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A Solid–Liquid Diffusion Couple Study of a Peritectic Reaction in Iron–Carbon System

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δ -iron and melted high carbon steel with carbon contents of the solvus and liquidus lines, respectively, in an iron–carbon equilibrium phase diagram, were held in contact with each other at 1 696 K. The thickness of the γ -phase formed between the δ -phase and the liquid phase was measured. The relationship between the thickness x (μm) and the holding time t (s) was found to be $x = 85.7t^{0.50}$.

The distribution of the carbon concentration over those three phases was also measured. The results showed a steep gradient of the carbon concentration in the γ -phase and an equilibrium conjugation relationship at both the δ/γ and γ/liquid interfaces.

These findings regarding the growth rate of the γ -phase and the distribution of the carbon concentration were both in good agreement with the results of a simulation of the peritectic reaction based on a diffusion-controlled mechanism.

KEY WORDS: peritectic reaction; solidification; transformation; diffusion; iron–carbon system.

1. Introduction

The austenitic structure in carbon steel has significant effects on the mechanical properties of the steel both during and after the manufacturing process. An example of these effects is the formation of surface cracks in continuously cast slabs due to coarse austenitic grains.¹⁾ A fine austenitic structure prevents this type of crack from developing and also produces a fine α -ferrite/pearlite structure after A_{r3} transformation, which results in the high strength and toughness of the steel. Consequently, control of the austenitic structure is very important, and it is useful to investigate the kinetics of its formation.

The austenitic phase (γ) is formed from the δ -ferritic phase (δ) and the liquid phase by a peritectic reaction, in steel with a carbon content of 0.09 to 0.53 mass%.²⁾ This reaction has been reported to be controlled by the diffusion of carbon from the liquid phase through the γ -phase to the δ -phase.^{3,4)} However, Takahashi *et al.*⁵⁾ recently proposed a new mechanism for the formation of the γ -phase. According to their report, the γ -phase formed between the δ -dendrite and the liquid phase by the peritectic reaction grows only to the liquid phase side by solidification and not to the δ -phase side. Furthermore, they suggested that the γ -phase is precipitated in the supercooled δ -phase without diffusion of carbon from the liquid phase.

Formation of the γ -phase by precipitation in the supercooled δ -phase may be possible if the cooling rate is high. The balance between the cooling rate and the peritectic reaction rate will determine which of the two

mechanisms for the formation of the γ -phase will be dominant. However, apparently no report has examined the experimentally measured rate of the peritectic reaction in the iron–carbon system.

In the present study, the rate of the peritectic reaction at a fixed temperature was measured by a diffusion couple method, and the kinetics of the growth process of the γ -phase was investigated.

2. Procedure

According to an iron–carbon equilibrium phase diagram,²⁾ the δ , γ and liquid phases co-exist in a temperature range between 1 768 and to 1 667 K. When the δ and liquid phases are in contact with each other at a temperature within this range, the γ -phase is formed between the two phases by a peritectic reaction. In the present study we measured the reaction rate at 1 696 K. At this temperature the δ -phase with 0.03 mass% C and the liquid phase with 1.85 mass% C react to produce the γ -phase with 0.05 to 0.59 mass% C. This wide range of carbon contents will make it easy to obtain a clear etched structure and a reliable result from the chemical analysis of the sample's carbon concentration.

Two types of steel were prepared. The chemical compositions are given in **Table 1**. In an argon atmosphere, Alloy A (Fe–1.61mass%C) was melted at 1 773 K in a high purity alumina crucible with an inside diameter of 35 mm and a depth of 50 mm. The alloy was then cooled to 1 696 K at a rate of 0.008 K/s to crystallize a small amount of the γ -iron to produce a residual liquid with an equilibrium carbon content at 1 696 K. Soon

Table 1. Chemical compositions of the diffusion couple. (mass%)

	C	Si	Mn	P	S	Sol. Al
Alloy A	1.61	0.02	0.10	0.003	0.004	0.01
Alloy B	0.03	0.03	0.14	0.003	0.003	0.01

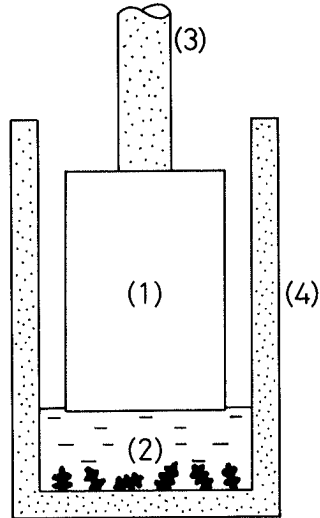


Fig. 1. Schema of the diffusion couple for the peritectic reaction.
 (1) Alloy B (2) Alloy A
 (3) Alumina tube (4) Alumina crucible

thereafter, a sample of Alloy B (Fe-0.03mass%C) with a diameter of 20 mm and a height of 30 mm was moved from a low temperature area in the furnace to a position just above Alloy A in the furnace. After both alloys were held at 1 696 K for 3.6 ks, they were brought into contact with each other as illustrated in Fig. 1. After a predetermined length of time had past, the diffusion couple was rapidly dropped into iced water.

