HOKKAIDO UNIVERSITY

Title	Rate of Peritectic Reaction in Iron-Carbon System Measured by Solid/Liquid Diffusion Couple Method
Author(s)	Matsuura, Kiyotaka; Maruyama, Hisashi; Itoh, Youichi; Kudoh, Masayuki; Ishii, Kuniyoshi
Citation	ISIJ International, 35(2), 183-187 https://doi.org/10.2355/isijinternational.35.183
Issue Date	1995-02-15
Doc URL	http://hdl.handle.net/2115/75740
Rights	
Type	article
File Information	ISIJ Int. 35(2) 183.pdf

Rate of Peritectic Reaction in Iron–Carbon System Measured by Solid/Liquid Diffusion Couple Method

Kiyotaka MATSUURA, Hisashi MARUYAMA, Youichi ITOH, Masayuki KUDOH and Kuniyoshi ISHII

Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, Kita 13-jo Nishi 8-chome, Kita-ku, Sapporo, Hokkaido, 060 Japan.

A model experiment was made for study on the effects of temperature on the reaction rate in isothermal peritectic reaction in iron–carbon system by using a solid/liquid diffusion couple method. Measurements of the variation in carbon concentration over δ, γ, and liquid phases show a decrease in the carbon concentration from the γ/liquid interface to the δ/γ interface and an equilibrium partition of carbon at both the interfaces. The γ-phase grows into both δ and liquid phases. A regression analysis of the thickness of the γ-phase, $x(\mu m)$, with the reaction time, $t(s)$, results in the following relations.

$$x = 36.6t^{1/2} \quad \text{at} \quad 1755\,\text{K}$$

$$x = 54.7t^{1/2} \quad \text{at} \quad 1722\,\text{K}$$

$$x = 71.0t^{1/2} \quad \text{at} \quad 1689\,\text{K}$$

These relationships imply that the peritectic reaction follows the parabolic law and that the reaction rate is higher at lower temperatures. It was found that about 90% of the γ-phase formed through the peritectic reaction is the transformation product from the δ-phase and about 10% the solidification product from the liquid phase.

KEY WORDS: peritectic reaction; reaction rate; diffusion couple; solidification; transformation; diffusion; iron-carbon system.

1. Introduction

The peritectic reaction in iron-carbon system is very important for steel casting techniques, because the peritectic reaction in this system may lead to generation of tensile stress on the surface of solidified shell,[1] segregation of alloying elements[2] and precipitation of manganese sulfide[3] during solidification of steel. The tensile stress will be a cause of cracking on the surface of continuously cast slabs, and the segregation and the precipitation will affect the mechanical properties of steel products. For optimum control of these phenomena, it is necessary to clarify the mechanism of the peritectic reaction and the effects of various factors on solute partition and interface mobility during this reaction.

Some proposals have been made on the mechanism of the peritectic reaction. According to Chuang et al.,[4] and Fredriksson and Stjerndahl,[5] the rate of the peritectic reaction depends on the rate of carbon diffusion in austenite (γ); the γ-phase grows with the diffusion of carbon passing through the γ-phase from liquid into δ-ferrite (δ) during the peritectic reaction. This mechanism is widely known as the diffusion-controlled theory. Other theories are the massive transformation theory by Singh et al.[6] and the precipitation-type

transformation theory by Takahashi et al.[7] The massive transformation theory assumes the occurrence of fine Widmanstätten-type γ-phase in the δ-phase. An experiment by Ueshima et al.[8] has confirmed that this mechanism operates in the formation of the γ-phase when the extent of carbon diffusion is insufficient because of a rapid cooling rate. On the other hand, the precipitation-type transformation theory assumes that the γ-phase nucleates in the δ-phase in an equilibrium conjugate relationship with the δ-phase during cooling, denying the possibility of the γ-phase generation by the diffusion-controlled mechanism even when the cooling rate is slow enough for carbon diffusion. No experimental evidence supporting this theory is available except for Takahashi's own report.[7] Mizoguchi[9] has reported that, although the massive transformation mechanism operates at extremely rapid cooling rates, the peritectic reaction usually take place by the diffusion-controlled mechanism. We[10] have also reported experimental results verifying quantitatively the validity of the diffusion-controlled mechanism for the peritectic reaction. Thus, from a number of results on the mechanism of the peritectic reaction, the reaction rate is thought to be primarily controlled by the diffusion of carbon in the conventional steel casting process. However, only a few

reports are available on the solute partition in the peritectic reaction, and the interface mobility during this reaction has hardly been studied.

