Diffusion of Silicon and Manganese in Liquid Iron. I : Diffusion in Liquid Iron Saturated with Carbon

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Synopsis

Diffusion coefficients of silicon and manganese in liquid iron (carbon-saturated) were determined in temperature range between 1,300° and 1,600° by the method of so-called semi-infinite medium. Blank values accompanied with the measurement of diffusion in liquid state were examined and the following results were obtained :

(i) Diffusion coefficients of silicon in Fe-C (saturated)-Si(1.5%) alloys can be expressed as follows :

$$\log D \,(\mathrm{cm^2 sec^{-1}}) = -3.62 - 0.179 \times 10^4 / T,$$

activation energy $Q = 8.2 \,\mathrm{kcal/g \cdot atom}$.

(ii) Diffusion coefficients of manganese in Fe-C(saturated)-Mn(2.5%) alloys can be expressed as follows :

$$\log D \,(\mathrm{cm^2 sec^{-1}}) = -3.71 - 0.127 \times 10^{-4} / T,$$

activation energy $Q = 5.8 \,\mathrm{kcal/g \cdot atom}$.

I. Introduction

Up to the present, many studies have been made on steelmaking reactions from the standpoint of equilibrium. However, many people have come to recognize that studies on the reaction-rate are also very important.

In our laboratory the studies on diffusion of several elements in liquid iron and slags are now being performed as the first step to the investigations from the viewpoints of the reaction of rate-process, and the results of the studies on the diffusion of sulfur in liquid $CaO\text{-}SiO_2\text{-}Al_2O_3$ slags[1] and the desulphurization of liquid iron by the same slags[2],[3] were already reported.

While many studies on diffusion coefficients in solid state were reported, investigations on diffusion in liquid metals are few, especially in metals of high melting point. Diffusion coefficients of several elements in liquid iron (carbon saturated) were measured by Holbrook, Furnas, and Joseph,[4] and those of silicon and manganese were measured by Paschke, and Houttmann.[5] But their results are old and seem to be unreliable, because of the inferiority of the experimental method and the scattering of values of diffusion coefficients. Therefore, it seems to be necessary to perform further experiments.

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(1) T. Saitô and K. Kawai, Sci. Rep. RITU, A5 (1953), 460.
(2) T. Saitô and K. Kawai, Sci. Rep. RITU, A7 (1955), 402.
(3) Y. Kawai, Sci. Rep. RITU, A8 (1956), 352 ; 9 (1957), 78 ; 520.
(4) W. F. Holbrook, C. G. Furnas, and T. L. Joseph, Ind. Eng. Chem., 24 (1932), 993.
(5) M. Paschke und A. Houttmann, Arch. Eisenhüttenw., 9 (1935), 305.

In the present report the diffusion coefficients of silicon and manganese were measured by the method of so-called semi-infinite medium, and blank values accompanied with the measurement of diffusion in liquid state were examined. The concentration changes of carbon corresponding to the penetration of silicon and manganese were also examined.

II. Method of experiment

1. Specimens

Electrolytic iron and iron containing silicon or manganese were melted in the graphite crucible, and saturated with carbon at 1,550°. These melts were cast in iron moulds to make the specimens (rods 4 mm in diameter and 30 mm in length). The Fe-C rod was inserted in the lower graphite vessel shown in Fig. 1 and melted at the same temperature as that of diffusion run. The top of this vessel was
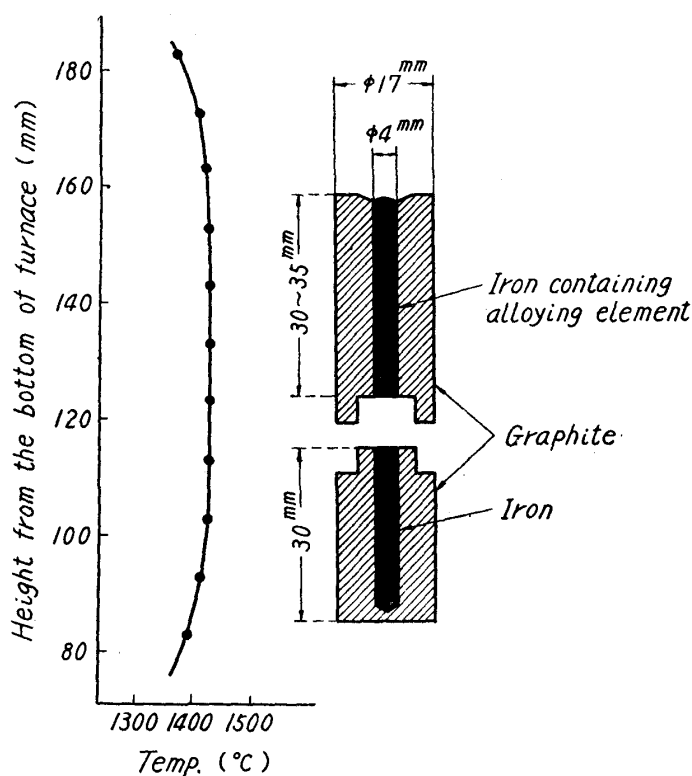