The longitudinal cross sectional surface was etched by nital and the thickness of the γ -phase formed between the δ -phase and the liquid phase was measured. The distribution of the carbon concentration over the δ , γ and liquid phases was also measured.

3. Results

Figure 2 shows the etched cross sectional surface of the sample held at 1 696 K for 7.2 ks. A γ -phase with a large columnar structure was formed between the δ -phase and the liquid phase. Each portion of the γ -phase transformed from the δ -phase or solidified from the liquid phase during the peritectic reaction was estimated from the total measured thickness of the γ -phase and from the initial height of Alloy B, which consisted entirely of the δ -phase before the reaction. Although the microstructure of the sample was observed minutely, unique structures, such as grain boundaries or inclusions, were not observed at the initial δ /liquid interface.

The relationship between the thickness of the γ -phase and the reaction time is given in Fig. 3. Three curves in the figure were regressed such that



Fig. 2. Microstructure of the sample held at 1 696 K for 7.2 ks. L, A and F are liquid phase, austenitic phase and δ -ferritic phase, respectively.

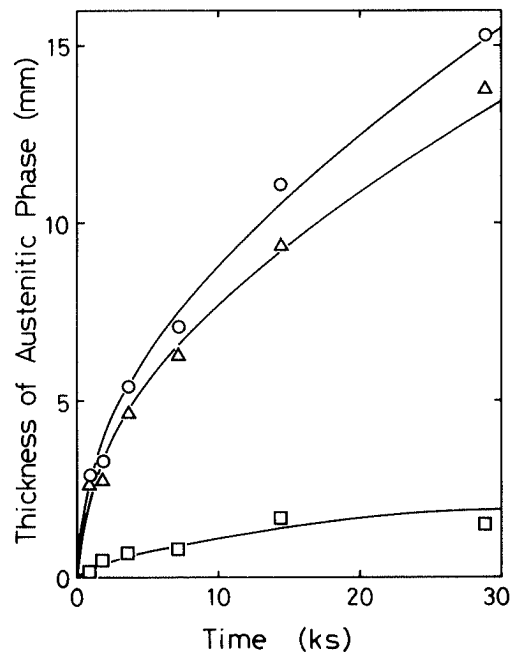


Fig. 3. Growth process of austenitic phase at 1 696 K.
 □: Austenite solidified from liquid.
 △: Austenite transformed from δ -ferrite.
 ○: Total austenite.

$$x_1 = 5.4t^{0.57}, \dots\dots\dots(1)$$

$$x_2 = 80.0t^{0.50} \dots\dots\dots(2)$$

and

$$x_3 = 85.7t^{0.50}, \dots\dots\dots(3)$$

where t is the reaction time (s), x_1 and x_2 are the thickness (μm) of the γ -phase solidified from the liquid phase and transformed from the δ -phase, respectively, and x_3 is the total thickness of the γ -phase. Each portion of the γ -phase increased in proportion to the approximate square root of the time, as seen in Eqs. (1) to (3).

The sample was cut transversely at about 2 mm intervals, and the carbon content of each slice was analyzed by a combustion method to obtain the longitudinal distribution of the carbon concentration in the sample. The result is shown in Fig. 4. Symbols C_1 to C_4 in Fig. 4 show the equilibrium carbon concentration

