



Title	Partition of Carbon between Solid and Liquid in Fe-C Binary System
Author(s)	Okamoto, Taira; Morita, Zen-ichiro; Kagawa, Akio et al.
Citation	Transactions of the Iron and Steel Institute of Japan. 1983, 23(3), p. 266-271
Version Type	VoR
URL	https://hdl.handle.net/11094/26397
rights	© 1983 ISIJ
Note	

The University of Osaka Institutional Knowledge Archive : OUKA

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

Partition of Carbon between Solid and Liquid in Fe-C Binary System*

By Taira OKAMOTO,** Zen-ichiro MORITA,**
Akio KAGAWA** and Toshihiro TANAKA****

Synopsis

In order to investigate carbon distribution between solid and liquid phases in Fe-C binary system, austenite-liquid phases equilibrated in the temperature range from 1 150 to 1 400 °C were quenched and the carbon concentrations in each phase were determined by EPMA.

The results obtained are summarized as follows.

(1) Solidus and liquidus obtained coincided well with the curves given in other recent works.

(2) Diffusion distance of carbon from liquid-solid interface into solid phase during quenching was calculated. From the results of the calculation, it became clear that carbon concentration in the center of solid phase was not influenced by the carbon diffusion during quenching.

(3) Equilibrium distribution coefficient of carbon in Fe-C system was determined thermodynamically. Solidus corresponding to the liquidus obtained experimentally was calculated by using the above coefficient and it was in good agreement with the experimental one.

1. Introduction

In discussing various phenomena during solidification of iron alloys, it is very important to know the equilibrium distribution behaviour of alloying element of iron alloys. Some studies have been carried out on the distribution of carbon between solid and liquid phases in the Fe-C binary alloy which is the most fundamental system of iron and steel. However, there seem to be some discrepancies, particularly, about solidus among them and no detail discussion on this point in those studies.

In this work, so as to investigate carbon distribution between solid and liquid phases in the Fe-C binary system, solid-liquid phases equilibrated were quenched and the carbon concentration in each phase was determined by EPMA. Since the diffusivity of carbon in the Fe-C alloy is known to be large, the validity of application of this experimental method to this alloying system was also investigated. Furthermore, solidus and liquidus obtained experimentally were compared with the curves given in other works, and the calculated results on solidus obtained using thermodynamic data.

II. Experimental

1. Apparatus for Quenched Specimens

The apparatus for preparing quenched specimens is shown in Fig. 1. A sample weighing 7 g was placed into an alumina crucible in purified argon atmosphere. After melting down of the sample, it was

cooled to a fixed temperature between 1 150 °C and 1 400 °C, at which austenite and liquid phases coexist, and held at that temperature for a given time. When equilibrium was achieved, by withdrawing the stopper, the sample fell through the hole at the bottom of the crucible and was quenched in oil, to make specimen including two phases having been liquid and solid before quenching.

As the vertical tube furnace used had a hot zone of 50 mm length and the height of the sample was within 10 mm, it is reasonable to expect that the solid distribution in the sample was uniform. However, there is a possibility that the ratio of solid at the bottom of crucible was larger than that of the upper part due to the density difference between solid and liquid. This problem will have to be investigated in the future.

2. Sample and Holding Temperature

Compositions of samples used and its equilibrium holding temperature are listed in Table 1. These samples were prepared in the high frequency induction furnace from electrolytic iron and pure graphite.

The equilibrium holding temperature was fixed to make the ratio of solid in the specimens from 5 to 10 %.

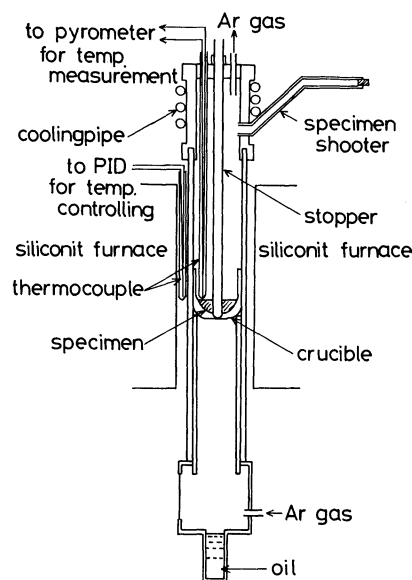


Fig. 1. Apparatus for quenching specimens.

