Modeling of Stable and Metastable Eutectic Transformation of Spheroidal Graphite Iron Casting

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In this work, a mathematical model for stable and metastable transformation of SG cast iron, coupling with microsegregation of some elements and latent heat resulted from different phase formation, was presented. The quantitative experimental results of specimens obtained from a step-shape sample casting were compared with the simulation, and two results of nodular counts and sizes agreed quite well. For white eutectic growth in mottled SG iron, the frequent impingement of white eutectic with austenite–graphite bulks might suppress its growth remarkably and result in quite lower growth rate than that from the melt exclusively. Meanwhile, the relationship of morphology of carbides and solidification was discussed, and it was indicated that the growth of white eutectic and carbide morphology could also be predicted by solidification simulation. It was found that neglecting silicon microsegregation, if metastable transformation was advantageous to stable, the simulated carbide fraction was higher, and vice versa.

KEY WORDS: spheroidal graphite cast iron; stable and metastable microstructure; eutectic transformation; modeling and simulation.

1. Introduction
Spheroidal graphite (SG) iron castings play a significant role in many industries especially in the automotive industry. The formation of carbide of SG iron castings during solidification decreases their machinability as well as the mechanical properties remarkably, and is a frequent reason for rejecting them. Although white microstructure can be transferred by heat treatment, however, the treatment would increase the cost of products reluctantly.

The modeling of gray-to-white transition of iron castings has been studied by a number of researchers, and the following factors should be taken into account, such as: nucleation and competitive growth of stable and metastable eutectics, microsegregation of various elements during solidification. Therefore, the mathematical models should be further improved and be verified with quantitative experimental results. Besides, the understanding of modeling stable to metastable transition of SG iron should be also studied. In this work, a mathematical model for stable and metastable transformation was presented and the influence of microsegregation of some elements and the latent heat of different phase formation were considered. The results of simulation and quantitative experiment of samples obtained from a step-shape casting were then compared, analyzed, and discussed.

2. Model Description
2.1. Nucleation
The research indicated that total number of nucleation was given by \( N = A \times (\Delta T)^n \), where \( \Delta T \) is the undercooling with respect to the equilibrium temperature of the phase transformation, \( A \) and \( n \) are constants reflecting the inoculation treatment. The nucleation rate is expressed as Eq. (1), and the number of nuclei appearing in liquid from calculation time \( t \) to \( t + dt \) can be calculated by considering the available liquid volume of nucleation with Eq. (2):

\[
\frac{dN}{dt} = nA(\Delta T)^{n-1} \frac{d\Delta T}{dt} \\
N_{t \rightarrow t + dt} = \int_{t}^{t + dt} f(\Delta T)^{n-1} \frac{d\Delta T}{dt} \, dt
\]

where \( f \) is volume fraction of liquid (%).

In this work, the gray and white transformation under their equilibrium temperatures, \( T_{\text{stable}} \) and \( T_{\text{metastable}} \) respectively, was considered and they were calculated by literature:

\[
T_{\text{stable}} (\degree C) = 1154 + 4(Si\%) - 2(Mn\%) - 30(P\%) \quad (3)
\]

\[
T_{\text{metastable}} (\degree C) = 1148 - 15(Si\%) + 3(Mn\%) - 37(P\%) \quad (4)
\]

where \( \langle Si\% \rangle, \langle Mn\% \rangle, \) and \( \langle P\% \rangle \) are weight percents of silicon, manganese, and phosphorus of liquid.

2.2. Growth
For hypereutectic SG iron investigated in this work, the solidification proceeds in two stages, pro-eutectic and eutectic transformation. In pro-eutectic transformation, the primary graphite spheres grow directly from the melt. While in the eutectic reaction, new nodules appear continu-
The growth rate of graphite spheres in liquid can be computed as follows:

\[
\frac{dR_g}{dt} = \frac{D_g^l}{\rho_l(C_G - C_{\gamma/G})} \frac{R_g}{R_g(R_g - R_{\gamma/G})} \times \frac{R_{g-dt} - R_{g-dt}}{1 - \exp \left( - \frac{D_g^l}{\delta} \right)} \quad \text{(5)}
\]

where \( R_g \) is radii of graphite spheres (m) (superscript \( t \) and \( t-dt \) are the calculation time) \( \rho_l \) and \( \rho_g \) are densities of liquid and graphite (kg/m³), \( D_g^l \) is diffusion coefficient of carbon in liquid (m²/s), \( C_g \) and \( C_{\gamma/G} \) are carbon content of initial liquid and graphite (%), \( C_{\gamma/G}^l \) is carbon content of liquid in equilibrium with graphite and equals to \( C_{\gamma/G} \) approximately (Fig. 1), and \( \delta \) is thickness of carbon diffusion boundary layer in front of liquid–graphite interface (m).

