Micro-segregation on the Mono-variant Line of an Iron–Carbon–Chromium Ternary Alloy

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To examine the effect of diffusion in the solid on the micro-segregation on a mono-variant line, a directional solidification experiment has been carried out in an iron–carbon–chromium ternary alloy. In an iron–carbon–metal ternary alloy, carbon is an interstitial solute in an iron-base solution (austenite or ferrite) and the diffusivity in the solution is not negligible, while the third metallic element in the iron-base solution is usually substitutional solute and its diffusivity is negligible compared with that of carbon. The second phase of the ternary alloy is usually a kind of carbide, and the diffusivity of carbon or the third metallic element can be neglected because of the strength of the bonding forces of the atoms. In such a situation with dendritic-eutectic mode, a micro-segregation model on the mono-variant line has been introduced, and it has been predicted that the progress of the solidification might terminate before reaching the three-phase eutectic point. If we assume a Scheil-type model of micro-segregation on a mono-variant line, the composition of the residual liquid will reach the terminal (for example, three-phase eutectic) point.

To confirm this prediction, an experiment has been carried out in an iron–carbon–chromium alloy. The initial composition is 3.17 mass% C and 25.6 mass% Cr and very near the eutectic valley of austenite–(Fe, Cr)7C3. With no diffusion of carbon in the austenite phase, the solidification will change to austenite–(Fe, Cr)3C eutectic reaction through the peritecto-eutectic point. With the effect of carbon, using the model, the solidification will end before reaching the peritecto-eutectic point and (Fe, Cr)3C formed during solidification will not be found. The metallographical observation revealed the existence of (Fe, Cr)3C phase but did not reveal the existence of (Fe, Cr)7C3 phase. The EPMA measurement between the dendritic arms showed that the measured minimum chromium compositions inside the austenite agree with the predicted values within an experimental error and uncertainties of parameters of the system. The identification of the phases by using XRD indicated that austenite–(Fe, Cr)3C eutectic did not form, as was predicted. These results suggest the validity of the model of micro-segregation on the mono-variant line in an iron–carbon–metal ternary system.

KEY WORDS: diffusion; carbon; austenite; carbides; metallographical methods.

1. Introduction

When considering the solidification of an iron–carbon–metallic ternary alloy, one sometimes encounters the situation where the solidification of the liquid proceeds on a eutectic mono-variant line with the liquid reducing its temperature to produce two solid phases (symbolically, $\alpha$ and $\beta$). Depending on the degree of freedom, the solidification mode can become cellular-eutectic or dendritic-eutectic. If all of the two solutes were not at all diffused in the either solid phase, the solute redistribution problem during the solidification would be “Scheil-type” (two solutes instead of one meaning that a couple of simultaneous differential equations instead of a differential equation would be used), so it could be solved easily. But in an iron–carbon–metallic ternary alloy, the $\alpha$ phase is usually austenite or ferrite, and carbon diffuses finitely. The diffusion of the metallic solute in austenite or ferrite is negligible compared with that of carbon. The $\beta$ phase is usually carbide (inter-metallic compound), and the diffusion of carbon or the third metallic solute can be neglected. With such an asymmetrical diffusion condition in the two solid phases, appropriate methods to predict the micro-segregation on a eutectic mono-variant line are needed.

Fortunately, a model to predict micro-segregation on a eutectic mono-variant line in which the first solute distributes in the solid phase has been carried out in an iron–carbon–chromium ternary alloy. The experimental study consists of three parts: the first employs a traditional metallographical method to consider the carbide phases which will occur during the solidification process; the second is the identifications of the carbide phases with XRD; and the third is a comparison between the prediction with the model and EPMA measurements.

