Interdiffusion in Molten Fe-C Alloy*

By Yoshimoto WANIBE,** Shoji TAKAI,** Takeshi KOJIMA***
and Hiroshi SAKAO**

Synopsis

The isothermal interdiffusivity was studied for molten binary Fe-C and quasi-binary Fe-C-Si alloys at 1 550°C by the diffusion couple method. The experiment was carried out by using a narrow alumina tube as a diffusion chamber under refined argon atmosphere in an electrical resistance furnace. The results can be summarized as follows;

$$\begin{aligned} D_C &= (1+0.24[\%C]) \times 10^{-4} \text{ cm}^2/\text{s} & (0.3 \sim 3\%C) \\ D_{Si}^I &= 1.0 \sim 1.4 \times 10^{-4} \text{ cm}^2/\text{s} & (0.5\%C, 0 \sim 1.34\%Si) \\ D_{Si}^C &= 6.9 \times 10^{-4} \text{ cm}^2/\text{s} & (0.3\%C, 0.4\%Si) \end{aligned}$$

where D_i^j is the interdiffusion coefficient of i in the quasi-binary Fe- i - j alloy. Discussion was held on the experimental procedure as well as the results investigated. Good agreement is concluded between the present measurement and some reference results, which have been measured by the different method and estimated by the other suitable way.

I. Introduction

The measurement of diffusion in liquid makes a useful contribution toward the study on liquid structure or toward the kinetic analysis of heterogeneous reactions, as well as those of viscosity, electric conductivity, etc. In steelmaking, the most reactions are heterogeneous at high temperature, so the chemical reactions themselves seem to proceed fast at interface. In the most cases, since the mass transfer to or from the interface is the rate-controlling step of the overall reaction, the diffusion in boundary-layer at interface is an important phenomenon. Thus, in order to clarify the mechanisms or the rates of the metallurgical reactions, it is necessary to know the diffusion coefficients of various elements in molten iron. It is, however, safe to say that the difficult measurement at high temperature has not yet satisfied the exact determination of these coefficients in spite of urgent requirement.

A good many reports have been published on the diffusion coefficient of carbon in molten iron as the most fundamental reference.¹⁻⁸⁾ By comparison, however, no obvious coincidence has been able to be obtained among those results, especially the concentration-dependencies of the diffusion coefficients.

In the present work, therefore, an experimental re-examination was carried out by means of the diffusion couple method to determine precisely the diffusion coefficient of carbon in molten iron, and the concentration-dependency. Moreover, an additional research was made into the interdiffusion in the quasi-binary Fe-C-Si system.

II. Experimental Method

1. Experimental Principle

Based on the Fick's second law for binary non-steady diffusion, the Boltzmann-Matano's method can be generally used to determine the concentration-dependent diffusion coefficient from the composition distribution measured. This method, however, brought no satisfactory results in the present investigation for the interdiffusion in molten Fe-C system due to the following experimental reasons:

- 1) no suitable means to obtain the sound diffusion couple with large concentration difference,
- 2) difficulty to determine precisely the tangent line on the concentration distribution curve measured, and
- 3) no exact ways to estimate the real diffusion time.

In the present work, therefore, the measurement was carried out by selecting the suitable initial concentration difference in the diffusion couple so that the diffusion coefficient D could be approximately supposed to be a constant and the measurement accuracy could be kept as high as possible.

For a constant D , the one-dimensional Fick's second law is

$$\partial C / \partial t = D \partial^2 C / \partial x^2 \quad \dots\dots\dots(1)$$

Under the initial and boundary conditions;

$$\begin{aligned} C &= C_A & (x < 0, t = 0) \\ C &= C_B & (x > 0, t = 0) \\ C &= C_A & (x = -\infty, t > 0) \\ C &= C_B & (x = +\infty, t > 0), \end{aligned}$$

Eq. (1) can be solved in

$$\frac{C - C_A}{C_B - C_A} = \frac{1}{\sqrt{2\pi}} \cdot \frac{1}{\sigma} \int_{-\infty}^x \exp\left(-\frac{x^2}{2\sigma^2}\right) dx \quad \dots\dots\dots(2)$$

where σ is the statistical variance of the diffusing distance of an element which has a following relation,

$$\sigma^2 = 2Dt \quad \dots\dots\dots(3)$$

Equation (2) also means that the curve of the relative concentration distribution corresponds to the one of the cumulative relative frequency of the normal distribution with a mean value of 0 and a variance of σ^2 . Thus, σ can be easily obtained from the straight

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** Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464.