We have developed a model experiment method for measuring the change in the thickness of the γ-phase during the peritectic reaction in iron-carbon system, and reported that both the δ/γ and the γ/liquid interfaces move in accordance with the parabolic law.[10] Furthermore, we have simulated the peritectic reaction process based on the diffusion-controlled mechanism by the direct finite difference method, and showed that the peritectic reaction rate is higher at lower temperatures.[10] In the present study, by applying this model experiment method, we intend to measure the rate of the isothermal peritectic reaction at several levels of temperature and to verify the preceding simulation results.

2. Experimental

Only the outline of the model experiment in the present study is described here, since the experimental method is detailed in a previous paper.[10] A δ-iron specimen of 25 mm in diameter and 35 mm in thickness was suspended by an alumina tube (outer diameter: 6 mm) from the top of a vertical type SiC furnace and was moved down to the position just above the surface of liquid metal (about 30 g) which was held at a predetermined temperature. After holding for 3.6 ks in this alignment, the δ-iron and the liquid metal were slowly brought into contact to form a solid/liquid diffusion couple.

After a predetermined time passed, the diffusion couple was dropped into vigorously stirred iced water together with the crucible. This experiment was performed at 1 755, 1 722, and 1689 K in an argon atmosphere. The initial carbon concentrations of the δ-iron and the liquid were those of the solvus line for the δ-iron and of the liquidus line for the liquid at the experiment temperature on an iron-carbon binary equilibrium phase diagram.[11] The purity of the δ-iron and the liquid was Si<0.01, Mn<0.01, P<0.002, S<0.002, and Sol.Al<0.01 mass%.

The rapidly quenched specimens were etched with nital etchant on the longitudinal section for the measurement of the thickness of the γ-phase formed at the interface of the δ and liquid phases. Furthermore, the variations of carbon concentration were measured over δ, γ and liquid phases by the EPMA method (JXA-8900M, JEOL).

3. Results and Discussion

3.1. Effect of Temperature on Peritectic Reaction Rate

Figure 1(a) shows the microstructure on the etched longitudinal section of a quenched specimen after reaction at 1 689 K for 3.5 ks. Each region of the prior δ, γ, and liquid phases before quenching is distinguished as the region of fine equiaxed γ-grains, coarse columnar γ-grains, and ultra-fine γ-grains, respectively. The location of the initial δ/liquid interface (shown by an arrow in the figure) is determined from the initial thickness of the δ-phase. Absence of γ-grain boundaries at the location of the initial interface suggests that both the γ-phases transformed from the δ-phase and crystallized from the liquid phase originate from an identical nucleus which nucleates in the δ-phase at the initial δ/liquid interface because of the lower latent heat for the $\delta \to \gamma$ transformation compared with that for the γ-solidification. The columnar shape of the γ-grains suggests a higher mobility of the δ/γ interface than the γ/γ interface. The mobility of the γ/γ interface is dependent on the diffusion velocity of iron at this interface,[12-14] while that of the δ/γ interface is dependent on the diffusion velocity of carbon in the γ-phase.[4,5,10] The difference in the diffusion velocity is thought to result in the formation of the columnar γ-grains. **Figure 1(b)** shows the distribution of carbon concentration measured for the sample shown in Fig. 1(a). According to Fig. 1(b), the carbon concentration decreases gradually from the γ/liquid interface to the δ/γ interface, and carbon is partitioned in equilibrium at both the interfaces.