2. Models

Micro-segregation models of a binary alloy system have
been explored in last seven decades. While enrichment of solute with equilibrium solidification is trivial, Scheil\textsuperscript{4} suggested a model where the liquid is completely mixed and no diffusion of solute works in the solid and made it possible to predict the amount of the nonequilibrium secondary phase, for example, in Al–Cu alloy. Brody and Flemings\textsuperscript{5} proposed a model with finite diffusion of solute in the solid and complete mixing the liquid. This model corresponds to the case where the solute atom is interstitial atom. Later, Clyne and Kurz\textsuperscript{6} suggested a modification equation of the intensity of the diffusion in the solid, “\( \alpha \)”, and modified the Brody-Flemings equation so that even if the local solidification time of the solid becomes infinity, the effect of the diffusion makes the equation of Brody and Flemings to become the equilibrium equation. Recently, Wolcynski et al.\textsuperscript{7},\textsuperscript{8} have made a new physical interpretation on the intensity of diffusion, “\( \alpha \)”, and proposed an analytical model to calculate the solute redistribution after solidification.

On a mono-variant line in a ternary alloy, the problem of the progress of solidification with equilibrium coidition is trivial. Extension of Scheil-type solidification (with complete mixing in the solid and no diffusion of solute in the solid) from a binary system to a ternary system is easy, and can be seen in, for example, the paper of Chen et al.\textsuperscript{9}

Here a model of micro-segregation for a ternary eutectic system on a eutectic mono-variant line is proposed.\textsuperscript{10} In the model, the dendrite-eutectic mode of solidification is assumed. Therefore, the liquid is assumed to be entrapped within the primary and secondary arms of the dendrite. Thus a volume element can be defined perpendicular to the growth direction of dendritic array (see Fig. 1). Neglecting the solidification shrinkage with solidification and transport phenomena of the liquid, micro-segregation problem reduces to a mass conservation problem with solidification. To make the problem simpler, we can assume that the liquid within the volume element is completely mixed. If the spacing between the same neighboring phases (\( \lambda \)) is much smaller than the width of volume element, (that is, \( \lambda \ll \lambda_1 \)), each solid phase (\( \alpha \) and \( \beta \)) can be treated as a continuous phase. In the case that only the diffusion of B solute (the first solute) works in the \( \alpha \)-solid and no other diffusions work in either solid, the basic assumption of the mass balance of the B elements is:

\[
\begin{align*}
\text{(solute rejected in the solid–liquid interface)} \\
= & (\text{solute increase in the liquid}) \\
+ & (\text{solute transported by the diffusion in the } \alpha\text{-phase})
\end{align*}
\]

...(1)

The mass balance equations for B solute and C solute (the second solid) are:

\[
(C^L_B - \ast C^a_B)d\alpha_a + (C^L_B - \ast C^B_B)d\beta_b = (1 - f_a - f_b)dC^a_B + \xi f_a d^* C^a_B
\]

...(2)

and

\[
(C^L_C - \ast C^a_C)d\alpha_a + (C^L_C - \ast C^B_C)d\beta_b = (1 - f_a - f_b)dC^a_C
\]

...(3)

The second term of the right-hand side of Eq. (2) means “solute transported by the diffusion in the \( \alpha \)” This term is dropped in Eq. (3), because of no diffusion of C solute.

Where, \( \xi \) in Eq. (2) is the intensity of the diffusion of the first solute (B) in the first solid (\( \alpha \)) and can be interpreted as \( D_\alpha/L_\alpha^2 \), analogous to Ref. 7, and where \( D_\alpha \) is the diffusion coefficient of the first solute in the first solid, \( t_f \) is the local solidification time of the dendritic eutectic, and \( L' \) is half of the spacing of the dendritic needles (=\( (1/2)\lambda_1 \)). \( f_a \) and \( f_b \) are the volume fractions of \( \alpha \) and \( \beta \) respectively. The solute content \( C \) can be expressed either in mass% or mole fraction (at%), because Eqs. (2) and (3) are based on Eq. (1), and a mass conservation equation holds, regardless of the kind of expression of content, as long as we use a consistent expression. Equations (2) and (3) hold even for the case where the densities of \( \alpha \) and \( \beta \) phase significantly differ from each other, because the effect of the diffusion of B solute is expressed by \( \xi \) as a non-dimensional parameter. For other symbols, see Nomenclature.