After the nodule was encapsulated by the austenite shell, its growth is dominated by the diffusion. On the basis of carbon diffusion through the shell, the growth rates of bulk graphite spheres were given as follows:

\[
\frac{dR_g}{dt} = D_g^l (C_{\gamma/G}^l - C_{\gamma/G}) = \frac{R_g}{R_g(R_g - R_{\gamma/G})} \times \frac{R_{g-dt} - R_{g-dt}}{1 - \exp \left( - \frac{D_g^l}{\delta} \right)} \quad \text{(6)}
\]

\[
\frac{dR_g}{dt} = D_g^l (C_{\gamma/G}^l - C_{\gamma/G}) = \frac{R_g}{R_g(R_g - R_{\gamma/G})} \times \frac{R_{g-dt} - R_{g-dt}}{1 - \exp \left( - \frac{D_g^l}{\delta} \right)} \quad \text{(7)}
\]

where \( R_g \) is radii of austenite shell of eutectic bulk, \( D_g^l \) is diffusion coefficient of carbon in austenite, \( \rho_G \) is density of austenite, \( C_{\gamma/G}^l \) and \( C_{\gamma/G} \) are carbon concentration of austenite and liquid in liquid–austenite interface respectively, and \( C_{\gamma/G}^l \) is carbon concentration of austenite in equilibrium with graphite.

The growth of graphite spheres during eutectoid transformation might be determined by calculating the growth of ferrite shells with the model in the former research. The growth of lamellar eutectic structure, such as ledeburite eutectic, was characterized by the well-known relationship:

\[
\Delta T = K' \sqrt{V} \quad \text{(8)}
\]

\[
V = K'' \times (\Delta T)^2 \quad \text{(9)}
\]

where \( K' \) and \( K'' \) are constants related materials properties, \( V \) is solidification rate (m/s).

Because of crystal defects, the white eutectic grain often grows bending, and eventually becomes spherical. Therefore, the white eutectic was usually simplified and assumed to be spherolitic in the simulation, whose growth was determined by Eq. (9). The volume fraction of carbide in white eutectic was calculated according to the volume ratio of carbides about 48.5 percent in white eutectic.

2.3. Microsegregation

Many researchers have done significant effort to describe the microsegregation behavior during solidification of different alloys including SG iron. It was proved that microsegregation of various elements had a significant effect on stable to metastable transition as well as the solid-state transformation or heat treatment. The microsegregation behavior is quite different among various elements, for example, silicon segregates negatively during stable while positively in metastable solidification; manganese segregates positively in both reactions, which makes the content of manganese in liquid increase during solidification. Therefore, stable and metastable eutectic equilibrium temperature must be calculated as a function of silicon and manganese concentration in the liquid.

At any time \( t \), the distribution of the element \( X \) in liquid, gray and white eutectics was approximately given by Eqs. (10) and (11):

\[
\langle X \rangle_{\text{gray}} = K_{X,\text{gray}} \langle X \rangle_0 \quad \text{(10)}
\]

\[
\langle X \rangle_{\text{white}} = K_{X,\text{white}} \langle X \rangle_0 \quad \text{(11)}
\]

where \( \langle X \rangle_{\text{gray}} \) and \( \langle X \rangle_{\text{white}} \) are concentrations of \( X \) element in gray and white eutectic at time \( t \), \( K_{X,\text{gray}} \) is partition coefficient of \( X \) element in liquid and gray eutectic and \( K_{X,\text{white}} \) is partition coefficient of \( X \) element in liquid and white eutectic, and \( \langle X \rangle_0 \) is initial content of \( X \) element in liquid at time \( t \).

Neglecting macro convection, the total content of an element of any mesh was assumed unchanged (Eq. (12)), and then the concentration of an element in liquid was determined by Eq. (13):

\[
\sum_{t=0}^{t} \langle X \rangle_{\text{gray}} = K_{X,\text{gray}} \langle X \rangle_0 \quad \text{(12)}
\]

\[
\langle X \rangle_{\text{gray}} = K_{X,\text{gray}} \langle X \rangle_0 \quad \text{(13)}
\]

where \( \langle X \rangle_0 \) is initial content of \( X \) element in the melt, \( d f_{\text{gray}}^t \) and \( d f_{\text{white}}^t \) is volume increase of gray and white eutectic at calculation time \( t \) respectively.

