KINETICS OF THE COUPLED GAS-IRON REACTIONS INVOLVING SILICON AND CARBON

by

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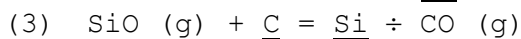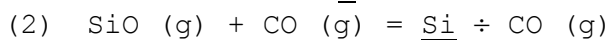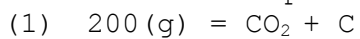School of Engineering and Engineering Technology
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ABSTRACT
The kinetic study of coupled gas-iron reactions at 1560^0 has been carried out for the system involving liquid iron containing carbon and silicon and a gas phase consisting carbon monoxide, silicon monoxide and carbon dioxide. The coupled reactions are:
(1) $200(g) = CO_2 + \underline{C}$
(2) $SiO(g) + CO(g) = \underline{Si} \div CO(g)$
(3) $SiO(g) + \underline{C} = \underline{Si} \div CO(g)$
in which reaction (3) proceeds as written for high initial carbon contents but proceeds in the reverse direction for high initial silicon contents. The rate-limiting factors seem to be the surface chemical reactions, with rate of supply of silicon monoxide probably contributing.

1   INTRODUCTION

In order to gain an insight into the nature of the coupled reactions existing between carbon and silicon when a gas phase containing carbon dioxide, carbon monoxide and silicon monoxide is in content with liquid iron at 1560^0C, the mechanisms and kinetics of these reactions must be understood. In a previous paper [1] the existence of these coupled reactions has been established and this paper reports the results of a kinetic study. The measurements reported in [1] are used here in computing relevant data needed in the discussion of the several possible rate limiting factors.

Silicon concentration in pig iron is one of the parameters that determine its quality. In practice, the silicon content of blast furnace is closely monitored [2]. The result of this research will help in the better understanding of the movement of carbon and silicon in the blast furnace.

2   LITERATURE REVIEW

Several researches have been reported on the study of the mechanism of silicon transfer into molten iron [3, 4]. There studies treat silicon transfer between slag and molten iron and none has been done involving molten iron with some initial silicon and carbon content exposed to an atmosphere of silicon monoxide and carbon monoxide. Extensive work has been done also on the thermodynamics of Fe-SiC systems [5-8) and thermodynamics of Fe-Si-C systems are now very much well understood.

Some kinetic studies have been done on silicon transfer into molten iron in contact with slag. Chipman and Fulton [9], employing a greaphite crucible in an induction furnance concluded that the slow step was the breaking of silicon- oxygen bonds. Yoshii and Tanimura [10] concluded that the silica reducion rate was limited by oxygen in the metal boundary layer at the slag-metal inter-face to be rate-limiting. Turkdogan et al [3] however pointed out that the rate of reduction from silicate metals by graphite-saturated iron is not as

slow as other investigators have shown. They maintained that in the presence
of carbon monoxide bubbles at the Slag - metal interface the rate of silicon transfer from the slag to the metal is controlled by interfacial reaction.

3. APPARATUS

An indication furnace using a motor enerator set with an excellent voltage stabilizer was used. The furnace, well described elsewhere [1], is shown in figure 1.

4. EXPERIMENTAL PROCEDURE

The main experiment entailed passing carbon monoxise through a packed bed of silica. A weight loss experiment established a range of optimum flow rates of carbon monoxide to ensure that equilibrium
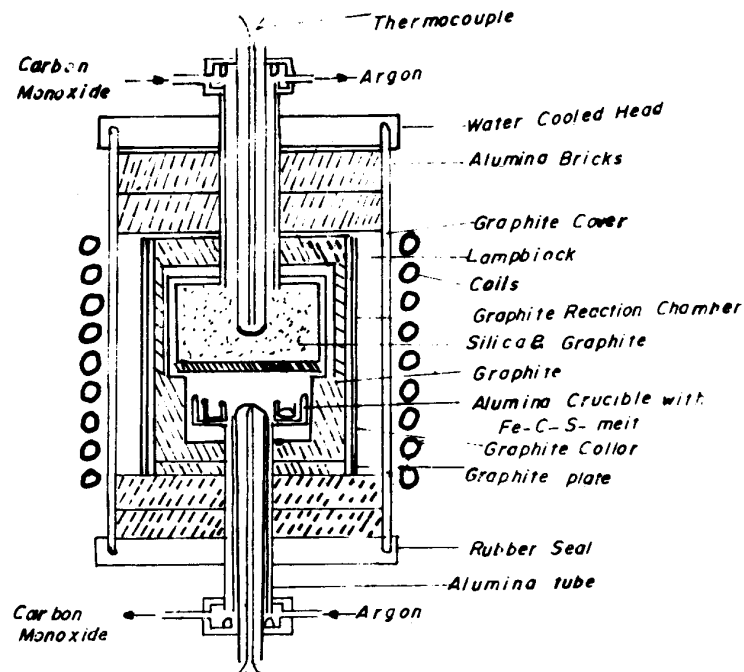

Fig. 1   Induction   Furnace

between solids and gases was reached.