Figures 2, 3 and **4** show the relationship between the thickness of the γ-phase and the square root of the reaction time. Since the location of the initial δ/liquid
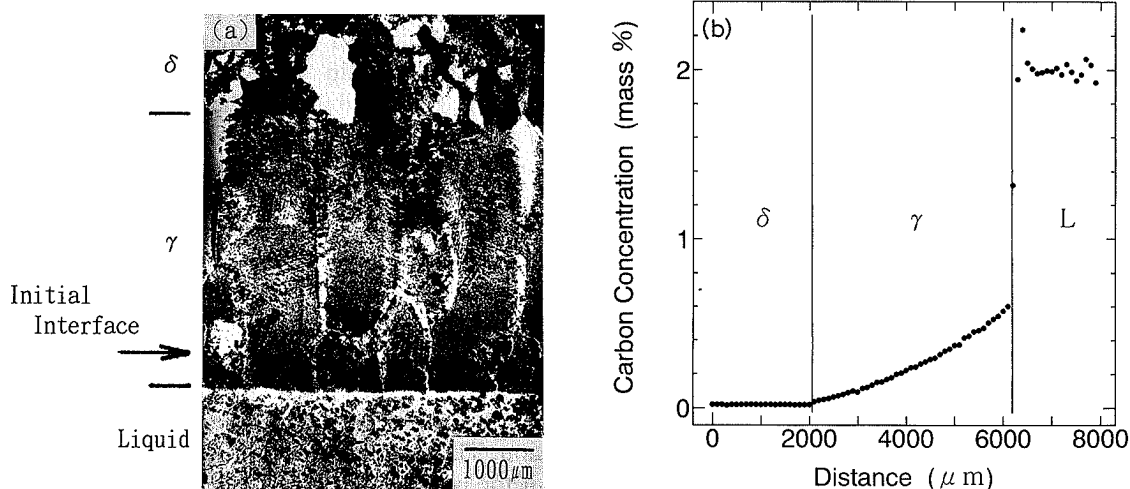

Fig. 1. (a) Microstructure on the longitudinal section of a specimen after reaction at 1 689 K for 3.5 ks.
(b) Distribution of carbon concentration for the sample shown in Fig. 1(a).
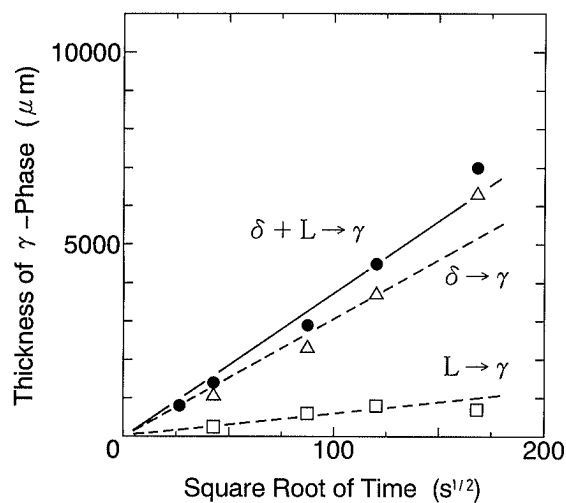
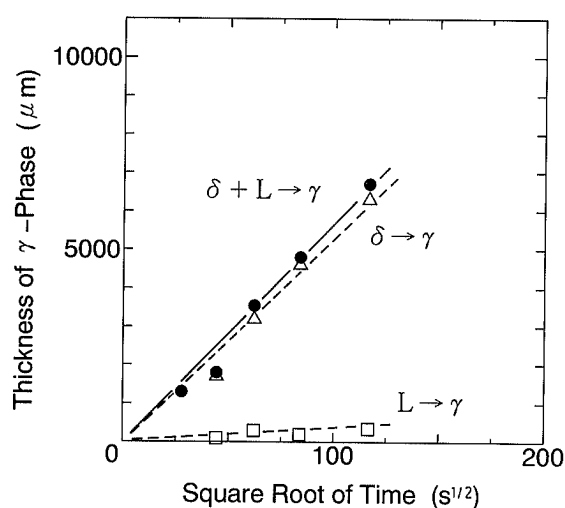Fig. 2. Relationship between the thickness of the γ-phase and the reaction time in square root at 1 755 K.