* Originally published in *Tetsu-to-Hagané*, **68** (1982), 244, in Japanese; Formerly presented to the 100th ISIJ Meeting, October 1980, at Kyushu University in Fukuoka. English version received August 9, 1982. © 1983 ISIJ

** The Institute of Scientific and Industrial Research, Osaka University, Yamadaoka, Suita 565.

*** Faculty of Engineering, Osaka University.

**** Graduate School, Osaka University.

3. Equilibration Time

To determine the time required to establish complete equilibrium between the two phases, a series of experiments were carried out on Fe-3.8 wt% C alloy, in which specimens were quenched after different holding times at 1 173 °C. The results of the analysis of carbon from the central regions of the solid phases are given in Fig. 2. This figure shows clearly that the equilibrium was achieved after holding the specimens for about 30 min. Consequently, the holding time was determined to be 1 hr.

4. Metallographic Structure of Quenched Specimens and Measurement of Concentration Distribution by EPMA

All the specimens were spherical, and the solid phases were distributed uniformly in each specimen.

Table 1. Chemical compositions (wt%) and equilibration temperatures (°C) for Fe-C specimens.

No.	Temp. (°C)	C	Si	Mn	P	S	Al
1	1 173	3.81	0.153	0.005	0.003	0.005	0.111
2	1 248	3.30	0.164	0.005	0.003	0.003	0.164
3	1 323	2.57	0.104	0.005	0.003	0.004	0.080
4	1 359	2.41	0.109	0.010	0.003	0.004	0.064
5	1 399	1.79	0.065	0.005	0.003	0.005	0.025

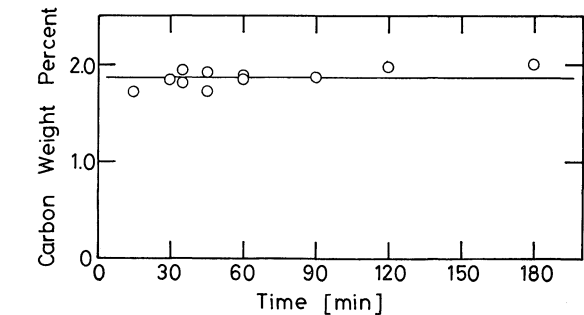


Fig. 2. Carbon concentration in austenite of the Fe-C alloy held at 1 173 °C with equilibration time.

Photograph 1 shows the metallographic structures of the quenched specimens, where circulars are solid phases and the other part is liquid one which had existed before quenching. In these photographs, Nos. 1 and 5 are the specimens held at the lowest and highest temperature, respectively. It is obvious from these photographs that the quantity of dendrites which crystallized in liquid phase during quenching increases as the temperature becomes higher and higher. Since the carbon content of No. 1 specimen is approximately equal to the eutectic one, the quantities of crystallized austenite are quite small during solidification as obvious from Photo. 2(A). On the other hand, although the carbon content of No. 5 specimen is less than the maximum carbon solubility in austenite, its structure consists of austenite grains surrounded by cementite divorced from ledeburite as shown in Photo. 2(B). As exhibited in Photo. 1, the average diameter of the solid phase is about 100~200 μ in the specimen held at lower temperature but about 300 μ in the specimen held at higher temperature because the rate of coarsening of the solid phase at higher temperature is larger than at lower one.

Electron microprobe analysis was carried out by scanning the focussed beam over a region which included both solid and quenched liquid. Since the structure of the liquid phase in the specimen was not so uniform as that of the solid phase, in the liquid phases, a focussed beam was moved over the distance which was 2 or 3 times of the diameter of the solid phase, and the concentrations at the liquid region of each specimen were averaged. In this experiment, using electrolytic iron, 0.69 wt% C steel and 4.24 wt% C cast iron, the relation between X-ray intensity and carbon content was established. The carbon concentrations were determined by use of the calibration curve as shown in Fig. 3.