For each experimental run, a charge of 5gm total weight containing a known weight percent of iron, silicon and carbon was used. A 1:1 ratio by volume of silica and graphite chips was thoroughly mixed and the graphite reaction chamber was filled with it. A thermocouple was inserted in the mixture. The system was flushed with argon passed through copper gauze furnace from the bottom of the furnace so that gases exited from the top. After 30 minutes of flushing with argon the generator was started and the furnace was heated up, at a slow

rate. Flushing with argon was still maintained until 1560 C was reached and stabilized. Flushing with argon was disctinued and a metered flow of carbon monixide was introduced from the top of the furnace into the reaction chamber the carbon monoxide acting as both a reactive gas and carrier gas. The gas exiting from t reaction chamber, containing SiO, CO and CO_2, comes in contact with the melt before exiting to the atmosphere where it was burnt to prevent CO from escaping into the laboratory. The flow of CO into the system was timed and at the end of this time the generator was turned off. Argon

flushing, by introducing the argon into the furnace from the bottom of the chamber, was again started. This removed any residual SiO and stopped any further reaction between the melt and the gaseous atmosphere. The melt solidified quickly and was later analysed for silicon and carbon. The results so obtained have been used to compute the data needed for the kinetic study.
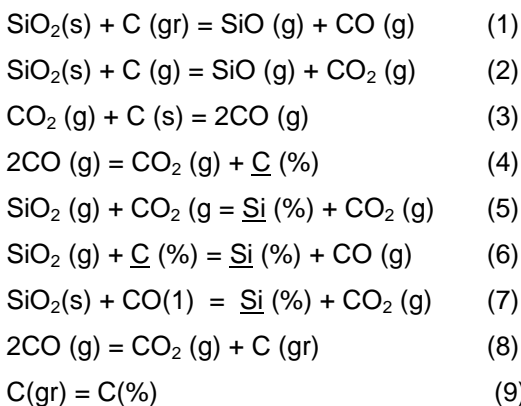
5. RATE – LIMITING FACTORS

The system studied in this investigation involves two phases; liquid and gas. The rate of pick-up of carbon or silicon may be limited by any or some of the following

(a) Rate of supply of silicon and carbon as silicon monoxide and carbon monoxide in the gaseous phase.

(b) Transport of silicon and carbon in the gaseous phase

(c) Transport of silicon and carbon in the liquid metal

(d) Chemical reaction at the interface

5.1 Relevant Reactions

The following are the relevant reactions for this study and will be referred to later

$$SiO_2(s) + C (gr) = SiO (g) + CO (g) \qquad (1)$$

$$SiO_2(s) + C (g) = SiO (g) + CO_2 (g) \qquad (2)$$

$$CO_2 (g) + C (s) = 2CO (g) \qquad (3)$$

$$2CO (g) = CO_2 (g) + \underline{C} (\%) \qquad (4)$$

$$SiO_2 (g) + CO_2 (g = \underline{Si} (\%) + CO_2 (g) \qquad (5)$$

$$SiO_2 (g) + \underline{C} (\%) = \underline{Si} (\%) + CO (g) \qquad (6)$$

$$SiO_2(s) + CO(1) = \underline{Si} (\%) + CO_2 (g) \qquad (7)$$

$$2CO (g) = CO_2 (g) + C (gr) \qquad (8)$$

$$C(gr) = C(\%) \qquad (9)$$

$$Si (1) = \underline{Si} (\%) \qquad (10)$$

Using Elliott and Gleiser [1] and JANAF [12] we obtain Table 1.

5.2 Rate of Gas Supply

The question of rate of gas supply is looked at from two viewpoints. These are gas-liquid equilibria in the system and the partial pressures of silicon monoxide and carbon dioxide in the gas phase.