*** Tokai Rika Co., Ltd., Nishibiwajima-cho, Nishikasugai-gun, Aichi 452.

line of the relative concentration distribution plotted in a normal probability paper. Then the diffusion time-dependency of σ can determine the diffusion coefficient through Eq. (3).⁹⁾

2. Experimental Apparatus and Procedures

1. Experimental Apparatus

An electric resistance furnace was used for the experiment (Fig. 1). A $56\phi \times 55\phi \times 400$ mm molybdenum tube heater was surrounded in the upper-, the lower- and the outer-sides with the radiation shields of molybdenum plates, and protected against the oxidation by a gas stream of Ar-7% H_2 mixture.

25 molybdenum disks of $33\phi \times 12\phi \times 0.5$ mm were also furnished within a $40\phi \times 35\phi \times 800$ mm alumina furnace tube ($Al_2O_3 > 99.5\%$) to obtain a broader uniform temperature zone. A $6\phi \times 4\phi$ or a $8\phi \times 5\phi \times 300$ mm alumina tube ($Al_2O_3 > 99.5\%$) was used for the diffusion cell on account of the reduced convection in the molten alloy and of the weak interaction between the alloy and the inside wall.

The temperature was measured with a Pt-6%Rh/Pt-30%Rh thermocouple inserted through the top of the furnace. A PID-type controller regulated the furnace temperature within $\pm 3^\circ C$ in combination with another W-5%Re/W-26%Re thermocouple whose junction was placed near the outside wall of the heater. The uniform temperature zone was obtained to be about 100 mm long at $1550^\circ C \pm 3^\circ C$.

2. Specimen for the Diffusion Experiment

About 500 g electrolytic iron (C, Mn, Cu, Si, S < 0.004%, P < 0.003%) was melted in a magnesia crucible under refined Ar stream by induction heating, and reduced at $1600^\circ C$ for about an hour with H_2 -Ar (1:1) mixture. The furnace atmosphere was again replaced with the Ar gas, then the suitable amount of carbon (and also silicon for the quasi-

binary experiment) was alloyed so as to compose the given concentration. After a while waiting for the uniform composition, the alloy was sucked into a silica tube (5 mm I.D.) and quenched in water.

A preliminary experiment showed no sound coupling of the specimens with 0.5% C after a 20 min heating at $1550^\circ C$. The reason seems to be due to the bubbling of CO formed with the reaction between the Fe-C alloy specimen and the easily reducible impurities in the alumina diffusion cell, such as SiO_2 , etc. A good result could be rewarded by the remedial addition of a small amount of aluminum during the alloying. Moreover, the thorough replacement of the atmosphere in the diffusion cell with the refined Ar could reduce the amount of the additive aluminum to less than 0.01% by repeating the procedures for degassing and Ar-fulfillment in the cell several times one after the other just before the diffusion experiment started.

For the diffusion measurement, the sucked specimen was polished to have the diameter suitable for the cell and cut to be 40 mm long.

3. Composition of the Diffusion Couple

The initial concentration difference between the specimens coupled was determined through the following selection steps:

(1) The optimum initial concentration difference was calculated throughout the experimental concentration range to minimize the measurement error based on the analytical accuracy ($\pm 0.01\%$ C) and the concentration-dependency of the diffusion coefficient (estimated by the Darken's equation⁴⁾).

(2) The concentration difference was determined so as to bring the couple into sound contact from the comprehensive preliminary experiments carried out in the light of the results of (1).

Also the couple was composed of the specimen with lower density in molten state as the upper half and the one with higher density as the lower half in order to prevent the convection due to the density difference during the diffusion experiment.

4. Experimental Procedure

The diffusion cell containing the specimens was inserted into the furnace previously heated at $1550^\circ C$ under the refined Ar stream after the thorough replacement of the atmosphere in the cell with the refined Ar according to the above-mentioned procedure. The diffusion experiment was carried out for a given duration, then the cell was rapidly taken out of the furnace and quenched by the Ar-blowing method. The couple was sawed into disks at a constant interval with a micro-cutter. The quantitative analysis of such disks gave us the solute concentration distribution.