Fig. 1. Uniformity of furnace temperature and sample for diffusion run.

Table 1. Chemical composition of raw materials.

Raw materials		Composition (%)					
		C	Si	Mn	P	S	Fe
Electrolytic iron	A	0.029	0.005	0.008	tr.	0.008	rest
„ „	B	0.019	0.021	0.005	0.063	0.007	rest
Ferrosilicon	A	—	96.62	0.02	0.03	—	3.06
„	B	—	85.67	0.05	0.03	—	13.97
Ferromanganese	A	5.96	1.36	70.1	0.20	—	rest
„	B	6.65	0.32	74.70	0.22	0.011	rest

cut down and polished and joined closely at the polished surface with the upper graphite tube containing Fe–C–X rod in a couple, as shown in Fig. 1. A pair of these two rods was used as the specimen in diffusion experiment. The chemical composition of raw materials for specimens is shown in Table 1.

2. Experimental procedure

In this experiments 20 kVA Tammann furnace was used and the arrangement of diffusion specimen in the furnace is shown in Fig. 2(a). A graphite heating element of the Tammann furnace was made in the shape shown in Fig. 2(b) and

(a) Arrangement in Tammann
    furnace

A : Mirror
B : Graphite heating element
C : Cooler
D : Specimen for diffusion experiment
E : Graphite block
F : Kryptol
G : Magnesia tube

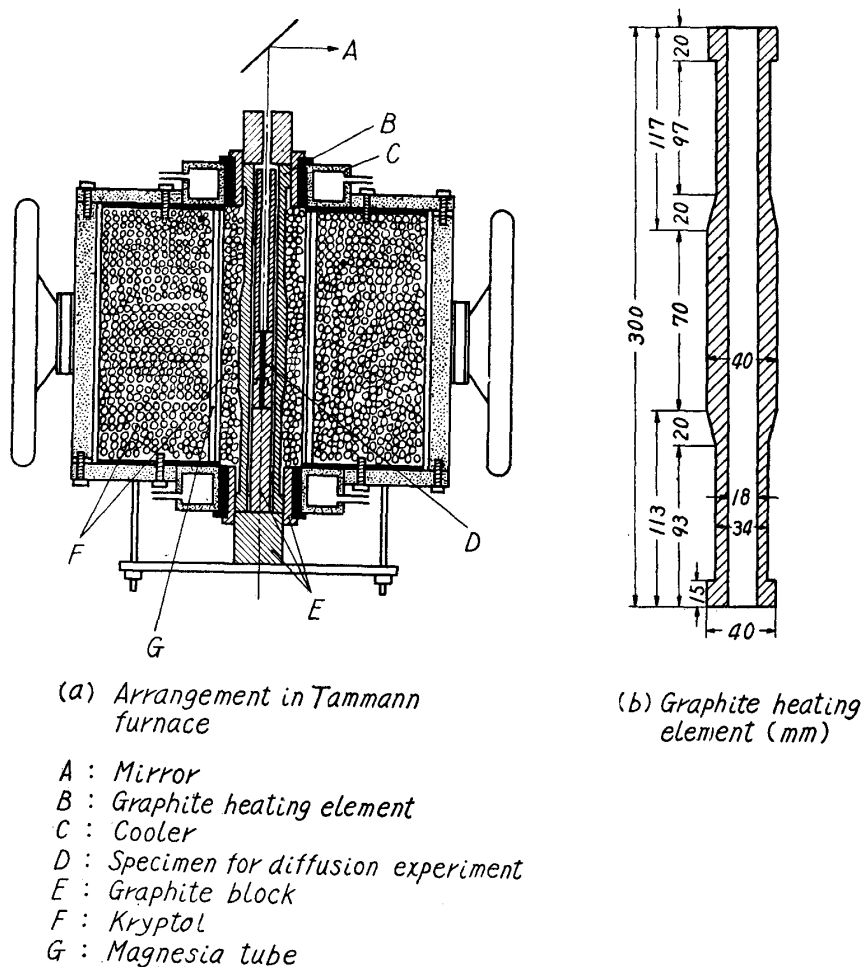(b) Graphite heating
    element (mm)