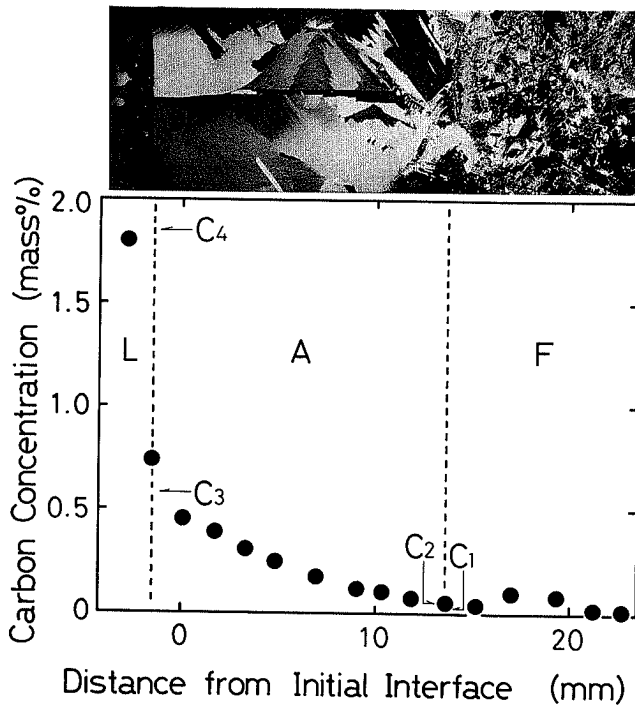


Fig. 4. Distribution of the carbon concentration in the sample held at 1696 K for 28.8 ks. C_1 to C_4 are the equilibrium concentrations at each interface, corresponding to those in Fig. 5. L, A and F are liquid phase, austenitic phase and δ -ferritic phase, respectively.

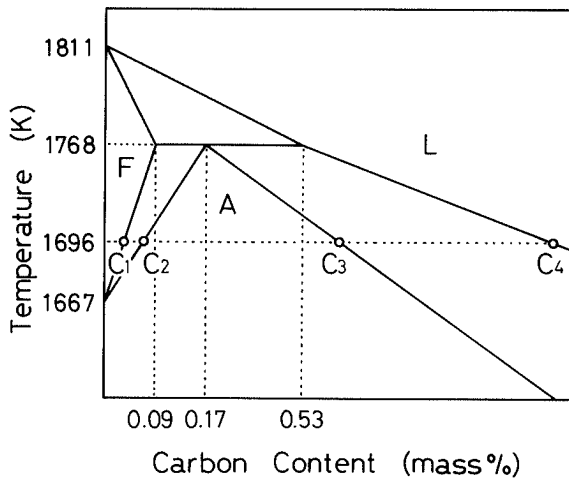


Fig. 5. Schema of an iron-carbon phase diagram.²⁾

at each interface, corresponding to those in Fig. 5. The equilibrium partition was recognized at each interface, and the carbon concentration in the γ -phase decreased steeply from the γ /liquid interface toward the δ / γ interface.

4. Discussion

4.1. Comparison with the Simulation

Chuang *et al.*³⁾ have reported that the peritectic reaction is controlled by the diffusion of carbon through the γ -phase formed between the δ -phase and the liquid phase. The parabolic growth of the γ -phase shown in Fig. 3 or in Eqs. (1) to (3) seems to support this mechanism. However, the γ -phase in the present

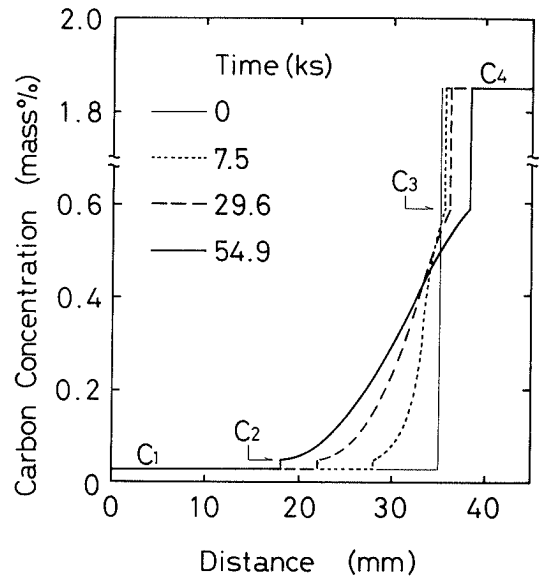


Fig. 6. Simulated distribution of the carbon concentration. C_1 to C_4 correspond to those in Fig. 5.

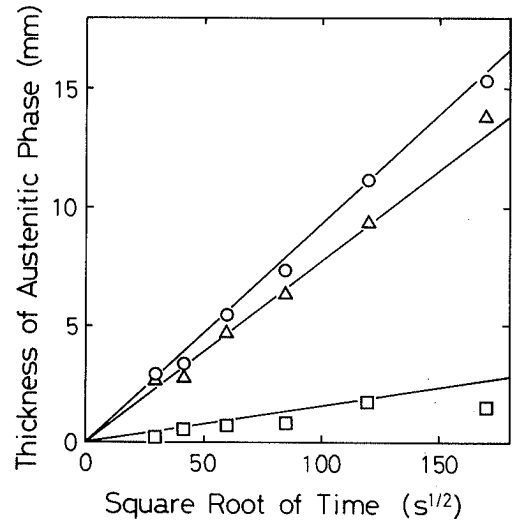


Fig. 7. Measured (plots) and simulated (lines) growth process of austenitic phase at 1696 K. Plotted marks correspond to those in Fig. 3.