2.4. Latent Heat Treatment

At any time \( t \), the latent heat released by formation of \( X \) phase, \( d Q_X^t \), may be calculated with Eq. (14):

\[
d Q_X^t = J_X V_m d f_{\text{gray}}^t \quad \text{(14)}
\]
where \( L_x \) is latent heat of \( X \) phase (Cal/m\(^3\)), \( V_m \) is volume of a mesh (m\(^3\)), \( d \) is fraction increase of \( X \) phase, and subscript \( X \) represents graphite, austenite, and white eutectic phases.

For any mesh with multi-phase (including liquid, graphite, austenite and white eutectic in this research), its density could be determined by a linear relationship involving the volume fractions of phases and their densities as shown in Eq. (15). Accordingly, its special heat can be obtained by Eq. (16). Then, the temperature change caused by released latent heat, \( \Delta T^* \), may be given by Eq. (17):

\[
\rho_{x+1} = \sum (\rho_x f_x) \quad \text{.................(15)}
\]
\[
C_{x+1} = \sum (\rho_x C_X f_x) / \sum (\rho_x C_X) \quad \text{.................(16)}
\]
\[
\Delta T^* = \sum \frac{dQ_X}{\rho_{x+1} C_{x+1} V_m} \quad \text{.................(17)}
\]

where \( \rho_{x+1} \) and \( C_{x+1} \) are density and special heat of a mesh with multi-phases in liquid–solid status (cal/kg/K), and \( \rho_x \) and \( C_X \) are density and special heat of \( X \) phase respectively.

### 3. Experimental Work

A step-shape sample SG iron casting was cast in green sand mold to verify the modeling of white formation. The shape and size of the sample casting are shown in Fig. 2. A steel chill of 50×100×10 mm (the shade area in Fig. 2) was used to promote the formation of the white eutectic. The pouring temperature was 1350°C. The melt casting was spheroidized with Mg(7.5wt%)-Re alloys and was inoculated with Si(75wt%)-Fe alloys. The final composition of the casting was listed in Table 1.

Twelve specimens, S1 to S12, were obtained from mirror section along L axis (black circles from right to left in Fig. 2). A quantitative microscope was used to get quantitative data of different phases of these specimens. Different fractions of carbides were found in specimens S1 to S6 as shown in Fig. 3 while no carbides in S7 to S12. The experiment was carried out in two steps: 1) the 2D densities and sizes of graphite spheres were analyzed from cross-section of unetched specimens, and according to the hypothesis reported in literature,\(^{21,22}\) the 3D densities of the spheres were derived from 2D data; 2) the volume fractions of carbides were obtained from etched specimens. The results of quantitative experiment are illustrated in Table 2.

### 4. Discussion of Simulation and Experiment

#### 4.1. Comparison of Simulation and Experiment

In the simulation, the constant \( A \) and \( n \) in nucleation equation were set to 1.8×10\(^{-3}\)/m²/K² and 2 respectively. Since the nucleation potential of white eutectic is greater than that of gray, the parameter of white nucleation was several times to gray,\(^{5,6}\) and so \( A \) for white was set to 9×10\(^{-10}\)/m\(^3\)/K². The parameters of density, special heat, latent heat of different phase were taken from reference.\(^{11}\) The diffusion coefficient of carbon in liquid was set to 2×10\(^{-8}\) m²/s,\(^{23}\) and the coefficient of carbon in austenite was given by\(^{24,25}\):

\[
D^*_C = D_0 \exp (-Q/RT) \quad \text{.................(18)}
\]

where \( Q \) is activation energy (cal/mol) and \( R \) is gas constant (cal/mol/K), \( D_0 \) and \( Q \) equal to 2.0×10\(^{-3}\) m²/s and 1.4×10\(^{7}\) J/mol respectively for carbon diffusion in austenite.