5. Concentration Distribution

Some examples of the concentration distribution measured by EPMA are given in Fig. 4. It is ob-

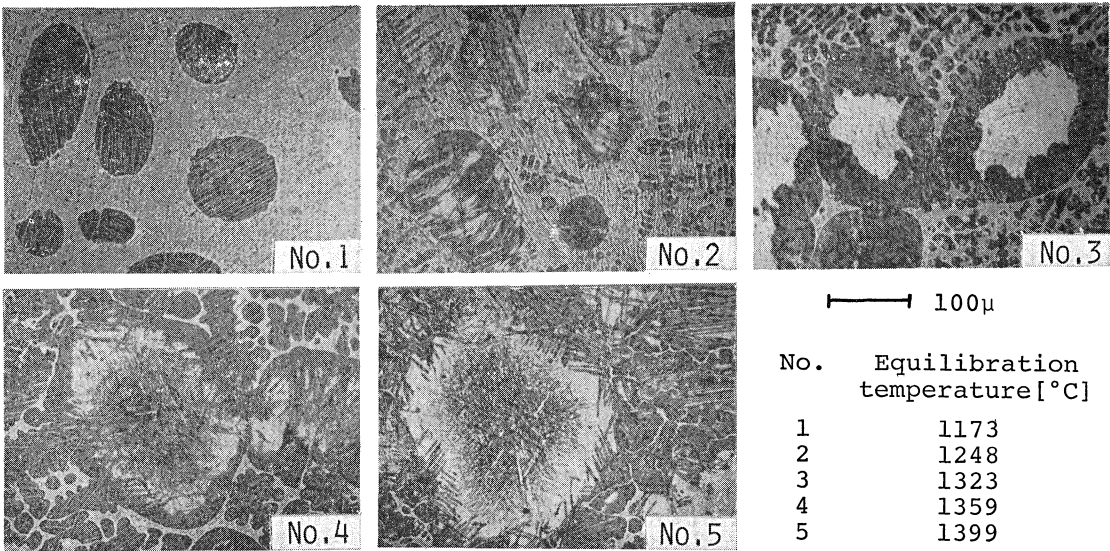


Photo. 1. Microstructures of quenched specimens.

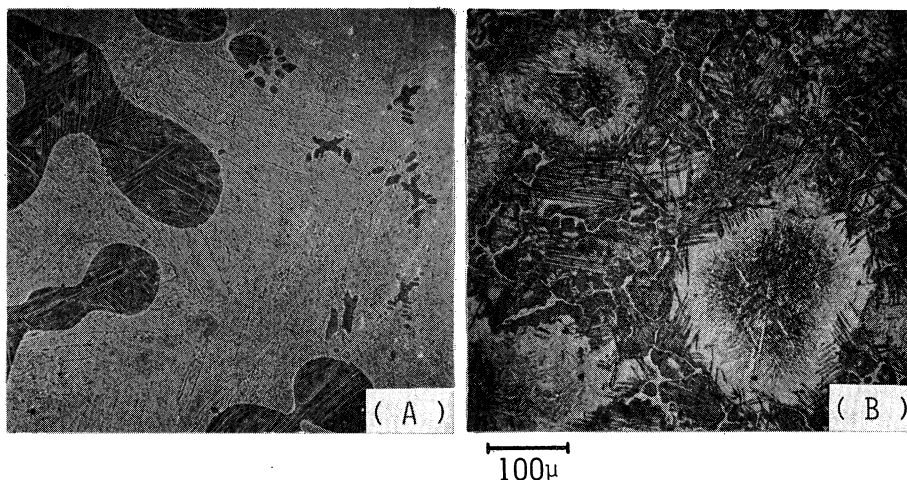


Photo. 2.
Microstructures of quenched specimens, (A) No. 1 and (B) No. 5.

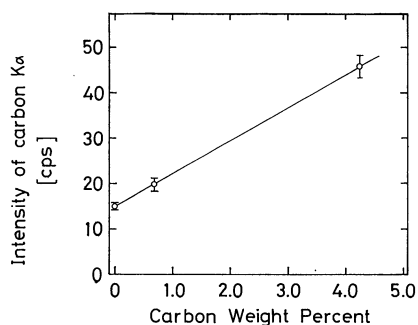


Fig. 3. The calibration curve for carbon in electron probe micro analysis.