Fig. 2. Furnace

a graphite block with a bore was introduced on the diffusion specimen to improve the uniformity of temperature distribution in the furnace.

Before the diffusion run, temperature distribution in the furnace was always measured, and diffusion specimen was introduced in a proper position in the furnace. An example of temperature distribution in the furnace is illustrated in Fig. 1. Temperature was measured by an optical pyrometer which was calibrated previously by comparing with a standard Pt–Pt·Rh thermocouple.

In the apparatus the diffusion specimen was melted in two minutes and reached a desired temperature in another 3~5 minutes. After being kept at this temperature

for 80~240 minutes, the specimen was cooled in the furnace to promote graphitization. The time required for solidification was 2~3 minutes. Each 5 mm layer of the cooled specimen was lathed for chemical analysis, and the concentration-penetration curve was obtained.

The loss of manganese in this experiment was little because the specimen was melted in CO atmosphere and the manganese content was low, and the effect is considered to be negligible.
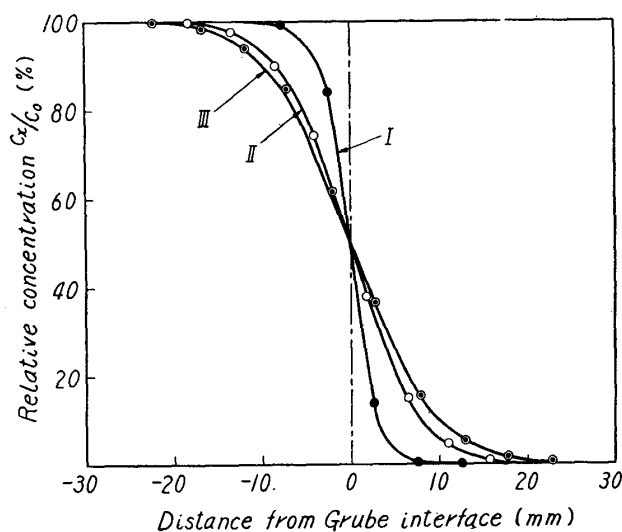
III. Blank value of diffusion experiment and results

Fig. 3. Relative concentration of silicon after diffusion.

I : 1,500°C, 0 min (8 min, above the melting point).
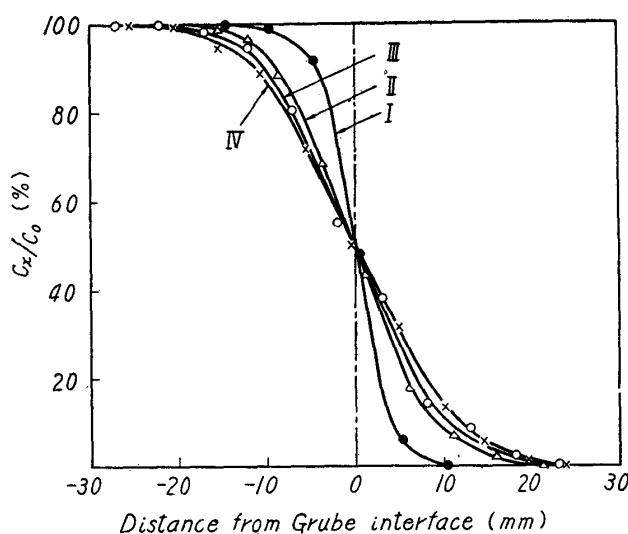II : 1,500°C, 85 min.
III : 1,500°C, 120 min.

Fig. 4. Relative concentration of manganese after diffusion.

