Ostwald Growth of Fe_3C and Distributions of Carbon Atoms in α -iron Annealed under a Constant Temperature Gradient

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When α -iron specimens are annealed for a long time under a temperature gradient, it is reported that coagulation of Fe_3C precipitates occurs at the high temperature side of the specimens. The coagulation process has been explained by the thermal diffusion of carbon under a temperature gradient. In this paper, the authors propose that the Ostwald coarsening of Fe_3C precipitate under a temperature gradient cause the Fe_3C coagulation.

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1. Introduction

Shewmon annealed α -iron specimens in a constant temperature gradient until diffusion of carbon became to zero, and then measured the carbon distribution along the temperature gradient.^{1,2)} The total carbon content measured at each temperature was normalized by dividing by that at the cold end of the specimen, and plotted versus to $1/T$.²⁾ Figure 1 shows one of the experimental result of Shewmon.²⁾ The carbon content of the specimen was 0.02 mass%, and the temperature range was 942 ~ 984 K.²⁾

Shewmon explained the steep rise in the normalized carbon content of the left side in the figure was due to coagulation of Fe_3C at the high temperature end of the specimen, and the gradual increase toward the left side was a distribution of solute carbon under the temperature gradient.¹⁾

We previously discussed on the carbon distribution in detail; however, we did not fully inquire into the coagulation of Fe_3C .³⁾

2. Ostwald Coarsening of Fe_3C under a Temperature Gradient

Figure 2 shows the temperature dependence of the Gibbs free energy of Fe_3C . The value of the free energy was calculated using database SGTE with THERM-CALC.³⁾ The temperature range of Fig. 2 covers that of Shewmon's experiments. Figure 2 shows that the Gibbs free energy of Fe_3C decreases with an increase in a temperature. Therefore, under a temperature gradient, Fe_3C precipitates existing in the highest temperature place in the specimen are considered to grow preferentially. As the results, after a long enough time, Fe_3C precipitates at the high temperature side of the specimen are thought to have coagulated.

3. Distribution of Solute Carbon under a Temperature Gradient

Figure 3 illustrates the distribution of carbon after the an-

Fig. 1 Comparison among the experimental data and calculated solubility limit values of carbon in α -iron. The total carbon content measured at each temperature and solubility limit values of carbon calculated taking Fe_3C and graphite as the standards were normalized by dividing by their respective values at the lowest temperature given to the diffusion specimen.

nealing. The Fe_3C layer exists at the high temperature end of the specimen, and the solute carbon in the α -iron must be in equilibrium with Fe_3C at the boundary between the Fe_3C layer and the α -iron.

When $J_C = 0$ under the temperature gradient, Shewmon derived the following equation to interpret the experimental results,²⁾

$$\frac{d \ln N_C}{dz} = \frac{-^*Q_C}{RT^2} \frac{dT}{dz}. \quad (1)$$

Here, J_C denotes diffusion flow flux, and N_C concentration of solute carbon, respectively. And z is a coordinate taken along the temperature gradient. The quantity *Q_C is called the reduced heat of transfer for carbon.

Since the experimental value of *Q_C was close to the value of the migration energy of carbon in α -iron, Shewmon sug-

Fig. 2 Temperature dependence of free energy of Fe_3C .

Fig. 3 Carbon distribution model in α -iron annealed in a constant temperature gradient.

gested the relation ${}^*Q_C = -\varepsilon_C^\alpha$.²⁾ Here ε_C^α is the migration energy of carbon in α -iron.