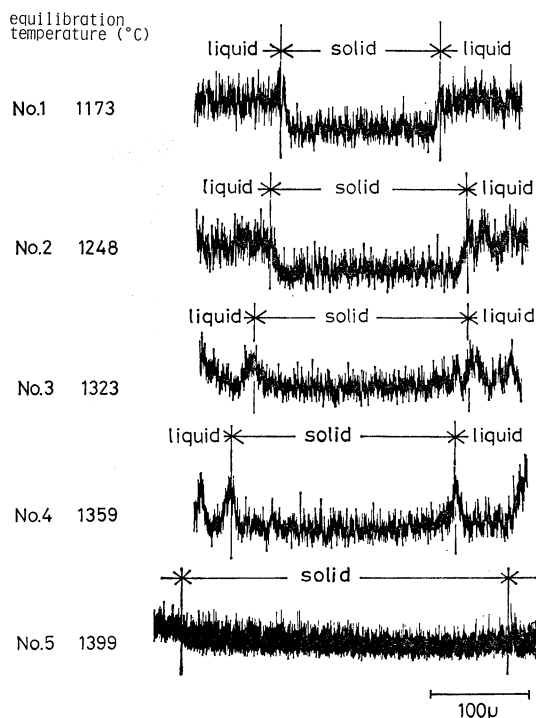


Fig. 4. Carbon distribution in quenched specimens.

vious from this figure that in the specimen held at higher temperature, the distortion of concentration distribution is remarkable because the quantity of dendrite crystallized in the liquid phases is large. In determination of equilibrium carbon concentration in the solid phase, the values at the center of the solid

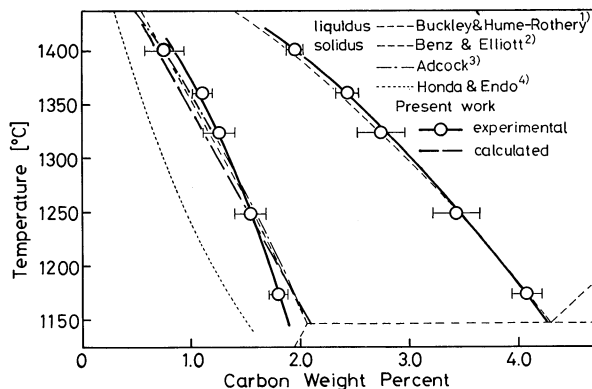


Fig. 5. Experimental and calculated results corresponding to the solidus and liquidus of austenite-liquid iron in the Fe-C system.

phase, in which carbon concentration is uniform as illustrated in Fig. 4, were used.

III. Results and Discussion

1. Experimental Results

Figure 1 shows the measured carbon concentration in both solid and liquid phases as a function of temperature in the Fe-C system, and the solidus and liquidus, which were obtained by fitting the plots by curves. This figure also indicates the liquidus by Buckley and Hume-Rothery,¹⁾ and the solidus by Benz and Elliott,²⁾ Adcock,³⁾ and Honda and Endo.⁴⁾ So far a number of studies have been carried out on the liquidus except Buckley and Hume-Rothery, but all these results coincide very well with that of Buckley and Hume-Rothery. So, those results are not shown in this figure. On the other hand, there are some types of solidus curves, for example, the curve convex downward by Honda and Endo, the one slightly convex upward by Adcock and the straight line by Benz and Elliott. This fact means that the determination of solidus is more difficult than that of the liquidus. The liquidus obtained in this work correspond to that of Buckley and Hume-Rothery, and extrapolating the liquidus of this work, it reaches the eutectic point which has already been established as most reliable. The solidus obtained in the present work coincides comparatively well with that of Benz

and Elliott. The solidus calculated using thermodynamic data is also shown in Fig. 5. The detail of this calculation will be discussed later in the Section III.3.

2. Validity of This Experimental Method and Results

When this experimental method is applied to Fe-C system in which carbon diffusivity is known to be large, it is considered that carbon diffuses even in the solid phase during quenching, and in some cases the carbon concentration in solid after quenching may differ from the equilibrium one. In this work, considering the change of carbon concentration at the solid-liquid interface and the change of carbon diffusivity in the solid phase with the temperature during quenching, the diffusion distance of carbon from the liquid-solid interface into the solid phase during quenching was calculated by use of the data of cooling rates obtained in this work.

First, supposing that these phenomena are based on one dimensional diffusion of carbon, Fick's second law in Eq. (1) is changed into the difference equation (2). In this work, the explicit method was used for this purpose as shown in Fig. 6. The diffusivity of carbon in austenite measured at 900~1 400 °C using the Fe-0.6wt%C alloy⁵⁾ is assumed to be applicable to the carbon content in this work.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \dots\dots\dots(1)$$

$$\frac{C_{i,j} - C_{i-1,j}}{\Delta t} = D \frac{C_{i-1,j-1} - 2C_{i-1,j} + C_{i-1,j+1}}{(\Delta x)^2} \dots\dots\dots(2)$$

$$D = 1.75 \times 10^{-2} \exp\left(-\frac{27.1 \times 10^3}{RT}\right)$$

$$= 1.75 \times 10^{-2} \exp\left(-\frac{27.1 \times 10^3}{R(T_0 - V\Delta t \cdot i)}\right) \dots\dots\dots(3)$$

where, *i, j*: step number of time on the vertical axis and distance on the abscissa, respectively, in Fig. 6
V: cooling rate [K/s]
*T*₀: equilibration temperature [K]
*T*₀ - *VΔt · i*: temperature at step *i* after start of quenching.