I : 1,400°C, 0 min (8 min, above the melting point).   II : 1,270°C, 90 min.
III : 1,400°C, 120 min.   IV : 1,560°C, 120 min.

Some concentration-penetration curves are shown in Figs. 3, 4 and 5. In Fig. 5, a diffusion run of silicon at 1,600° for 0 minutes (for 8 minutes above the melting point) was intended to serve as a blank to examine the influence of disturbance during melting, thermal expansion, difference of surface tension between liquid Fe-C and Fe-C-Si metal and shrinkage during solidification on the shape of interface, because the shape of interface was more or less changed during diffusion experiment. That is, from the comparison of the blank run with others, it was found that the penetration of silicon in the blank run was greater than that predicted by the diffusion coefficient of silicon. Therefore, it was necessary to correct the concentration-penetration curve of each diffusion run. The appropriate correction method for this disturbing effect (this correction value will be called blank value of diffusion hereafter) was adopted as follows.

Heating and cooling process in this diffusion experiment is shown schematically in Fig. 6. Penetrations at ab and gh in the figure (solid state) are negligible, because diffusion coefficients in solid state
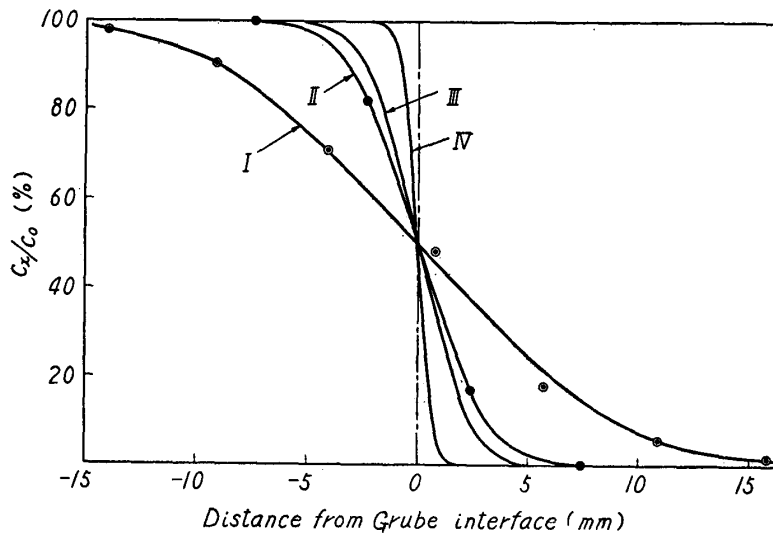
Fig. 5. Diffusion curves and correction curve in diffusion experiment.
(1,600°C, 1.5 per cent Si)

I : 100 min.   II : 0 min (8 min, above the melting point).
III : Calculated curve with use of D'''.
IV : Penetration due to disturbance during melting and freezing, (blank value of diffusion).
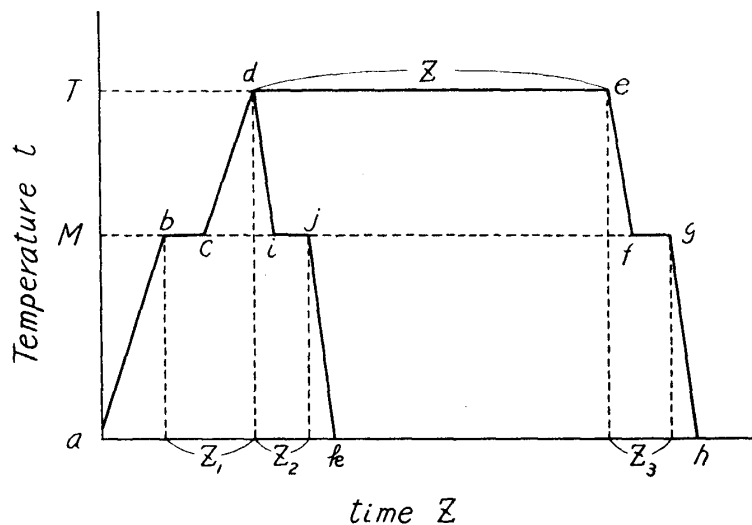

Fig. 6. Heating and cooling process of diffusion experiment.
a : Room temperature
M : Melting point of specimen
T : Temperature of diffusion

are nearly of the order of $10^{-8}\text{cm}^2\text{sec}^{-1}$ which are very small values compared with the diffusion coefficients in liquid state and, furthermore, the time of diffusion is short. In *bcd*, interface moves (less than 0.3 mm in 4 cm length) and is stirred because of the melting and expansion of specimen. After arrival at *d*, specimen is held at a desired temperature for a fixed time *de*, in which period the greater part of diffusion proceeds. At *e*, specimen is cooled by switching off the power of the furnace. In *efg*, liquid specimen shrinks and solidifies, but the disturbance in this period will be small compared with that of *bcd*.