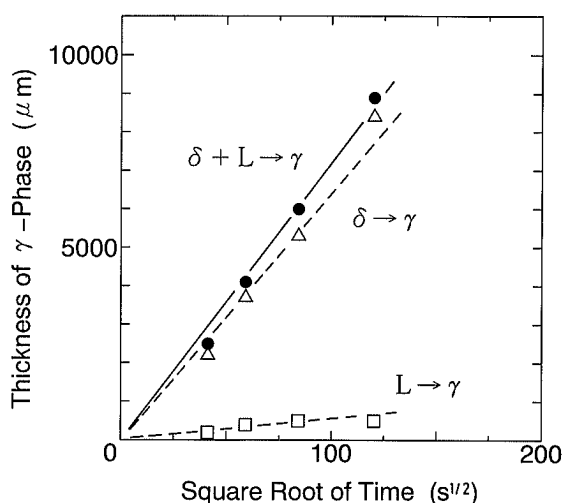Fig. 3. Relationship between the thickness of the γ-phase and the reaction time in square root at 1 722 K.

Fig. 4. Relationship between the thickness of the γ-phase and the reaction time in square root at 1 689 K.

interface is known, the total thickness of the γ-phase formed in the peritectic reaction $[\delta + L \rightarrow \gamma]$ is divided into the fraction of the γ-phase formed in the

transformation $[\delta \rightarrow \gamma]$ and that formed in the solidification $[L \rightarrow \gamma]$; the results are shown in the figures. Regression analysis of the relationships between the total thickness of the γ-phase and the reaction time is summarized as follows:

$$x = 36.6t^{1/2}, \quad (1\,755\,\text{K}) \quad \dots\dots\dots\dots\dots(1)$$

$$x = 54.7t^{1/2}, \quad (1\,722\,\text{K}) \quad \dots\dots\dots\dots\dots(2)$$

$$x = 71.0t^{1/2}, \quad (1\,689\,\text{K}) \quad \dots\dots\dots\dots\dots(3)$$

Equations (1), (2) and (3) suggest that the peritectic reaction proceeds in accordance to the parabolic law, and that the reaction rate is higher at lower temperatures. This result agrees with our previous result of the simulation[10] on the peritectic reaction based on the diffusion-controlled mechanism by the direct finite difference method.[8] The rapid progress of the peritectic reaction at lower temperatures is thought to be a result of the larger extents of carbon concentration range at lower temperatures in the iron-carbon binary equilibrium phase diagram. The carbon concentration of the γ-phase is higher at the γ/liquid interface than at the δ/γ interface, and the difference in the concentration increases with lowering temperature; the difference of the carbon concentration at 1 700 K amounts as much as about 13 times of the difference at 1 760 K.[11] The large difference in the carbon concentration at both the interfaces indicates the high gradient of the concentration throughout the γ-phase. On the other hand, the temperature dependence of the diffusion coefficient of carbon in the γ-phase is small; the value of the diffusion coefficient decreases only about 70 % with a temperature drop from 1760 to 1 700 K.[8] Therefore, with lowering temperature, while the diffusion coefficient of carbon decreases slightly, the concentration gradient becomes extremely steep. Since the amount of diffusion is the product of the diffusion coefficient and the concentration gradient, the rate of peritectic reaction becomes higher at lower temperatures. Thus, the effect of temperature on the peritectic reaction rate is explained.

3.2. Comparison between Amounts of Transformation and Solidification during Peritectic Reaction

In each of Figs. 2 to 4, during the peritectic reaction $[\delta + L \rightarrow \gamma]$, the transformation $[\delta \rightarrow \gamma]$ is shown to produce a much larger amount of the γ-phase than the solidification $[L \rightarrow \gamma]$. The parabolic rate constants for the growth of the γ-phase in the transformation and the solidification are obtained from the slope of the straight lines in the figures. The results are shown in **Fig. 5**, where the solid marks represent the experimental results of the present study and the open marks the results of our previous study.[10] The curved lines represent the results of the simulation of the isothermal peritectic reaction at various levels of temperature[10] based on the diffusion-controlled mechanism by the direct finite difference method.[8] A fairly good agreement of the simulation results with the experimental ones confirms the validity of this simulation method. In the previous results, larger values of the parabolic rate constant were obtained for both the transformation and the solidification.
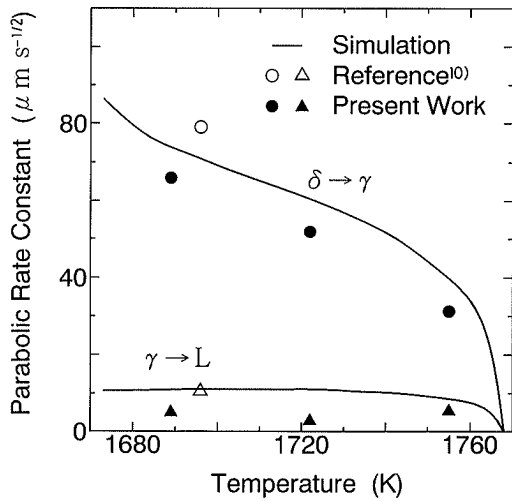
185