Also, initial and boundary conditions are shown in Eqs. (4) and (5), respectively.

$$C_{0,j} = C^o \dots\dots\dots(4)$$

$$C_{i,0} = C^o + \frac{V}{m} \Delta t \cdot i \dots\dots\dots(5)$$

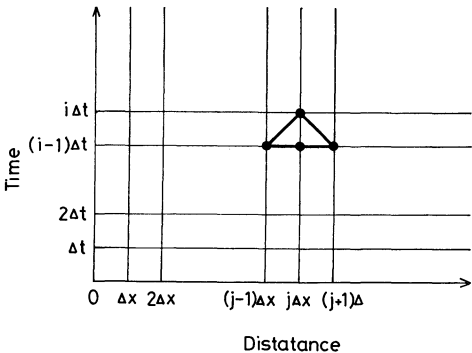


Fig. 6. Explicit method.

where, *C*^o: equilibrium concentration in the solid phase [wt%]
m: gradient of the solidus [K/wt%].
Cooling rate *V* was calculated by using Eq. (6)⁶⁾

$$V = \left[\frac{340 \times (1/\%C - 1/4.3)^{0.35}}{Z} \right]^{100/27} \dots\dots\dots(6)$$

where, *Z*: the second dendrite arm spacing [μ], obtained from Photos. of microstructure of the quenched specimens in this work.

Figure 7 indicates the measured cooling rate. Since dendrite structures could not clearly be observed in liquid phases in Nos. 1 and 5 specimens, the extrapolated values obtained from linear approximation of the relation between the cooling rate and temperature of other specimens were adopted as the cooling rates of these specimens.

Thus, the changes of concentration distribution in the solid phase due to carbon diffusion during quenching were calculated by using Eq. (2). Some examples of the calculated results are given in Fig. 8, which shows the concentration distributions of carbon in the solid phase at the end of solidification when it is assumed that each specimen solidifies completely at temperature of 100 °C under than eutectic one. It is obvious from Fig. 8 that the diffusion distance of carbon in even the specimen held at higher temperature is less than 100 μ from solid-liquid interface. Comparing these diffusion distances with the diameters of solid phases as shown in Photo. 1, that is to say, about 100~200 μ of the specimen held at low temperature and about 300 μ held at high one, and also from Fig. 8, which shows that the calculated diffusion distances of carbon into austenite during quenching are larger than the measured values from the C Kα intensity profiles in Fig. 4, it is supposed that present experimental results were in the equilibrium state enough as far as the carbon concentration at the center of the solid phase was used in the quenched specimens obtained in this work.

There may exist the depression of temperature dur-

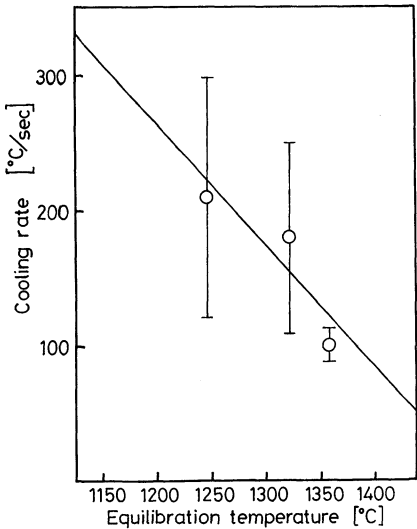


Fig. 7. Change of cooling rates of the Fe-C alloy with equilibration temperature before cooling.

ing quenching, namely, until the specimen dropped into oil after withdrawing the stopper. In this regard, it was found from the preliminary experiments that it took 0.35 sec during quenching and the depression of temperature was 15 °C. Then, assuming that the depression of temperature of the specimen is 15 °C during quenching and calculating the carbon diffusion distance in the same way as described above, the results are found to be as same as in Fig. 8. Thus, the depression of temperature during quenching can be neglected.

Another question included in this experiment seems to be the influence of impurity in the samples. But in this work, this effect has not been made clear. So, this problem will have to be investigated in the future.