The present authors deduced an alternative equation instead of eq. (1):

$$\frac{d \ln N_C}{dz} = \frac{h_C^\alpha}{RT^2} \frac{dT}{dz}, \quad (2)$$

where, h_C^α is the partial molar enthalpy of carbon in α -iron.^{3,4)} By substituting the relation, $d/dz = d/dT \cdot (dT/dz)$, into eq. (2):

$$\frac{d \ln N_C}{dT} = \frac{h_C^\alpha}{RT^2}. \quad (3)$$

This equation means that h_C^α can be interpreted as the heat of solution for carbon in α -iron,^{3,4)} then the solute carbon under the temperature gradient must be distributed in proportion to the solubility limit curve of the iron-carbon phase diagram.³⁾

The solubility limit curves for Fe_3C - α -iron and graphite- α -iron systems were calculated using SGTE with THERMOCALC. Each calculated value was normalized by dividing by that at the lowest temperature given to the cold end of the

specimen, and plotted in Fig. 1 versus to $1/T$, together with the experimental data.

It is clear from Fig. 1 that the experimental data fall in between two solubility limit curves, and are rather close to that of Fe_3C - α -iron system.

4. Discussion

4.1 Carbon segregation

The experimental value of *Q_C reported by Shewmon was $100 \pm 6.1 \text{ kJ/mol}$. Values of h_C^α (graphite) and h_C^α (Fe_3C) calculated using SGTE with THERMOCALC are 108 and 128 kJ/mol, respectively.¹⁾ Here, graphite and Fe_3C in the round parentheses denote the reference states on which the values of h_C^α are calculated.¹⁾ Comparing these three values, the authors interpreted as ${}^*Q_C = -h_C^\alpha$ (graphite), in the previous paper.³⁾ However, Fig. 1 clearly shows that *Q_C must have the intermediate value between 108 and 128 kJ/mol. Considering this and the coexistence of Fe_3C precipitates in the specimen, we may reasonably conclude as ${}^*Q_C = -h_C^\alpha$ (Fe_3C).

4.2 Fe_3C coagulation

The carbon diffusion toward the high temperature side looks like a reasonable process for the Fe_3C coagulation, however, this process is not possible.

Let's assume Fe_3C precipitates are distributed uniformly before annealing in a temperature gradient. At the beginning of the annealing, the precipitates start to dissolve, and soluble carbon increases toward the solubility limit value. When the carbon concentration reaches the solubility limit value at each temperature, the condition which satisfies eq. (2) will be realized. Since eq. (2) is obtained under the condition, $J_C = 0$, the carbon diffusion toward the high temperature side can not advance anymore.

If $|{}^*Q_C|$ were larger than h_C^α (Fe_3C), the carbon diffusion could continue beyond the equilibrium to build up the Fe_3C coagulation. Shewmon introduced the larger value by summing *Q_C ($=\varepsilon_C^m$) and h_C^α (Fe_3C) due to his considering that the coagulation was the result of thermal diffusion of carbon and a carbon distribution in proportion to its solubility limit curve.¹⁾ However, this summation is not allowed since two equations are defined in different vector spaces. Equation (2) is formulated using an usual heat flow flux, J_Q , and eq. (1) is defined upon the reduced heat flow flux, $J'_Q = J_Q - h_C^\alpha J_C$.^{3,4)} If we would admit the summation, the experimental data in Fig. 1 should lie below the solubility limit curve for the Fe_3C - α -iron system. However, as shown in Fig. 1, the experimental data locate in between two solubility limit curves.

In contrast, the Ostwald coarsening of Fe_3C can continue until all Fe_3C precipitates have been swept up into the high temperature end of the specimen. Thus, we can conclude that the mechanism of the Fe_3C coagulation is the Ostwald coarsening.

5. Conclusion

It is shown here that Fe_3C coagulation and solute carbon segregation toward the high temperature side of a specimen

annealed under a constant temperature gradient for a long time can be explained by the Ostwald coarsening of Fe_3C precipitates and a carbon distribution in proportion to the solubility limit curve of the Fe_3C - α -iron phase diagram.

REFERENCES

- 1) P. G. Shewmon: Trans. Amer. Inst. Min. Eng., **212** (1958), 642–647.
- 2) P. G. Shewmon: Acta Metall., **8** (1960), 605–611.
- 3) R. Habu and W. Yamada: Mater. Trans., JIM, **39** (1998), 351–356.
- 4) R. Habu: Mater. Trans., JIM, **40** (1999), 1355–1360.