Now, suppose that A_{Z_1}, A_{Z_2}, A_Z and A_{Z_3} are respectively the penetration distance of diffusion during the time Z_1, Z_2, Z and Z_3 shown in Fig. 6, and that B_{Z_1}, B_{Z_2} and B_{Z_3} are the penetration due to disturbance in the respective time above mentioned.

Then, amount (1) is measured in this experiment,

$$A_{Z_1} + A_Z + A_{Z_3} + B_{Z_1} + B_{Z_3} , \qquad\qquad (1)$$

where only A_Z is desired for the computation of D.

Because the temperature dependency of diffusion coefficient in liquid metal is small,[6],[7] the error will be relatively small in estimating the diffusion penetration for a short time $(Z_1 + Z_3)$ as being equal to that at the desired temperature $T°$ for the same period of time.

Assuming that the shape of interface was unchanged, the diffusion coefficient D' of silicon was calculated as the first approximation from the concentration-penetration curve held for 100 minutes (i. e., $Z_1 + Z + Z_3$) at 1,600° shown in Fig. 5, curve I and the penetration of silicon due to disturbance during melting and freezing (i. e., $Z_1 + Z_3 = 8$ minutes) was estimated by applying this diffusion coefficient D' to the blank run (curve II in Fig. 5).

Next, the interfacial disturbance obtained above was eliminated from the curve I, and the more accurate value of the diffusion coefficient of silicon D'' was calculated. Further, more accurate value of interfacial disturbance was estimated by applying this diffusion coefficient D'' to the blank run (curve II). By repeating this procedure, the interfacial disturbance curve gradually approaches a fixed one. Curve III in Fig. 5 is the calculated penetration curve due to diffusion held for 8 minutes at 1,600°, which was drawn by the use of $D'''=2.7\times10^{-5}$cm²sec⁻¹. The difference of diffusion penetration between curve II and curve III shows the more accurate interfacial disturbance,

$$B_{Z_1} + B_{Z_2} , \qquad\qquad (2)$$

which is shown in curve IV. On the other hand, the difference of the penetration distance between another experimental diffusion curve and the calculated diffusion curve obtained by the use of D''' under the same condition is equal to

$$B_{Z_1} + B_{Z_3} . \qquad\qquad (3)$$

Subtracting (2) from (1), the penetration due to diffusion only is expressed as follows:

$$A_{Z_1} + A_Z + A_{Z_3} + (B_{Z_3} - B_{Z_2}), \qquad\qquad (4)$$

There is a difference in concentration gradient between initial and final stage of diffusion run and $B_{Z_3} < B_{Z_2}$, but both B_{Z_2} and B_{Z_3} are much smaller than B_{Z_1},

(6) T. Saitô and K. Maruya, Bulletin Research Inst. Mineral Dress. Metallurgy, **9** (1953) ; 271 ; **10** (1954), 167.

(7) K. Niwa, M. Shimoji, S. Kado and Y. Watanabe, J. Japan Inst. Metals, **18** (1954), 266; 271 ; 274.

so (4) may be nearly equal to the penetration $(A_{Z_1} + A_Z + A_{Z_3})$ due to the diffusion penetration held only for 100 minutes (i.e. $Z_1 + Z + Z_3$).

Some numerical examples will be given. By comparing (2) with (3) at the relative concentration of 80 per cent of the experimental diffusion curve held for 85 minutes at 1,600°, the following results were obtained:

$$B_{Z_1} + B_{Z_2} = 0.060 \text{ cm}$$
$$B_{Z_1} + B_{Z_3} = 0.063 \text{ cm}$$

So, it is in the form $B_{Z_3} - B_{Z_2} \doteqdot 0$ in the range of the accuracy of this experiment, and (4) may be considered to be equal to $A_{Z_1} + A_Z + A_{Z_3}$.