These two equations are the general formulation of the solute redistribution at the solid–liquid interface of the problem, and include special cases of the problem. For example, in the case of \( \xi = 0 \), Eq. (2) reduces to

\[
(C^L_B - \ast C^a_B)d\alpha_a + (C^L_B - \ast C^B_B)d\beta_b = (1 - f_a - f_b)dC^1_B ....(4)
\]

which, with Eq. (3), is a “Scheil-type” formulation for solidification on a eutectic mono-variant line of a ternary system. In the case of \( \xi = 1 \), Eq. (2) reduces to

\[
(C^L_B - \ast C^a_B)d\alpha_a + (C^L_B - \ast C^B_B)d\beta_b = (1 - f_a - f_b)dC^1_B + \xi f_a d^* C^a_B
\]

...(5)

which is the case where the first solute completely diffuses in \( \alpha \)-phase, and that the solidification process about B solute in \( \alpha \)-phase is in equilibrium. Therefore, the physical validity of Eqs. (2) and (3) at the limit has been proven.\textsuperscript{10}

Whether we may take \( \xi \) to be unity or a finite value in an actual iron–carbon–metallic alloy will be discussed later.

It would also be meaningful to calculate with a hypothetical phase diagram the progress of the micro-segregation and what the residual liquid will “enrich” with its solute contents. Calculations for this diagram have been carried out in Fig. 2, and some features have been predicted as shown in Fig. 3. In Fig. 3 the horizontal axis shows the normalized content \( s = E_X/E_aE_b \) on the mono-variant line “\( E_aE_b \)”, where the composition of the liquid is denoted by “\( X \)”. The vertical axis shows the volume fraction for solids, and lower symbols illustrate the volume fractions of the \( \alpha \)-phase respectively, while the differences between the uppers symbols and the lower symbols are the volume fractions of \( \beta \)-phase. From these calculation, the solidification ends at
the stage of $x=0.136$ when $\xi=1$ and at $s=0.201$ when $\xi=0$. The value of the diffusion intensity, $s=0.1$, is a possible value for carbon in austenite, and might be somewhat underestimated. From this calculation, it is suggested that a situation could exist where the solidification on a mono-variant eutectic line ends before the liquid reaches the end point of the line.

3. Experimental

3.1. Why Did We Adopt an Iron–Carbon–Chromium Alloy?

To examine this model, we adopted an iron–carbon–chromium system. In this system, three types of carbides are known, that is, (Cr, Fe)$_7$C$_3$ phase, (Cr, Fe)$_3$C$_2$ phase and (Fe, Cr)$_3$C phase. In Fig. 4, a part of the liquidus projection of the Fe–C–Cr phase diagram calculated by Thermo-Calc is shown. On the austenite+$\gamma$+(Cr, Fe)$_3$C$_2$ eutectic line, there exists the peritecto-eutectic point, $P$, and beyond this point the eutectic reaction changes to form austenite and (Fe, Cr)$_3$C phase, although the chromium content decreases on these lines. Fortunately, one can distinguish (Fe, Cr)$_3$C phase from (Cr, Fe)$_7$C$_3$ phase by traditional metallographic techniques, i.e. etching. Table 1 shows comparison of the effect of etchants. Murakami’s reagent changes color for (Cr, Fe)$_7$C$_3$ but does not change color for (Fe, Cr)$_3$C. On the contrary, the solution of the mixture of picric-acid and caustic soda changes color (Fe, Cr)$_3$C but does not change color for (Cr, Fe)$_7$C$_3$. Including the measurement of the solute distribution after solidification, one can estimate the contents of the liquid on the line where the solidification ended. Murakami’s reagent contains 10 g of red prussiate of potash ($K_3[Fe(CN)_6]$) and 10 g of potassium hydroxide (KOH) per 100 ml of water. The solution of the mixture of picric-acid and caustic soda contains 2 g of picric-acid and 25 g of caustic soda per 100 ml of water.

