed., p. 988, John Wiley and Sons, London, 1962.
13. D. W. Morgan and J. A. Kitchener: *Trans. Faraday Soc.,* 1954, vol. 54, pp. 51-58.
14. *Handbook of Chem. & Phy.,* p. 3380, Chemical Publishing Co., Cleveland, Ohio, 1969.
15. K. Schwerdfeger: *Trans. TMS-AIME,* 1967, vol. 239, p. 135.
16. K. Gunji, Y. Katase, and Y. Aoki: *Tetsu To Hagane,* 1964, vol. 50, p. 1828.
17. K. C. Sahoo and D. N. Ghosh: *J. Iron Steel Inst.,* 1972, June, pp. 406-11.