3. Thermodynamic Treatment of the Equilibrium Distribution Coefficient

In order to discuss thermodynamically the distribution of carbon between solid and liquid phases, the solidus corresponding to the liquidus obtained in this experiment was calculated using the thermodynamic data and compared with the experimental results.

Equilibrium between liquid and solid phases in an Fe-C alloy is represented by Eqs. (7) to (9)

$$\mu_c^l = \mu_c^s + RT \ln \gamma_c^l N_c^l \dots\dots\dots(7)$$

$$\mu_c^s = \mu_c^s + RT \ln \gamma_c^s N_c^s \dots\dots\dots(8)$$

$$\mu_c^l = \mu_c^s \dots\dots\dots(9)$$

- where, μ_c : the chemical potential of carbon
 μ_c^s : the chemical potential of carbon in standard state
 N_c : mole fraction of carbon
 γ_c : activity coefficient of carbon
 R : gas constant
 T : absolute temperature
 l, s : the liquid state and solid one.

From the equilibrium condition Eq. (9), the equilibrium distribution coefficient of carbon, k_o , is obtained as follows.

$$k_o = \frac{N_c^s}{N_c^l} = \frac{\gamma_c^l}{\gamma_c^s} \exp \left(\frac{\mu_c^s - \mu_c^l}{RT} \right) \dots\dots\dots(10)$$

If the standard state of carbon in both liquid and solid phases is taken to solid graphite, i.e.,

$$\mu_c^l = \mu_c^s \dots\dots\dots(11)$$

Eq. (10) can be written as

$$k_o = \frac{\gamma_c^l}{\gamma_c^s} \dots\dots\dots(12)$$

Thus, substituting the values of activity coefficients γ_c^l, γ_c^s reported by other investigators into the above equation (12), and also using the equilibrium distribution coefficient obtained from Eq. (12), the solidus corresponding to the liquidus obtained experimentally can be calculated.

4. Validity of the Thermodynamic Data Used in the Calculation

When the equilibrium distribution coefficient k_o is calculated in Eq. (12), the thermodynamic data have to be correct and reasonable. Then, the data previously obtained on the activity of carbon in liquid iron and austenite were investigated. Among these data, the values, which are applicable to the temperature range (1 150~1 400 °C) in this work, and also are being given as a function of both temperature and concentration, were selected. Furthermore, in determination of the data used in the above calculation, the values, whose degrees of the quotation and the convergency are high, were adopted. Figures 9 and 10 show some representative data of activity coefficients in liquid iron and austenite, respectively, at 1 200, 1 300 and 1 400 °C as a function of N_c . From

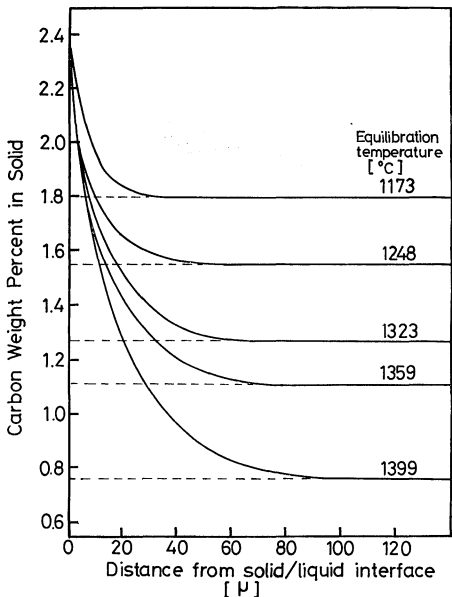


Fig. 8. Carbon diffusion distances in the solid phase during quenching.

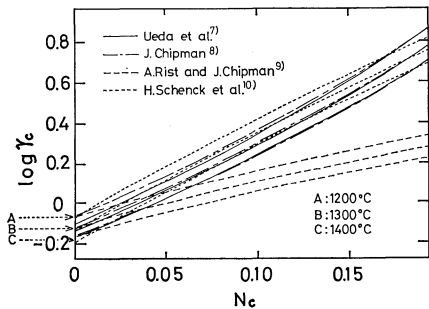


Fig. 9. Activity coefficients for carbon in liquid iron.