3.2. Chemical Composition of Specimen and Uni-directional Solidification Experiment

The chemical composition of specimen is shown in Table 2. The composition is illustrated by the open circle in Fig. 4. In this figure, the eutectic mono-variant line curves sharply, so it appears difficult to calculate the progress of the micro-segregation by using the similar method to Fig. 3. In reality, we calculated the micro-segregation by using the phase diagram presented with mole fraction. In this diagram, the meander of the mono-variant line is weak, and we might calculate the progress by assuming the mono-variant line is straight. The conservation from mole fraction to mass% is

$$x' = \frac{M_A x}{M_A x + M_B y + M_C z} \text{ ............(6)}$$

e tc., where, $M_A$, $M_B$, or $M_C$ is the atomic weight of A atom, B atom or C atom respectively, $x$, $y$, or $z$ is the mole fraction of A element, B element or C element of the ternary alloy and $x'$ is the content of A expressed in mass%. The conservation from mass% to mole fraction is carried out by solv-
ing these three simultaneous equations about \((x, y, z)\).

It is predicted that the composition denoted by the open square in the diagram will terminate its solidification at the composition denoted by the solid square when \(\xi=0.1\). The composition of the open square is very similar to the initial composition. Therefore the solidification will end before reaching the peritecto-eutectic point.

The Experiment was conducted in the following manner. A sample having the chemical composition listed in Table 2 was broken into small granular pieces, and these were placed into an alumina crucible for heating in a Bridgeman-type furnace. The crucible was heated to 1 660 K for fifty minutes. Then the body of the furnace was pulled out by a motor leaving the crucible in a constant position, and a unidirectional solidification started from the bottom of the crucible. When the temperature of the crucible dropped to 1 550 K, it was immersed in water to cool the sample. The temperature of the crucible was measured by two thermocouples and the solidification condition of the sample was estimated. Needless to say, the temperature measurements were based on the air near the sample and not the sample itself, but when the heat capacity of the furnace system is much greater than that of the sample and the moving speed of the furnace heating is low, the measured temperature approximately indicates the temperature of the sample. The mass of the sample was about 50–60 g, which is much less than that of the furnace system, and the moving speed of the furnace heating was about 0.04 mm/s.

### 3.3. Estimate of Solidification Conditions

The solidification parameters were estimated from the measurements of two thermocouples such that the temperature gradient was \(G=3.1\) K mm\(^{-1}\) and the growth rate of the solid was \(V=0.036\) mm s\(^{-1}\). The primary dendrite spacing was about 0.41 mm (see Fig. 6(a)), and the spacing of dendritic eutectic, \(\lambda_1\), can be taken as the same length. \(D_0\) would be about \(1 \times 10^{-10}\) m\(^2\) s\(^{-1}\) at the experimental temperature. Therefore, the intensity of diffusion of carbon in austenite phase, \(\xi\), might be about 0.5.

### 3.4. Prediction of Micro-segregation with \(\xi=0.5\)

Now that we have estimated the \(\xi\)-value, we can calculate the solute distribution profile after solidification of this sample. As in Fig. 4, the starting composition of this specimen could be replaced by the open square of Fig. 4 because the amount of primary dendrites was less than 0.05.

The result of the calculation is shown in Fig. 5. In this calculation, the possibility of decomposition of carbide during solidification has been neglected. The content of chromium in austenite will decrease from 15.3 to 11.8 mass\%. The content of chromium in (Cr, Fe),\(C_3\) will decrease from 60.5 to 50.8 mass\%. As the diffusion of chromium in austenite or (Cr, Fe),\(C_3\) after solidification is negligible, the minimum content of chromium in sample will be 11.8 mass\%. In the case of carbon, the situation is somewhat complicated. The content of carbon in austenite will increase from 1.12 to 1.40 mass\%. But these values are at the solid-liquid interface. The content at the first solidification stage would increase a little due to the diffusion after solidification. The content of carbon in (Cr, Fe),\(C_3\) will decrease from 8.81 to 8.76 mass\%. Naturally, (Cr, Fe),\(C_3\) is a stoichiometric compound, only changing the ratio of chromium to iron, but the content of carbon indicated by mass\% changes as the content of chromium changes. Thus the carbon contents in austenite and (Cr, Fe),\(C_3\) approach to each other, and it is hard to examine the extent of the progress of the micro-segregation from the measurement of carbon contents in the sample. However, it can be estimated that the carbon contents in the austenite phases in the sample would be about 1.1 to 1.4 mass\%, while the carbon contents in the (Cr, Fe),\(C_3\) phases would be about 8.8 mass\%.