The concentration of carbon was determined by the coulometric titration method, and that of silicon by the molybdenum blue absorption spectrophotometric method (JIS-G1212).

III. Experimental Results

As an example, Fig. 2 shows the concentration distribution curve in the couple with the initial com-

Fig. 1. Schematic illustration of the furnace used for diffusion experiment.

positions of Fe-0.3%C/Fe-0.5%C solidified after a 30 min diffusion. The accurate determination of the diffusion coefficient, however, requires the curve based on the actual diffusing distance realized at the experimental temperature. Therefore, there must be a correction of the distance measured in the solidified couple from the viewpoint of the contractions of the couple and the alumina cell during the solidification and the cooling. The couple cooled was observed to be in close contact with the inside wall of the cell without shrinkage cavity. So it may be reasonably presumed that the cooling couple solidifies and contracts with filling the diffusion cell. Here the couple length or the diffusing distance was corrected on the assumption that the diameter of the couple always corresponded equally to that of the cell at any temperature throughout the experiment, *i.e.*, from the experimental to the room temperature. 7.8 g/cm³ was used for the density of the couple at room temperature, regardless of the little effect of the composition changes in carbon and silicon. According to L. D. Lucas' measurement,¹⁰⁾ 6.9 g/cm³ is the mean density of the Fe-C and Fe-Si alloys averaged over the present experimental composition range at 1550°C where the composition-dependence is negligibly small ($\pm 1.5\%$). The thermal expansion coefficient of alumina is $8.0 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ (in the catalogue of Nippon

Kagaku Togyo Co., Ltd.). From these data, then the actual diffusing distance could be evaluated to be 1.09 times as long as that measured at the room temperature after the experiment.

The concentration distribution curve corrected in the above manner was re-plotted in a normal probability paper as graphically shown in Fig. 3, where the ordinate represented the relative concentration (%) and the abscissa the distance from an end of the couple. The value of σ was obtained from the gradient of the straight line on this plot. Thus, the diffusion coefficient could be calculated from the slope of the linear relation between the values of σ^2 obtained and the apparent diffusion time according to Eq. (3). Figure 4 shows such an example and the calculated results are summarized in Table 1. The diffusion of carbon becomes faster in the higher con-

Fig. 2. Concentration profile in the couple Fe-0.3%C/Fe-0.5%C diffused at 1550°C for 30 min.

Fig. 3. Concentration profile on a probability paper re-plotted from Fig. 2 to estimate σ .

Fig. 4. Time-dependency of σ^2 for the determination of D_C in the couple shown in Figs. 2 and 3.

Table 1. Results of Fe-C binary, Fe-C-Si quasi-binary systems.

Couple No.	Composition of couple (%)				$D_C \times 10^4$ (cm ² /sec)	Inner diameter of diffusion chamber (mm)
	(C _C) _A	(C _C) _B	(C _{Si}) _A	(C _{Si}) _B		
1	0.47	0.31	0	0	1.1	5
2	0.70	1.10	0	0	1.3	5
3	1.06	1.80	0	0	1.4	4
4	1.50	2.20	0	0	1.3	5
5	1.98	2.89	0	0	1.5	4
6	2.40	3.37	0	0	1.7	5
7	2.62	3.68	0	0	1.8	4
Q-1	0.27	0.75	0.49	0.49	1.13 (D_C^{Si})	5
Q-2	0.27	0.75	1.03	1.03	1.33 (,,)	5
Q-3	0.27	0.75	1.34	1.34	1.37 (,,)	5
Q'-1	0.29	0.51	0.81	0.81	1.0 (D_C^{Si})	5
Q''-1	0.31	0.29	0	0.81	0.69 (D_{Si}^{C})	5

centration range and has a tendency to be accelerated by the addition of silicon.