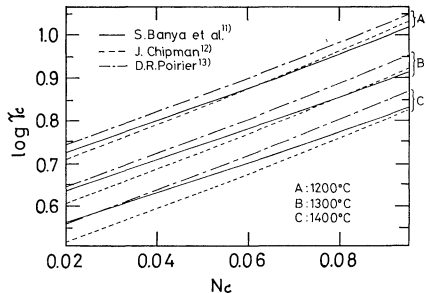


Fig. 10. Activity coefficients for carbon in austenite.

Fig. 9, the agreement between the data of Chipman⁸⁾ and that of Ueda *et al.*⁷⁾ is very good. However, since the data of Chipman was calculated from the activity in austenite using the equilibrium condition between solid and liquid phases, it is thought to be unsuitable for this discussion. On the other hand, as the data of Ueda *et al.* was reported more recently than that of Chipman, and was obtained by measuring the rate of effusion of iron vapour, it is considered to be more suitable for this discussion than that of Chipman. Then, the data of Ueda *et al.* was adopted as

$$\log \gamma_c^l = \left(\frac{5300}{T} + 0.507 \right) \frac{N_c^l}{1 - N_c^l} + \left(\frac{694}{T} - 0.587 \right) \dots \dots \dots (13)$$

About the data of activity of carbon in austenite in Fig. 10 the value of Ban-ya *et al.*¹¹⁾ approaches that of Chipman¹²⁾ at higher temperature range and also that of Poirier¹³⁾ at lower temperature range. So, the data of Ban-ya *et al.* was adopted as

$$\log \gamma_c^s = \left(\frac{3770}{T} - 10.5 \right) + \left(0.43 + \frac{3900}{T} \right) \frac{N_c^s}{1 - N_c^s} + 2.72 \log T - \log (1 - N_c^s) \dots \dots \dots (14)$$

5. Thermodynamically Calculated Results

Substituting Eqs. (13) and (14) into Eq. (12) and also using the relation $N_c^s = k_o N_c^l$, the solidus corresponding to the liquidus obtained experimentally can be calculated. The result is shown in Fig. 5. From this figure, the calculated result is comparatively good agreement with the experimental one. Thus, present experimental results are thought to be appropriate also in the thermodynamical standpoint.

Consequently, obtaining solidus corresponding to the liquidus by use of the thermodynamic data is thought to be useful as the way to estimate or identify the solidus when the information about solidus is unreliable because of experimental difficulties.

IV. Summary

In order to investigate carbon distribution between solid and liquid phases in the Fe-C binary system, austenite-liquid phases equilibrated were quenched and the carbon concentrations in each phase were determined by EPMA. The diffusion of carbon in the solid phase during quenching was discussed. Also, the solidus corresponding to the liquidus obtained experimentally was calculated thermodynamically. It was found from these discussions that this experimental method and results were reasonable.

Though this kind of experimental method has recently been used by many investigators in order to obtain the distribution coefficient of alloying elements, there are few studies applied to the Fe-C system. Consequently, this result is considered to be useful as the fundamental data for the studies of application of this method to Fe-C base multicomponent systems.

REFERENCES

- 1) R. A. Buckley and W. Hume-Rothery: *JISI*, **196** (1960), 403.
- 2) M. G. Benz and J. F. Elliott: *Trans. Met. Soc. AIME*, **221** (1961), 323.
- 3) F. Adcock: *JISI*, **135** (1937), 720.
- 4) K. Honda and H. Endo: *Science Reports Tohoku Univ.*, **16** (1927), 235.
- 5) D. F. Kalinovich, I. I. Kovenskii and M. D. Smolin: *Izv. Vyssh. Ucheb. Zaved, Fiz.*, **9** (1971), 116.
- 6) T. Okamoto and H. Matsumoto: 39th International Foundry Congress, AFS, Philadelphia, May 1972.
- 7) A. Ueda, K. Fujimura and T. Mori: *Tetsu-to-Hagané*, **61** (1975), 42.
- 8) J. Chipman: *Met. Trans.*, **1** (1970), 2163.
- 9) A. Rist and J. Chipman: *Rev. Mét.*, **53** (1956), 796.
- 10) H. Schenck, E. Steinmetz and M. Gloz: *Arch. Eisenhüttenw.*, **42** (1971), 307.
- 11) S. Ban-ya, J. F. Elliott and J. Chipman: *Met. Trans.*, **1** (1970), 313.
- 12) J. Chipman: *Trans. Met. Soc. AIME*, **239** (1967), 2.
- 13) D. R. Poirier: *Trans. Met. Soc. AIME*, **242** (1968), 685.