Similar relations hold also in other experiments. For example, at 1,500°, $B_{Z_1} + B_{Z_3} = 0.58$ cm. This is about the same with the value at 1,600°. Blank value in the diffusion experiment of manganese also accords with that of silicon.

In this study the concentration of silicon and manganese were low. So, diffusion coefficients D of these elements were calculated by (5), the solution of the second equation of Fick's law taking D as constant independent of their concentration.

$$C = \frac{C_0}{2}\left\{ 1 - \psi\left(\frac{x}{2\sqrt{Dt}}\right) \right\}, \tag{5}$$

where, C is the concentration of diffusion element at a distance x from the interface after diffusion time t; C_0 is the initial difference of concentration between Fe-C-X and Fe-C specimens; ψ is the Gauss' error function.

Table 2. Diffusion coefficients of silicon in liquid iron (carbon-saturated).

Specimen	Temperature (°C)	Diffusion time(min)	Si (%)	Diffusion coefficient $D \times 10^5$ (cm² sec⁻¹)
1	1,600	100	1.43	2.6
2	1,600	100	1.50	2.6
3	1,600	85	1.58	2.8
4	1,600	61	1.43	2.8
5	1,500	135	1.65	2.5
6	1,500	101	1.71	2.5
7	1,500	100	1.98	2.4
8	1,500	62	4.19	2.2
9	1,470	96	1.59	2.1
10	1,460	97	1.47	2.3
11	1,400	175	1.35	1.9

Table 3. Diffusion coefficient of manganese in liquid iron (carbon-saturated).

Specimen	Temperature (°C)	Diffusion time(min)	Mn (%)	Diffusion coefficient $D \times 10^5$ (cm² sec⁻¹)
1	1,610	100	2.46	3.9
2	1,550	130	2.47	4.1
3	1,500	130	2.26	3.8
4	1,450	100	2.64	3.6
5	1,400	131	2.59	3.7
6	1,400	131	2.56	3.3
7	1,350	195	2.76	3.3
8	1,300	115	2.67	2.8
9	1,300	90	2.76	3.0
10	1,250	190	2.56	2.5
11	1,200	130	2.61	2.0

The calculated diffusion cofficients of silicon and manganese are given in Tables 2 and 3.

IV. Discussion

By plotting the logarithms of the diffusion coefficients of silicon and manganese against the reciprocal of absolute temperature, linear relations can be obtained as
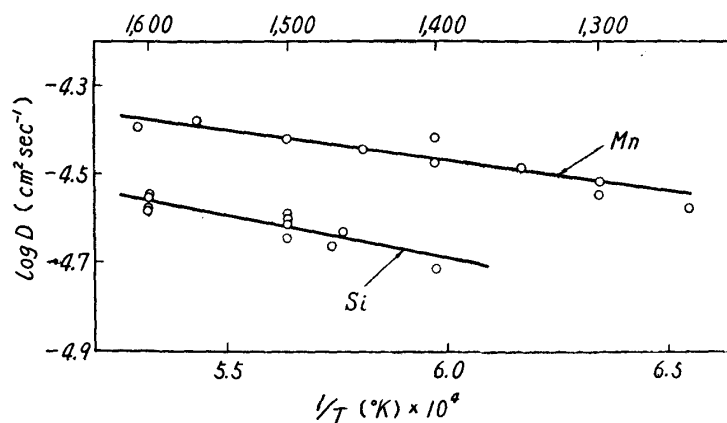

Fig. 7. Relation between diffusion coefficients of silicon and manganese and the reciprocal of absolute temperature.
○   1.5% Si : $\log D$ (cm²sec⁻¹) = −3.62 − 0.179×10⁴/T.
◉   2.5% Mn : $\log D$ (cm²sec⁻¹) = −3.71 − 0.127×10⁴/T.

shown in Fig. 7. They accord with the Arrhenius' equation, and can be expressed as follows:

i)   In the case of silicon

$$\log D \text{ (cm}^2\text{sec}^{-1}) = -3.62 - 0.179 \times 10^4/T$$

$$\text{or} \quad D \text{ (cm}^2\text{sec}^{-1}) = 2.40 \times 10^4 \, e^{-4.12 \times 10^3/T} \qquad (6)$$

activation energy $Q = 8.2$ kcal/g·atom.

ii)   In the case of manganese

$$\log D \text{ (cm}^2\text{sec}^{-1}) = -3.71 - 0.127 \times 10^{-4}/T$$

$$\text{or} \quad D \text{ (cm}^2\text{sec}^{-1}) = 1.93 \times 10^4 e^{-2.92 \times 10^3/T} \qquad (7)$$

activation energy $Q = 5.8$ kcal/g·atom.