IV. Discussion

1. Concentration-dependency of the Diffusion Coefficient of Carbon

Figure 5 is a plot of the diffusion coefficient of carbon D_C determined in the present binary system against the representative composition of the couple [%C] (the mean initial concentration in the specimens composing the couple). Here the dispersion range is also presented according to the following estimation:

- 1) The investigation on how the value of σ^2 scatters by the deviation in the gradient of the concentration distribution straight line in the normal probability paper within the individual measurement
- 2) The estimation on how such scattered σ^2 conduces to the dispersion of the diffusion coefficient through the variation in the gradient plotted against the apparent diffusion time

The experimental function of the concentration dependent diffusion coefficient obtained by the least square method is

$$D_C = (1.00 + 0.24[\%C]) \times 10^{-4} \text{ cm}^2/\text{sec} \dots\dots\dots(4)$$

as shown by a line in Fig. 5. Moreover, the 95% confidence limit was estimated with the calculation of the variation of the D_C ¹¹⁾ when this linear regression relation was applied for any [%C]. The results are shown by two one-dotted chains in the same figure.

Now the detailed observation of Fig. 5 has resulted in a remark: while the value of D_C at about 1.8% C satisfies Eq. (4) within the dispersion of the measurement, it is beyond the 95% confidence limit. Since each mark in Fig. 5 represents a mean value of the several measurements as shown in Fig. 4, if the deviation signifies much in the relation against the concentration of carbon, there seems to be a discontinuity in the straight line at about 1.8% C.

The existence of such a discontinuity in molten Fe-C alloy has been observed in the measurements of the density,¹²⁻¹⁵⁾ the viscosity¹⁶⁻²⁰⁾ and the surface tension.²¹⁾ There has been an X-ray analysis of molten Fe-C alloy structure supporting the observation, too.²²⁾

On the other hand, a recent more trustable X-ray

structure analysis has denied the above result.²³⁾ As for the viscosity of molten Fe-C alloy, the unusual behavior might be explained by the effect of very small difference in the concentration of co-existing oxygen (0.001~0.006%).²⁴⁾

At present, no conclusion can be drawn about whether the discontinuity at about 1.8% C in the present study is significant or not, and if so, what causes it. The solution of the problem is in need of an idea about a new measurement method with much higher accuracy.

2. Diffusion Time and Mixing Disturbance

For the determination of diffusion coefficient, the present method used requires only the apparent diffusion time instead of the actual one. But, since the knowledge of the actual diffusion time is very much interesting and important information for the further development in this kind of investigation, a few discussions have been considered as follows:

First, the necessary period from the insertion of the couple into the uniform heating zone to the melting was examined in supplementary experiments. 2.5 min heating did not fuse completely the couple, did only partially the interfaces. This has a perfect coincidence with the results which the authors have already reported.²⁵⁾

According to Y. Ono and S. Matsumoto,⁹⁾ the plot of σ^2 against each apparent diffusion time has to be a straight line with the assumption of a steady mixing disturbance. In Fig. 4 shown as an example, the intersection between the time-axis and the extrapolated straight line can be taken for the starting time of the diffusion, integrated with the period from the setting of the diffusion cell in the heating zone to the moment when the couple temperature reaches the experimental one through the melting (a negative correction for the apparent diffusion time) and the equivalent diffusion time due to the mixing disturbance during the melting and the solidification (a positive correction). In the present investigation, the beginning time ranged in between -2.5 min and +1.5 min with a mean value of -1.0 min.

From the above two informations there seems to be a certain mixing in the couple during the melting and the solidification.

No distinction was found in the result of the further investigation on the effect of the different cell size, 4 ϕ mm and 5 ϕ mm I.D. (Table 1).

3. Comparison with References

The interdiffusion coefficients D_C in molten Fe-C system which have been reported are summarized in Table 2 and shown in Fig. 6 in comparison with the present work. The diffusion couple method has been used only in the present investigation. The results are plotted together with the previously mentioned dispersion range and regression straight line in that figure. The present results show a good agreement not only with the data measured by mean of the different method (the capillary-reservoir method) by B. M. Lepinskikh *et al.*,³⁾ Tu. A. Savelev *et al.*⁶⁾ and

Fig. 5. Concentration-dependency of D_C at 1550°C.

Table 2. Diffusion coefficient of C in molten binary ferro-alloys.