5.1.1 Gas-Liquid Equilibria in the System

There are two possible extreme cases. Each case consists of equilibrium in the Sio producer and equilibrium in the melt.
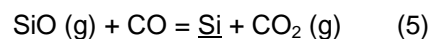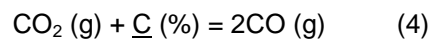
Case 1

(i) Sio producer equilibrium

$$SiO_2 (g) + CO(g) = SiO (g) + CO_2 (g) (2)$$
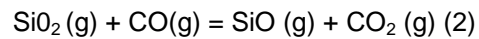
Where $PC_O = 1$ Partial pressure of carbon monoxide

$P_{sio} = Pco_2$

a_{sio2} = activity of silicon dioxide = 1

(ii) Equilibrium in the melt
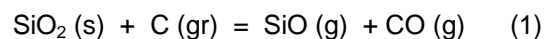
$$CO_2 (g) + \underline{C} (\%) = 2CO (g) \qquad (4)$$

$$SiO (g) + CO = \underline{Si} + CO_2 (g) \qquad (5)$$

Where $P_{sio} = P_{co2}$ as in (1) above and $Pco = 1$

Case 2

(iii)   Equilibrium in the reaction chamber

$$SiO_2 (s) + C (gr) = SiO (g) + CO (g) \qquad (1)$$

where $= a_{sio_2} = a_c(gr) = 1 \ and \ P_{co} = 1$

Table 1: Gibbs Free Energe of reacton at 1833^0K

AG^o1	AG^o2	AG^o3	AG^o4	AG^o5	AG^o6	AG^o7	AG^o9	AG^o10 (cal
14775	50027	−35252	22022	−9925	−31947	29738	−13230	−39663

(iv) Melt equilibrium

$$2CO(g) = CO_2(g) + C(s) \qquad (3)$$

$$SiO(g) + CO = \underline{Si} + CO_2 \qquad (5)$$
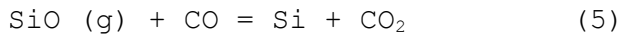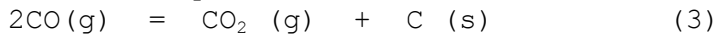
where P_{co2} is calculated from eq. (3). We note that partial pressure of carbon dioxide calculated from eq. (3) in case 1(ii) is different from that calculated in case 2(iv).

$P_{sio} = P_{CO2} = 1.04 \times 10^{-3}$ atmosphere for case 1

$P_{CO2} = 6.25 \times 10^{-5}$ atmosphere, $P_{sio} = 0.0173$ atmosphere for case 2

Thus,

For P_{sio}, max = 0.0173 atmosphere;

min = 1.04×10^{-3} atmosphere

for P_{CO2}, max = 1.04×10^{-3} atmosphere,

min = 6.25×10^{-5} atmosphere

using the values obtained for Psio, silicon pick-up for these values are

When Psio = 0.0173 atmosphere, rate of silicon pick-up = 0.0432% Si per minute

When Psio = 1.04×10^{-3} atmosphere, rate of silicon pick-up = 0.0026% Si per minute

5.3 Experimental rate of silicon pick-up

The experimental rate of silicon pick-up is higher than that possible if the actual P_{SiO} in the system is given by (P_{sio}) min. above.

But the rate is lower than that possible if the actual P_{sio} in the system is given by (P_{sio}) max. Table 2 below suggests that the actual value of P_{sio} is nearer 1.04×10^{-3} atmosphere than 0.0173. It seems then that the rate of SiO supply could be a rate-limiting factor.

5.4 Transport of silicon and carbon in gas phase.

In most high-temperature metallurgical processes involving diffusion in the gas phase and in the liquid, gas phase diffusion is not usually rate-limiting. At these high temperatures, there is also convection which enhances diffusion transport.

Hirschfelder [13] has, from kinetic theory, given the diffusion coefficient of gases according to a formula of the following type:

$$D_i \, 1.8583 \times 10^{-3} \, \frac{T^{3/2}}{p \times 16 \times 1} \frac{2}{M_i}$$

Where

D_i = coefficient of diffusion of gas species, i. (cm^2/sec)

T = Temperature (o$_K$)

M_i = Molecular weight of the gas

P = Total pressure in the system (atmospheric)

Volumes of unity and 16 have been inserted for the collision integral and the square of the collision diameter respectively.

Thus,

D_{SiO2} 1.9cm^2 /sec 1.9cm^2 /sec; DC02 1.9cm^2 /sec and
D_{CO} 2.4cm^2/sec at 1560°C.

These may be compared with the diffusion coefficients of carbon [14] silicon [15] in the liquid iron at 1600^{0}C, $D_C = 6.7 \times 10^{-S}2$/sec and $D_{si} =^-$ $^{5cm2/sec}$ 3.8x10^{-5} cm^2/sec. We note that diffusion in the gas phase is many

orders of magnitude faster than that in the liquid phase. However, the diffusion boundary layer thickness in the gas phase is bigger than that for the liquid and boundary layer thickness for diffusion is proportional to square root of diffusion coefficient. Thus the ratio of diffusion coefficient to diffusion boundary layer thickness, $\underline{D}$ in the gas phase is always greater than that in the liquid phase. Consequently diffusion of silicon and carbon in the gas phase is not likely to be rate- limiting.