That is, diffusion coefficients of silicon were 2.0~2.8 × 10⁻⁵cm²sec⁻¹ in the temperature range from 1,400° to 1,600°, and those of manganese were 3.0~4.1×10⁻⁵ cm²sec⁻¹ in the temperature range from 1,300° to 1,600°. These values are smaller than those of Holbrook, Furnas, Joseph and Paschke, Houttmann. The differences are probably attributed to the neglection of the blank values in diffusion experiments by other workers. The results obtained by Holbrook et al. and Paschke et al. seem to be unreliable because of the inferiority of experimental method and the scattering of the values of diffusion coefficients.

Since the solubility of carbon in liquid iron increases with temperature, the composition of the solvent is slightly different from one another at different temperatures. Therefore, the equations (5) and (6) may be regarded as equations showing the temperature dependency of diffusion coefficients of silicon and manganese in liquid iron containing about 5 per cent carbon.

Because the melts are saturated with carbon, the concentration of carbon in equilibrium with silicon or manganese will change with the penetration of these diffusing elements. The distribution of carbon content accompanied with the penetration of silicon (Fig. 8) and manganese (Fig. 9) are shown together with their concentration-pentration curves. In these figures, solid line ($C_{exp.}$) shows the values of carbon analysis and dotted line ($C_{estim.}$) is the estimation of carbon content from the solubility curves of carbon in liquid Fe–Si–C (saturated)[8] and Fe–Mn–C (saturated) alloys.[5]

As shown in these figures, C_{exp} is not equal to C_{estim}, but corresponds to C_{estim}. The difference may be attributed to the dissimilarity of cooling conditions. To determine the solubility curve of carbon in melts, specimens are quenched into watercooled moulds of copper after melts are saturated with carbon at a fixed temperature. In this experiment, however, specimens were cooled in the furnace. It is well-known that the diffusion-rate of carbon[9] in austenite is about 70 times as large as that of silicon or manganese at temperatures from 1,100° to 1,200°. So, it may be suggested that the diffusion rate of carbon in
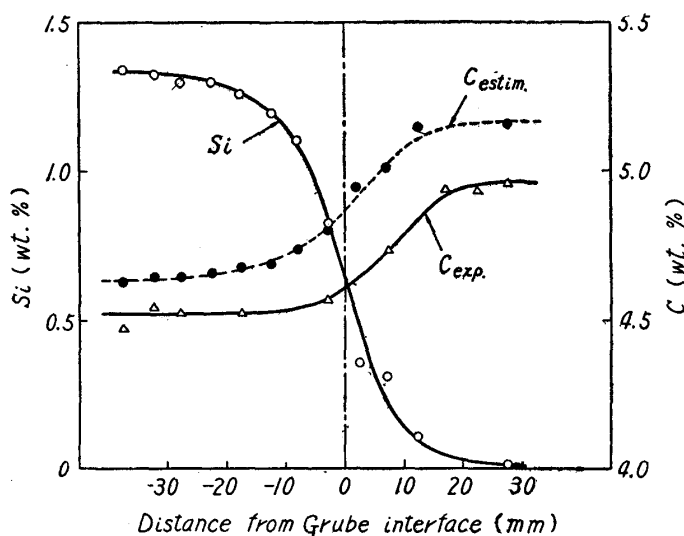