Investigators	Measuring technique	wt% C	Temperature (°C)	D_C (cm ² /sec)		$D_C \times 10^4$ at 1550°C (cm ² /sec)
				D_0 (cm ² /sec)	Q (kcal/mol)	
Grace-Derge ¹⁾	C-R	1.63~Sat.	1410~1600	1.6×10^{-2}	14.0	3.2
		2.53~Sat.	1340~1505	3.9×10^{-2}	16.0	4.7
Heisterkamp-Löhberg ²⁾	C-R	2.55~Sat.	1350~1500	8.27×10^{-3}	12.0	3.0
Lepinskikh <i>et al.</i> ³⁾	C-R	2	1400~1500	1.74×10^{-3}	9.2	1.4
Mori-Nomura ⁴⁾	Evaluation of Literature	0.0~2.5	1350~1600	$1.74 \times (1+0.52\%C) \times 10^{-3}$	11.3	1.8 (2.5%C)
Kosaka-Saito ⁵⁾	D-R (Solid Fe)	4.15	1190~1510	1.76×10^{-2}	15.0	2.8
Savelev <i>et al.</i> ⁶⁾	C-R	2.96	1430~1600	1.1×10^{-2}	15.0	1.8
Goldberg-Belton ⁷⁾	C-R & D-R	0.0~Sat.	1560	$(1.1+0.21\%C) \times 10^{-4}$		1.8 (3.5%C)
Ono-Ezaki ⁸⁾	C-R	1.73~Sat.	1350~1550	$2.5(\pm 1.7) \times 10^{-3}$	8.8 (± 2.3)	2.2 (± 0.3)
This work	D-C	0.31~3.68	1550	$(1.00+0.24\%C) \times 10^{-4}$		

C-R=capillary-reservoir method, D-C=diffusion couple method, D-R=estimation from resolution rate

Fig. 6. Illustration of Table 2 for the comparison.

Y. Ono and Y. Ezaki,⁸⁾ but also with the one estimated in combination with the measurement through the capillary-reservoir method and the calculation based on the dissolution rate of carbon into molten iron by C. D. Goldberg *et al.*⁷⁾ Also, the results have a relatively good coincidence with the following equation;

$$D_C = (0.76 + 0.33 [\%C]) \times 10^{-4} \text{ cm}^2/\text{sec} \dots\dots\dots (5)$$

which has been applicably modified for the present experimental condition ($C < 3.0\%$, at 1550°C) by the re-calculation of the K. Mori and H. Nomura's equation for the estimation of D_C ,⁴⁾ dependent upon the self diffusion coefficients of Fe and C and the activity coefficient of carbon in molten iron based on the Darken's equation.

4. Comparison with the Diffusion Coefficients of the Other Elements in Molten Iron

Many authors²⁶⁻³³⁾ have tried to formulate theo-

retically the diffusion in molten iron through the fluctuation theory, *etc.*, and or to discuss empirically it based on the indirect estimations in colloidal science, hydrodynamics and so on. However, there has been no satisfaction yet.

Recently, the diffusion coefficient in molten iron has been related to the free energy of solution^{34,35)} or to the atomic radius.³⁵⁾ Thus, the present result was compared with both the relations; the former showing in Fig. 7 and the latter in Fig. 8, where the present data was figured as a region totalized throughout the whole concentration range of the experiment. Both the relations seem to be well conserved in the present investigation in spite of a certain uncertainty due to the temperature difference (50°C). These relationships, however, should be further investigated.

5. Quasi-binary Diffusion Coefficient

There have been no references about the effect of the third element on the diffusion coefficient of carbon in molten iron in spite of practical importance. This is owing not only to the requirement of much more accuracy in ternary measurement than in binary one, but also, exactly speaking, to the inadequacy of the treatment for ternary diffusion as the effect of the third element on binary one.

Ternary diffusion requires actually the very complicated analysis written in details in the other reports,^{36,37)} and the result has a disadvantage not to be directly applicable to the analysis for reaction kinetics. For all practical purposes, however, the effect of silicon or carbon on the diffusion coefficient of carbon or silicon in molten iron was investigated, respectively, although they were theoretically problematic.

First, the diffusion of carbon for the quasi-binary Fe-C-Si (a constant) system was examined in the couple with the same initial concentrations of silicon. The concentration profiles of silicon were checked up to be almost same within the range of the analytical error in the couples before and after the diffusion experiment. Then, the diffusion coefficient of carbon D_C^{Si} was obtained at each concentration of silicon. In

Fig. 7. Relation between the diffusivity and the standard free energy of solution for various solute elements in liquid iron at 1 600°C, after Y. Kojima *et al.*³⁵⁾

Fig. 8. Relation between the diffusivities and the radius of diffusates in liquid iron at 1 600°C; atomic (A), Covalent (C) and effective (E) radius, after Y. Kojima *et al.*³⁵⁾

order to investigate the effect of silicon on these D_C^{Si} , it is necessary for the representative concentration of carbon to be a constant.