Fig. 5. Relationship between the parabolic rate constant and the reaction temperature.
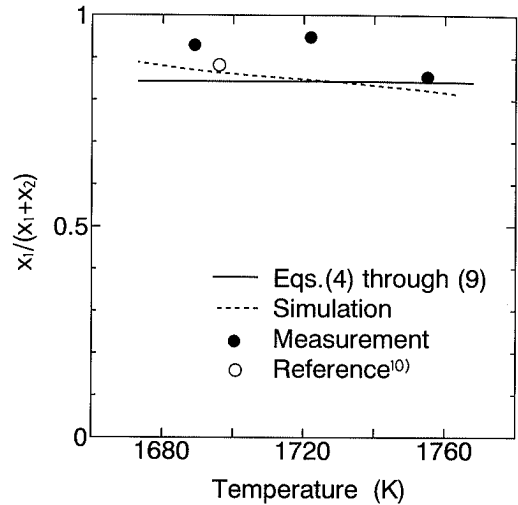

Fig. 6. Schematic representation of the distribution of carbon concentration during the peritectic reaction.

Fig. 7. Temperature dependence of the fraction in the thickness of the γ-phase formed by the transformation from the δ-phase. x_1 represents the γ-phase thickness formed by the transformation from the δ-phase and x_2 by the solidification from the liquid phase.
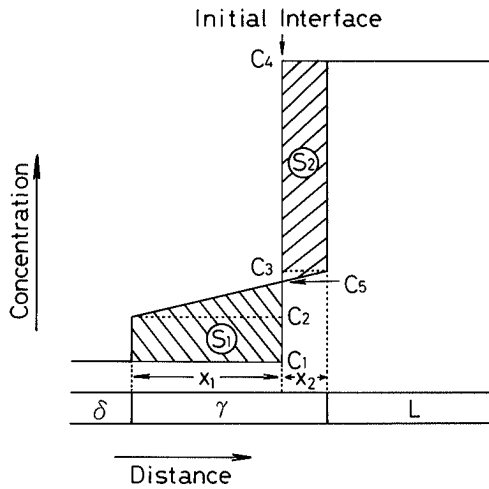
phase through the initial δ/liquid interface, respectively. Since $S_1 = S_2$,

$$(C_2 - C_1 + C_5 - C_1)x_1/2 = (C_4 - C_3 + C_4 - C_5)x_2/2 \quad ...(4)$$

where C_1, C_2, C_3 and C_4 are expressed in Eqs. (5) to (8) as linear functions of temperature, T, based on the iron–carbon binary equilibrium phase diagram.[11]

$$C_1 = 8.91 \times 10^{-4}T - 1.48 \quad ....(5)$$

$$C_2 = 1.68 \times 10^{-3}T - 2.81 \quad ....(6)$$

$$C_3 = -5.86 \times 10^{-3}T + 10.53 \quad ....(7)$$

$$C_4 = -1.83 \times 10^{-2}T + 32.89 \quad ....(8)$$

and C_5 is expressed in terms of x_1 and x_2 as follows:

$$C_5 = (x_1 C_3 + x_2 C_2)/(x_1 + x_2) \quad ....(9)$$

The solid line in **Fig. 7** represents the relationship between $x_1/(x_1 + x_2)$ and T derived from Eqs. (4) through (9). The dotted line in the figure represents the simulation results calculated from the results in Fig. 5. The solid and open marks in the figure are replotted from Fig. 5. From both the results of the measurement and the simulation in Fig. 7, about 90 % of the total amount of the γ-phase formed in the peritectic reaction is produced through the transformation from the δ-phase. Since these results agree well with the calculation results from Eqs. (4) though (9), the mass balance of carbon as expressed in Eq. (4) will be a primary cause for the transformation mechanism to predominate over the solidification mechanism in the whole process of the peritectic reaction. Figure 6 suggests that the large difference in carbon concentration at the γ/liquid interface induces a large amount of outward flow of carbon from the liquid phase upon the slight movement of the γ/liquid interface, while this amount of carbon flowing in is consumed in a large migration of the δ/γ interface because of the small difference in carbon concentration at the δ/γ interface.