From this calculation, it can be determined that the solidification on the mono-variant line would end before reaching the composition of the solid square, and before reaching the peritecto-eutectic point.

### 3.5. Three Methods to Examine the Prediction

Three methods were employed to examine the prediction. Two of them were qualitative, but one was quantitative.

1. The prediction suggested that austenite–(Cr, Fe),\(C_3\) eutectic would be formed but austenite–(Fe, Cr),\(C_3\) eutectic was not be formed. As described in Sec. 3.1, one can distinguish between (Fe, C),\(C_3\) and (Cr, Fe),\(C_3\). In addition, it is said that the solution of the mixture of picric-acid and caustic soda changes color for the (Fe, C),\(C_3\) phases formed by solidification but that it does not change color for (Fe, Cr),\(C_3\) phases formed by solid state decomposition because of their small size.

2. Identification of carbides can be made directly with XRD.

3. The solute distribution profiles of chromium and carbon can be measured by EPMA. These measurements can be compared with the prediction shown in Fig. 5. In particular, it would be meaningful to compare the minimum content of chromium in the sample with the minimum content of prediction.

### 4. Results of the Three Methods

#### 4.1. Identification of Carbides by Etching

Figure 6 shows the transverse sections of the sample in its solid state. The three photographs are: (a) the sample etched with 3% nital, (b) the sample etched with Murakami’s reagent after nital, and (c) the sample etched with a solution of picric-acid and caustic soda after nital.

![Fig. 5. Predictions for solute content for the specimen.](image-url)
Each photograph covers almost the same area of the sample. At a glance, photograph (c) looks like photograph (a). And a closer look reveals the two-phase mixture in the fine colored particles observed between cross-like dendritic structures in photograph (b). The two-phase mixture might be austenite–(Cr, Fe)7C3 eutectic.

4.2. Identification of Carbide Phases with XRD

Figure 7 shows the XRD peaks after smoothing. In this figure the open squares coincides the peaks of (Cr, Fe)7C3 phase. Weak peaks of Fe3C are observed. These peaks were not predicted with etching experiment, but this problem will be discussed in Sec. 6.

4.3. Comparison of the Predicted and Experimental Solute Profile Distributions

Figure 8 shows the chromium content profile measured with EPMA. The minimum content is 13.5 mass% and the difference compared to the prediction is 1.7 mass%. This is within the error tolerance of the measurement. The maximum content is 60.5 mass% and coincides the prediction. Figure 9 shows the carbon content profile measured with EPMA. The values near the lower contents levels are within the range of the prediction. However, the values near the higher contents levels are a little larger than predicted. Although the carbon content in (Fe, Cr)7C3 changes slightly, it appears that errors in measurement, which are not small, are included. Nevertheless, the agreement of prediction with the austenite level is good. In addition, the first seven points of the left-side of this figure are the results of measurement within a primary dendrite. The carbon contents display a slight successive decrease. This is evidence that the solidification proceeded with finite rather than complete diffusion of carbon in the austenite. If this solidification process were to be made with $\xi=1$, the carbon content within the dendrite would remain constant. Thus, our use of the finite value of $\xi$ rather than unity in the calculation is justified.

5. Complementary Experiment

The results of the three methods to examine the prediction might suggest that the prediction holds true. But a question arises in consideration of the first method in re-
gards to the identification of the carbide by etching. Did a small amount of (Fe, Cr)\(_3\)C phases crystallize during solidification and possibly escape detection due to their small size? To eliminate this doubt, a complementary experiment was carried out for Fe–2.8mass%C–13.5mass%Cr alloy.

The composition of this alloy is illustrated with cross symbol in Fig. 4. Since the chromium content is lower than that of open circle, it is expected that (Fe, Cr)\(_3\)C will crystallize during solidification. In Fig. 10, the XRD peaks of this experiment are shown. Apparent Fe\(_3\)C peaks are observed and (Cr, Fe)\(_7\)C\(_3\) peaks are also observed. In Fig. 11, the microstructures of this sample are shown. (a) is a photograph etched with Murakami’s reagent after nital, and (b) is a photograph etched with a solution of picric-acid and caustic soda after 3% nital.