experiment initially grew about $86 \mu\text{m}$ in 1 s. This was much higher than expected. Some experimental data reported by other authors^{5,6)} have suggested that the growth rate is fairly slow. Therefore, to examine whether the high growth rate measured in this study coincides quantitatively with the result estimated from the diffusion-controlled mechanism, we simulated the diffusion of carbon during the peritectic reaction by the method proposed by Ueshima *et al.*⁷⁾

The simulated distribution of the carbon concentration is given in Fig. 6. The simulated distribution at 29.6 ks (broken line) approximately agrees with the measured distribution at 28.8 ks in Fig. 4. The simulated growth process of the γ -phase is shown in Fig. 7. Each portion of the γ -phase solidified from the liquid phase and transformed from the δ -phase is perfectly proportional to the square root of time and is in good agreement with the measured result. Thus, the present results coincide

quantitatively with the results estimated from the diffusion-controlled mechanism.

The measured growth rate of the γ -phase in this experiment coincided with the calculated growth rate based on the diffusion-controlled mechanism. However, it was much higher than what would be estimated from other reports. We examined various possibilities to explain this difference.

A photography by Suzuki *et al.*⁶⁾ showed the clear trace of the residual δ -phase inside the dendrite in 0.25 mass% C steel. If the δ/γ interface moves as quickly as is estimated from Eq. (2), then, based upon the size of the dendrite in their sample, the δ -phase should have disappeared within 1 s. It would have been almost impossible to stop the rapid movement of the interface by quenching the sample.

Takahashi *et al.*⁵⁾ measured the distribution of the carbon concentration in a quenched sample of Fe-0.29 mass% C alloy, and found that to entirely eliminate the low carbon spots corresponding to the carbon content of the δ -phase in the comparatively high carbon area of the γ -phase it was necessary to reduce the cooling rate to 0.06 K/s between the temperatures 1771 and 1713 K. This means that it took more than 900 s for the entire δ/γ transformation. On the other hand, for the size of the dendrite in Takahashi's sample, the entire transformation should require less than 5 s, according to Eq. (2).

The significantly rapid movement of the interface measured in the present study may have been the results of: 1) the large difference between the carbon concentration C_3 and C_2 in Fig. 4, because the temperature in the present experiment was lower than 1768 K, at which the peritectic reaction starts in continuously cooled steel, and also because 2) the δ -phase in the present experiment had an equilibrium concentration from the beginning of the reaction, while the concentration of the δ -dendrite which was solidified during the continuous cooling was somewhat lower because of the segregation.

We investigated the effect of the reaction temperature and the initial carbon content of the δ -phase.

4.2. Effect of the Reaction Temperature

The process of the peritectic reaction at various temperatures was calculated by the same method as described above.⁷⁾ Figure 8 shows the effect of the reaction temperature on the rate constant for the movement of the δ/γ interface during the peritectic reaction. As seen in this figure, the interface moves faster as the temperature decreases. This tendency is the reverse of the general relationship between the reaction rate and the temperature.

The rate of the peritectic reaction is controlled by the diffusion of carbon in the γ -phase, as confirmed in Sec. 4.1. Therefore, the rate should be related to the gradient of the carbon concentration, and to the diffusion coefficient of carbon in γ -phase, according to Fick's first law. Although the concentration gradient changes with position and time, the effect of the reaction temperature on the concentration gradient may be ascertained

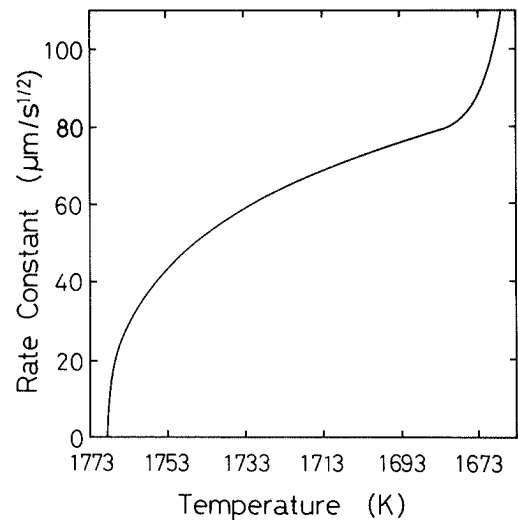


Fig. 8. Effect of temperature on the rate constant for the movement of the δ/γ interface during the peritectic reaction.