Fig. 8. Relation between diffusion of silicon and concentration of carbon. (1,500°C, 120 min)
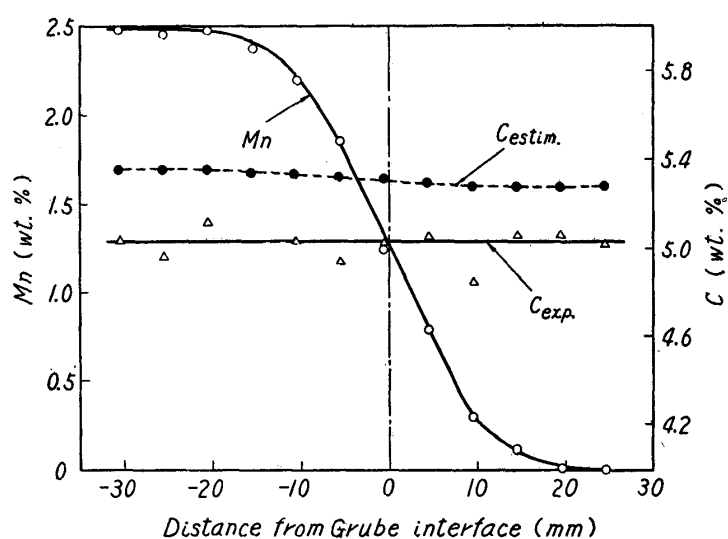
Fig. 9. Relation between diffusion of manganese and concentration of carbon. (1,560°C, 120 min)

(8) J. Chipman, R.M. Alfred, L.W. Gott, R.B. Small, D.N. Wilson, C.N. Thomson, D.L. Gurney and J.C. Fulton, Trans. A.S.M., **44** (1952), 1215.

liquid iron is larger than that of silicon or manganese, and carbon diffuses in the state of quasi-equilibrium with the pentration of silicon or manganese.

The present results are compared with those already published in Table 4.

Table 4.　Diffusion of various elements in liquid iron.

Diffusion element	Specimen	Diffusion coefficient $D \times 10^5 (cm^2 sec^{-1})$ at 1,550°C	Activation energy of diffusion (kcal/g·atom)	Workers
C*	Fe-C unsaturated	6.0	10	Morgan, Kitchener[9] (1954)
Co*	pure iron	4.6	11	Morgan, Kitchener[9] (1954)
S*	Fe-C saturated	3.5	7.5	Kawai[3] (1955)　[10]
P	pure iron	4.7	8	Maekawa, Nakagawa (1955)
S	pure iron	4.5	8.6	Kawai[3] (1956)
Si	Fe-C saturated	2.5	8.2	Saitô, Maruya
Mn	Fe-C saturated	4.0	5.8	Saitô, Maruya

　*　Radioisotope

Diffusion coefficients of silicon and manganese and their activation energies were both much the same as those of cobalt,[9] sulfur[3] and phosphorus[10] investigated already in pure liquid iron.

Summary

Studies on the diffusion of silicon and manganese in liquid iron (carbon saturated) were carried out in temperature range between 1,300° and 1,600° by the method of so-called semi-infinite medium.

An appropriate method was adopted for the calculation of diffusion coefficient in liquid state and the following results were obtained :

(i)　Diffusion coefficients of silicon in Fe-C (saturated)-Si (1.5 per cent) alloy can be expressed as follows:

$$\log D \ (cm^2 \ sec^{-1}) = -3.62 - 0.179 \times 10^4/T,$$

or　　　　$$D \ (cm^2 \ sec^{-1}) = 2.40 \times 10^{-4} e^{-4.12 \times 10^3/T},$$

activation energy　　　$Q = 8.2$ kcal/g·atm.

That is, diffusion coefficient D between 1,400 and 1,600° were $2.0 \sim 2.8 \times 10^{-5} cm^2 sec^{-1}$.

(ii)　Diffusion coefficients of manganese in Fe-C (saturated)-Mn (2.5 per cent) alloy can be expressed as follows:

$$\log D \ (cm^3 \ sec^{-1}) = -3.71 - 0.127 \times 10^{-4}/T,$$

or　　　　$$D \ (cm^2 \ sec^{-1}) = 1.93 \times 10^{-4} e^{-2.92 \times 10^3/T},$$

activation energy　　　$Q = 5.8$ kcal/g·atom.

That is, diffusion coefficients D between 1,300° and 1,600° were $3.0 \sim 4.1 \times 10^{-5} cm^2 sec^{-1}$.

The distribution of carbon content accompanied with the penetration of silicon and manganese was also examined.

(9)　D. W. Morgan and J. A. Kitchener, Trans. Faraday Soc., 50 (1954), 51.
(10)　S. Maekawa and Y. Nakagawa, Report at the Kanazawa Meeting of Japan Institute of Metals, October, 1955.