Minimum content of chromium is about 5 mass%. This might correspond with the peritecto-eutectic point. The statement “substance in existence can be observed” stands in contraposition to the statement that “not observed” implies “nonexistence”. Therefore, the doubt raised in the question above is erased.

6. Discussion

From the results of the two experiments above, it can be stated that the prediction of micro-segregation of the model holds. Then, why are the weak Fe\(_3\)C peaks found in XRD measurement in the first experiment? In this experiment, the austenite compositions where the dendritic-eutectic solidification ended are nearly 13.5 mass% chromium and 1.3 mass% carbon. This means that the solidification ends before the peritecto-eutectic point. The most probable explanation is that (Fe, Cr)\(_3\)C was formed during solid-state decomposition of austenite after solidification. In Fig. 13, an iso-thermal section (700°C) of Fe–C–Cr alloy phase diagram\(^{11}\) is shown. The hatch-marked area shows the above mentioned compositions. If a slight change of composition occured, a little amount of M\(_3\)C might form.

7. Conclusion

A micro-segregation model has been introduced. This model is mainly for an iron–carbon–metal alloy with a dendritic-eutectic solidification mode. As an actual ternary system, an iron–carbon–chromium alloy has been examined. Two qualitative approaches and one quantitative approach were employed to examine the prediction based on the model. Comparisons between the predictions of the analytical model and the results of experiment have been made.
for the uni-directional solidification of Fe–3.17mass%C–25.6mass%Cr alloy.

(1) (Fe, Cr)$_7$C$_3$ phase was identified, but cementite was not identified by the etching technique.

(2) The peaks of (Fe, Cr)$_7$C$_3$ were strong, but the peaks of cementite were weak in the XRD measurement.

(3) The minimum contents of Cr by calculation and by EPMA measurement agreed well.

A complementary experiment was made for Fe–2.8mass%C–13.5mass%Cr alloy, and colored areas indicating a (Fe, Cr)$_7$C$_3$ phase and a cementite phase were found by etching, and apparent peaks of cementite occurred in XRD.

From this evidence, it can be stated that the predictions of the proposed model for micro-segregation model agreed with the results of experiment. The model can be useful to predict the amount of micro-segregation on the mono-variant line in a Fe–C–Metal ternary alloy system.

Acknowledgements

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Nomenclature

B : The first solute element of the ternary alloy
C : The second solute element of the ternary alloy
$C^L$ : Solute content in the liquid (mole fraction)
$C^\alpha$ : Solute content in the $\alpha$-phase (mole fraction)
* $C^\alpha_B$ : Solute content in the $\alpha$-phase at the solid–liquid interface (mol fraction)
$C^\beta$ : Solute content in the $\beta$-phase (mole fraction)
* $C^\beta_B$ : Solute content in the $\beta$-phase at the solid–liquid interface (mole fraction)
$D_s$ : Diffusion coefficient in the solid (m$^2$s$^{-1}$)

$E$ : End of the mono-variant line
$E_B$ : The content of B solute at E (mole fraction)
$E_C$ : The content of C solute at E (mole fraction)
$f_i$ : Volume fraction of $i$-phase (–)
$M_J$ : Atomic weight of element J
$t_i$ : Local solidification time of a cellular/dendritic eutectic (s)

x : Mole fraction of A element in a ternary alloy
x' : Weight percent of A element in a ternary alloy
y : Mole fraction of B element in a ternary alloy
z : Mole fraction of C element in a ternary alloy
$\alpha$ : The first phase of the solids
$\beta$ : The second phase of the solids
$\lambda_e$ : The spacings of the neighboring $\alpha$ or $\beta$ phase, see Fig. 1 (m)
$\lambda_1$ : Spacing of the needles of the cellular/dendritic eutectic, see Fig. 1 (m)
$\xi$ : Dimensionless intensity of diffusion in the solid, $D_s t_i/L^2$ (–)

REFERENCES

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