Figure 9 shows the relation between the molar fraction of silicon N_{Si} and the ratio of the diffusion coefficient of carbon in the quasi-binary Fe-C-Si (a constant) system to that in the binary Fe-C system at the same concentration of carbon D_C^{Si}/D_C (in logalythmic measure). According to the figure, D_C^{Si} increases with the increasing concentration of silicon. This trend

Fig. 9. Effect of silicon content on D_C^{Si} in Fe-0.5% C-Si quasi-binary alloy at 1 550°C.

was tried to be explained on the usual assumption of inverse proportion between diffusion coefficient and viscosity, but no obvious conclusion could be drawn from the reference values.³⁸⁾

H.-D. Kunze³⁹⁾ has studied comprehensively the effect of the third element on the interdiffusion coefficient of nitrogen in molten iron in arrangement with the following equation;

$$\ln D_N^{(3)} = \ln D_N^{(2)} + \partial_N^x \cdot N_x \dots \dots \dots (6)$$

and found a relation between the interaction parameter ϵ_N^x and the variation rate of the diffusion coefficient due to the addition of the third element ∂_N^x as follows:

$$\partial_N^x = 0.5 \epsilon_N^x \dots \dots \dots (7)$$

Supposed that these relations are valid for the diffusion of carbon, the straight line can be drawn in Fig. 9 through Eqs. (6) and (7) in connection with $\epsilon_C^{Si} = 10.0$.⁴⁰⁾ The tendencies are in good agreement with each other out of consideration for the experimental error.

Next, the apparent diffusion coefficient of silicon in the quasi-binary Fe-C (a constant)-Si system D_{Si}^C was investigated in the above mentioned manner. The present D_{Si}^C are a little larger than D_{Si} reported by K. Saito *et al.*⁴¹⁾ and F. P. Calderon *et al.*⁴²⁾ among the references values measured in the binary Fe-Si system as summarized in Table 3.

V. Summary

The isothermal diffusion experiments were carried out by means of the diffusion couple method in the binary Fe-C and the quasi-binary Fe-C-Si system at 1 550°C. The results are summarized as follows:

$$D_C = (1 + 0.24[\%C]) \times 10^{-4} \text{ cm}^2/\text{sec} \quad (0.3 \sim 3\% \text{ C})$$

$$D_C^{Si} = 1.0 \sim 1.4 \times 10^{-4} \text{ cm}^2/\text{sec} \quad (0.5\% \text{ C}, 0 \sim 1.34\% \text{ Si})$$

$$D_{Si}^C = 6.9 \times 10^{-5} \text{ cm}^2/\text{sec} \quad (0.3\% \text{ C}, 0.4\% \text{ Si})$$

Although there have been no reports like the present work in which the concentration-dependent diffusion coefficient of carbon has been precisely measured, the present results can be concluded to be quite reasonable in comparison with those measured by the different method or estimated by the other suitable calculation.

Table 3. Diffusion coefficient of Si in molten binary ferro-alloys.

Investigators	Measuring technique	wt% Si	Temperature (°C)	D_{Si} (cm ² /sec)		$D_{Si} \times 10^4$ at 1550°C (cm ² /sec)
				D_0 (cm ² /sec)	Q (kcal/mol)	
Saito <i>et al.</i> ⁽⁴¹⁾	D-C	2.59~2.78 0~30 at%	1 575~1 680 1 600	5.0×10^{-4} D increases with %Si	10.2	0.3
Calderon <i>et al.</i> ⁽⁴²⁾	D-C	0~4.4	1 550~1 725	5.1×10^{-4}	9.15	0.41
		8.0~17.0		2.1×10^{-3}	13.20	0.55
		17.0~23.0		2.8×10^{-3}	11.90	1.05
Majdic <i>et al.</i> ⁽⁴³⁾	D-C	1.0	1 500~1 690	1.4×10^{-2}	23.7	0.20
This work	D-C	0.0~0.81	1 550			0.69 (D_{Si}^C)

D-C=diffusion couple method

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