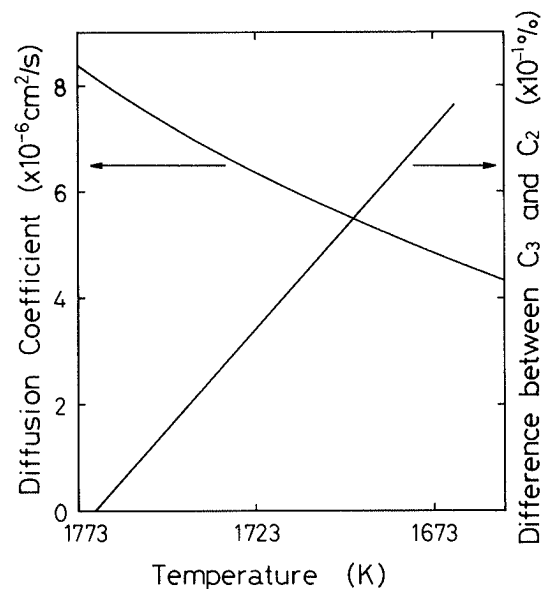


Fig. 9. Effect of temperature on the diffusion coefficient of carbon in γ -iron and on the difference between the carbon concentration at the interfaces of austenite, C_3 and C_2 .

qualitatively from the relationship between the temperature and the difference between the carbon concentration at both interfaces of the γ -phase.

Figure 9 shows the effect of the reaction temperature on the difference between C_3 and C_2 in Fig. 5 and on the diffusion coefficient of carbon in γ -iron.⁷⁾ The difference between the carbon concentration increases dramatically with decreasing temperature, while the decrease in the diffusion coefficient is small. This may explain the reason why the reaction rate is higher at a lower temperature.

4.3. Effect of the Initial Carbon Content in the δ Phase

The δ -iron used in the present experiment was carbon-saturated from the beginning of the reaction, while the δ -dendrite which was solidified in the manufacturing process may have had a somewhat lower

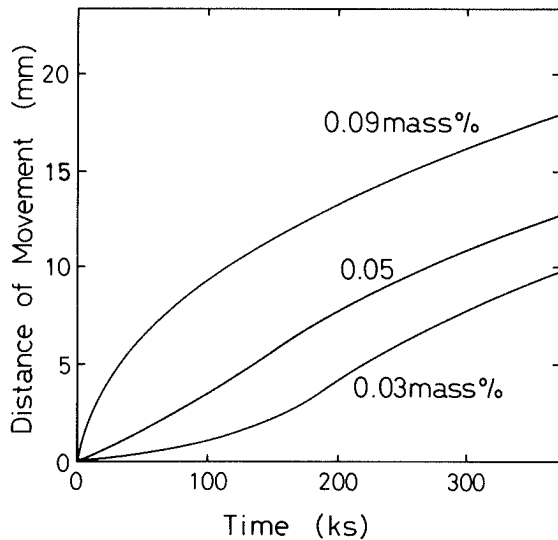


Fig. 10. Movement of the δ/γ interface during the peritectic reaction at 1763 K for various initial carbon contents of δ -phase.

carbon content than the saturation level because of microsegregation during solidification. We calculated the kinetics of the peritectic reaction between a δ -phase with a lower carbon content than the saturation level and a liquid phase with an equilibrium concentration.

Figure 10 shows the movement of the δ/γ interface during the peritectic reaction at 1763 K for various initial carbon contents of the δ -phase. The carbon concentration of the solvus line of the δ -phase is 0.09 mass% at this temperature, according to an iron-carbon equilibrium phase diagram.²⁾ In a δ -phase with an initial carbon content of 0.09 mass%, the interface moves in a parabolic manner from the outset. However, in a δ -phase with a lower initial carbon content, the interface initially moves very slowly, but the movement gradually becomes

parabolic over time. This behavior which is associated with a lower initial carbon content implies that the interface does not move until the carbon concentration in the δ -phase in the vicinity of the interface increases to the saturation level due to carbon atoms diffusing from the liquid phase through the γ -phase into the δ -phase.

5. Conclusions

The rate of the isothermal peritectic reaction in the iron-carbon system was measured by a diffusion couple method. The distribution of the carbon concentration in the sample was also measured. By comparing these results with the simulated results of the peritectic reaction based on a diffusion-controlled mechanism, the following conclusions were derived.

- (1) The peritectic reaction in the iron-carbon system is controlled by the diffusion of carbon through the γ -phase from the liquid phase to the δ -phase.
- (2) The rate of the reaction increases with decreasing temperature.
- (3) The low initial content of the δ -phase reduces the initial rate of the reaction, although the rate becomes more parabolic with time.

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