5.5 Transport of silicon and carbon in the liquid phase
5.5.1 Consideration of diffusion only

Neglecting convection, we can solve Fick's equations to obtain the average concentration of the melt after a time interval, t, assuming diffusion in the liquid is rate - limiting. Newman [16] solved pick's equation for a slab of finite thickness for long time and obtained.

$$\frac{D_t}{L^2} = 0.0851 - 0.933 \log (1 - F)$$

$$where\ F = \frac{C_m - C_o}{C_s - C_o}$$

Table 2. Values of Reaction Time, using Experimental Data and the calculated Values of the Limiting cases of silicon monoxide, Assuming supply of silicon monoxide in the gas is rate-limiting

$(\%C)_o$	$(\%Si)_t$	$(\%Si)_o$	t (Min) Experimental	t (Min) for Psio = 0.017atm	t (Min) for Psio = $1.04\times10^{-3}_{atm}$
0.0	0.16	0.0	60	6	99
0.0	0.32	0.0	120	11.7	195
0.3	0.15	0.0	60	5.5	93
0.3	0.35	0.0	120	12.7	212.7
0.3	1.00	1.0	60	2.6	43.6
0.3	1.16	1.0	120	5.16	86.6
0.5	0.27	0.0	60	9.9	165
0.5	*0.36*	0.0	120	13.0	218.5
0.5	1.26	1.0	60	8.4	140.1
0.5	2.13	2.0	120	4.0	66.6

C_m = average bulk concentration after time T.
C_o = uniform initial bulk concentration
C_s = constant interface equilibrium concentration
L = half thickness of slab (cm)
D = diffusion coefficient.

In using Newman's equation above we have to approximate our melt to a slab where L is the thickness of the melt. Using time interval of one hour, C_m is calculated and compared with experimental values as shown in Table 3.

Table 3: Calculated Values of Average Composition of the Melt, Considering Diffusion only, compared with Experimental Values

Species	Time (sec)	Initial Composition	Final Composition (Calculated		Final Composition Experimental
			Case 1	Case 2	
Silicon	3600	2.0%	3.9%	19.44% %	2.11%
Carbon	3600	0.5%	0.825%	0.720% %	0.58%

From Table 3 above it is seen that experimental values are much less than the calculated values. The shows that there is another process which is slower than diffusion in the liquid.

5.5.2 Consideration of both diffusion and convection

The mass of the melt was 5 grams in each run; the volume 0.7 cubic centimeter and the melt depth 0.31 centimeter. There was also some induction stirring.

In order to get some quantitative parameters that will characterize transport in the melt, the effective diffusion boundary layer thickness is calculated from the results of some of the runs. Assumptions made are that the concentration of the solute *is* uniform in the bulk of the melt, a concentration gradient exists only in the boundary layer thickness, the surface of the melt contains the equilibrium concentration of the solute and the diffusion coefficient, D, *is* constant.

Using silicon as the solute, the rate of the solute transfer through the boundary layer thickness is given by

$$J_{si} = \frac{D_{si}}{si} \left(N_{si}^b - N_{si}^i \right)$$

Where J_{si} flux of silicon (moles/cm^{2}sec)
D_{si} = coefficient of diffusion for silicon (moles/cm^{2}sec)

N_{si}^b
= *concentration of silicon in the bulk melt (moles/cm^3)*
N_{si}^i
= *concentration of silicon in the interface (moles/cm^3)*
Si = effective diffusion boundary layer for silicon (cm)

The above formula is converted from moles to percentage to get

$$\frac{D\,(\%si)}{dt} = \frac{A_m\,D_{si}}{Vm\,si} \left((\%Si)^i - (\%Si)^b \right)$$