This may be a result of a higher manganese content in the previous experiment; it is about 10 times higher than the present experiment. We have started a study on the effects of coexisting elements on the peritectic reaction rate. Figure 5 shows that the amount of the transformation is several times larger than that of the solidification at every temperature studied. The evidence can be understood in the following way.

Figure 6 shows schematically the distribution of the carbon concentration over the δ, γ and liquid phases. In the figure, C_1 and C_2 represent the carbon concentration of the δ-phase and that of the γ-phase at the δ/γ interface, respectively, and C_3 and C_4 that of the γ-phase and the liquid phase at the γ/liquid interface, respectively. By approximating the distribution of the carbon concentration in the γ-phase as a straight line, C_5 is obtained as the carbon concentration at the intercept of the straight line with the initial δ/liquid interface. The distance of the movement of the δ/γ interface is x_1, and that of the γ/liquid interface, x_2. The areas of the hatched regions in the figure, S_1 and S_2, represent the amounts of carbon flowing into the prior δ-phase and out of the prior liquid

4. Conclusions

A model experiment of the isothermal peritectic reaction in the iron-carbon system was made by using the solid/liquid diffusion couple method to study the effects of temperature on the rate of peritectic reaction. The results are summarized below.

(1) The relation between the thickness of the γ-phase, $x(\mu m)$, and the reaction time, $t(s)$, is described by the following equations.

$$x = 36.6t^{1/2}, \quad (1\,755\,K)$$

$$x = 54.7t^{1/2}, \quad (1\,722\,K)$$

$$x = 71.0t^{1/2}, \quad (1\,689\,K)$$

The peritectic reaction proceeds in accordance with the parabolic law and the rate constant is larger at lower temperatures. This is a result of larger extents of the carbon concentration range of the γ-phase at lower temperatures in the iron–carbon binary equilibrium phase diagram.

(2) In analyzing the total rate of the peritectic reaction $[\delta + L \rightarrow \gamma]$, the transformation process $[\delta \rightarrow \gamma]$ predominates over the solidification process $[L \rightarrow \gamma]$; the rate of the transformation process amounts as much as 90 % of the total rate of the peritectic reaction. The predominance of the transformation mechanism is caused by the significantly smaller difference in carbon concentration at the δ/γ interface than at γ/liquid interface.

REFERENCES

1) T. Matsumiya, T. Saeki, J. Tanaka and T. Ariyoshi: *Tetsu-to-Hagané*, **68** (1982), 1782.
2) H. Fredriksson: *Scand. J. Metall.*, **5** (1976), 27.
3) Y. Itoh, N. Narita and K. Matsubara: *Tetsu-to-Hagané*, **67** (1981), 755.
4) Y. Chuang, D. Reinisch and K. Schwerdtfeger: *Metall. Trans. A*, **6A** (1975), 235.
5) H. Fredriksson and S. Stjerndahl: *Met. Sci.*, **16** (1982), 575.
6) J. Singh, G. R. Purdy and G. C. Weatherly: *Metall. Trans. A*, **16A** (1985), 1363.
7) T. Takahashi, K. Ohsasa and J. Tanaka: *Tetsu-to-Hagané*, **73** (1987), 99.
8) Y. Ueshima, S. Mizoguchi, T. Matsumiya and H. Kajioka: *Metall. Trans. B*, **17B** (1986), 845.
9) S. Mizoguchi: *Bull. Jpn. Inst. Met.*, **26** (1987), 490.
10) K. Matsuura, Y. Itoh and T. Narita: *ISIJ Int.*, **33** (1993), 583.
11) T. B. Massalski: Binary Alloy Phase Diagrams, Vol. 1, ASM, Metals Park, (1986), 842.
12) D. Turnbull: *Trans. AIME*, **191** (1951), 661.
13) M. Hillert: *Acta Metall.*, **13** (1965), 227.
14) T. Nishizawa: *Tetsu-to-Hagané*, **70** (1984), 194.