Where V_m = volume of the melt (cm^3)
A_m = area of the interface (cm^3)
$(\%Si)^i$ = silicon concentration at liquid-gas interface
$(\%Si)^b$ = silicon concentration in the bulk melt.
Integrating the above we get:
$$-In\{(\%Si)^i - (\%Si)^t + In\{(\%Si)^o\}$$
$$= \frac{A_m\,D_{si}}{Vm\,si}\,t$$
Where i = concentration at liquid-gas interface
t final bulk concentration after time t

o = initial bulk concentration at time t=o

Plotting the left hand side of the above equation against, time we obtain a straight line whose slope is given by slope = $\frac{A_m\,D_{si}}{Vm\,si}$ as shown in Figure 2. si is then obtained from the slope using A_m = .227cm^2
V_m = .704cm^3, D_{Si} [15] = 3.8x10^{-5}cm^2/sec at 1600^{0}c $(\%Si)^i$ = 19.94 %Si = equilibrium concentration
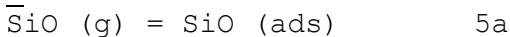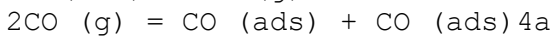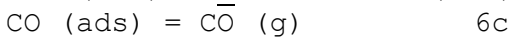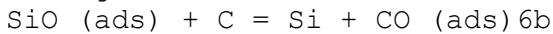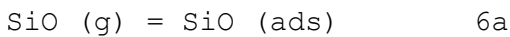
of silicon.

From the values of maximum and minimum slopes we get (Si) max = 1.43×10^{-4} cm, (Si) min = 5.88×10^{-5} cm. These value seem rather small compared with values [17,18] one would expect if transport in the liquid is rate-limiting. Thus we can conclude that transport in the liquid phase is not the rate-limiting factor.

5.6 Chemical Reaction at the Interface

The rate-limiting step may be chemical reaction at the liquid-gas interface. The following reactions of importance here:

SiO (g) + $\underline{C}$ = Si + CO (g)   (6)
$2CO$ (g) = $\underline{C}$ + CO_2 (g)   (4)
SiO (g) + $\overline{CO}$ (g) = S + CO_2 (g) (5)
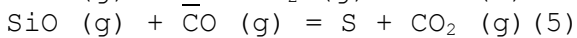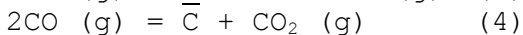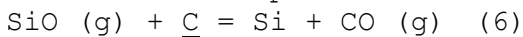
The reactions are further broken down to consider adsorption steps below:

SiO (g) = SiO (ads)   6a
SiO (ads) + $\underline{C}$ = Si + CO (ads) 6b
CO (ads) = $\overline{CO}$ (g)   6c
$2CO$ (g) = CO (ads) + CO (ads) 4a
CO (ads) + Co (ads) + CO (ads) + $\underline{C}$ 4b
SiO (g) = SiO (ads)   5a
CO (g) = CO (ads)   5b
SiO (ads) + CO (ads) = $\underline{Si}$ + Co_2 (ads) 5c
cO_2 (ads) = CO_2 (g)   5d
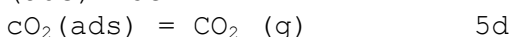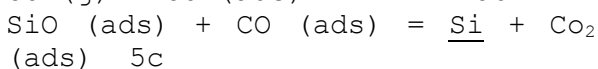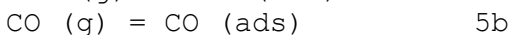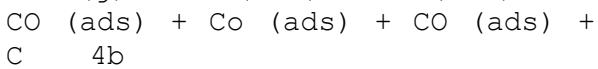
We note that reaction of elemental adsorbed species going into or coming from solution in the melt is-considered to be a fast step, [19] reaction between two adsorbed gaseous species is more difficult than reaction involving one adsorbed gaseous species and that reaction between adsorbed species is more difficult than the adsorption or desorption process itself. According to this reasoning, reactions (4) and (5) are more difficult than reaction (6) because both involve reactions between two adsorbed gaseous species.

The rate-limiting factors seem to be surface chemical reactions but the rate of supply of SiO may also have to be considered

although in this situation rate of supply of SiO is not likely to be rate-limiting. Clearly the elimination of transport of silicon and carbon in the gaseous phase and in the liquid phase quantitatively, and the use of optimum flow rates of carbon monoxide ensuring equilibrium strongly make chemical reactions the more liely rate-limiting factors.

6. CONCLUSION

The kinetic study of coupled gas-iron reactions at 1560^0C has been done for the system involving liquid iron containing carbon and silicon and a gas phase consisting or carbon monoxide, silicon monoxide and carbon dioxide. The possible rate-limiting steps-rate of supply of silicon and carbon as silicon monoxide and carbon monoxide in the gaseous phase, transport of silicon and carbon in the liquid metal and chemical reaction at the gas- liquid interface - Were each considered. It was found that surface chemical reactions to be rate - limiting and the rate of supply silicon monoxide may also have to be recognized as a contributory factor in the rate limiting processes.

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