The partition coefficients of silicon in stable and metastable eutectics were determined according to the results of reference and were set to 1.23 and 0.8 respectively,\(^{18}\) and the coefficients of manganese in both eutectics were set to 0.7.\(^{20}\)

The comparison of nodule counts and sizes between simulation and quantitative experiment is shown in Fig. 4. It was indicated that two results agreed quite well with each other, which means that the nucleation and growth of graphite spheres in the modeling were accurate. The growth parameter of white eutectic, \( J \), was selected to 8×10\(^{-3}\) m²/s and 1.4×10\(^7\) J/mol respectively for carbon diffusion in austenite.

The partition coefficients of silicon in stable and metastable eutectics were determined according to the results of reference and were set to 1.23 and 0.8 respectively.\(^{18}\) Different parameters from references\(^{5,6}\) were also used to predict the fraction of white eutectic. Meanwhile, the impingement was considered with Johnson-Mehl model.\(^{25}\) The results of carbide fraction of different simulations are shown in Fig. 5. By comparing the results of simulations with experiment, the growth rate of white eutectic in sample mottled SG iron was approximately 1–2×10\(^{-6}\) m²/s/K², quite less than the growth rate of white eutectic, 3.97×10\(^{-3}\) m²/s/K², in the melt alone provided by Magnin.\(^{16}\) For the white eutectic growing in mottled SG iron, the melt is divided into a lot of micro-melts by large numbers of nodules and the frequency of impingement of white eutectic with austenite–graphite bulks is very high. This impingement might suppress the growth of white eutectic remarkably and result in quite lower growth rate.

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**Table 1.** Chemical composition of SG iron sample casting.

| Elements | C   | Si   | Mn | P   | S   | Mg  | Re |
|---------|-----|------|----|-----|-----|-----|-----|
| wt%     | 3.74 | 2.52 | 0.26 | 0.05 | 0.016 | 0.04 | 0.033 |

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Fig. 3. Microphotographs of specimens S1 to S6 (top: S1 to S3 from left to right; bottom: S4 to S6 from left to right).

Fig. 4. Comparison of results of simulation and experiment of nodular counts and sizes.

Fig. 5. Results of carbide fraction of experiment and simulation with different growth parameters.

Table 2. Results of quantitative experiment.

| Specimens | Nodular count $N_{e0} \times 10^3 \text{mm}^{-3}$ | Nodular diameter $D_{0e} \times 10^{-3} \text{mm}$ | Fraction of carbides $f_{\text{carb.}}$, % |
|-----------|---------------------------------|-----------------|-------------------------------|
| S1        | 84.3                            | 6.2             | 36.7                          |
| S2        | 71.1                            | 6.3             | 15.3                          |
| S3        | 61.8                            | 8.9             | 14.8                          |
| S4        | 66.1                            | 8.9             | 9.0                           |
| S5        | 70.0                            | 9.3             | 7.9                           |
| S6        | 50.2                            | 9.9             | 2.1                           |
| S7        | 19.7                            | 14.7            | -                             |
| S8        | 20.2                            | 15.0            | -                             |
| S9        | 8.8                             | 20.7            | -                             |
| S10       | 5.2                             | 26.4            | -                             |
| S11       | 4.9                             | 29.7            | -                             |
| S12       | 5.2                             | 26.3            | -                             |
4.2. Relationship of Carbide Morphology and Solidification

The simulated cooling curves and the variation of carbide fraction of S1 and S2 are shown in Fig. 6. For S1, the white nuclei continuously nucleated and grew in the melt after time $t'$, and so the final morphology of carbides was large free carbides (Fig. 3(a)). Different from S1, the white eutectic growth of S2 proceeded in three periods as shown in Fig. 6(b): period a, the white nucleated and grew; period b, metastable transformation was interrupted; period c, the white nucleated and grew again from liquid remained among austenite and graphite eutectic bulks. Then, small intercellular carbides were formed in S2 as shown in Fig. 3(b). The above explains why the morphology of carbides of S1 and S2 is so different. It is indicated that the white eutectic growth and carbide morphology could be predicted by solidification simulation.

4.3. Influence of Microsegregation on Carbide Fraction

Kagawa indicated that the lower chill fraction was obtained by using constant equilibrium eutectic temperature without considering microsegregation in the simulation. However, a different result was obtained in this work. Neglecting microsegregation and using constant equilibrium eutectic temperature in the simulation, as shown in Fig. 7, the carbide fraction of S1 was higher than that of microsegregation condition, while those fractions of other five samples (S2 to S6) were lower.

Figure 8 shows the simulated cooling curves, and the change of carbide fraction of S1 and S6 during solidification under two cases: considering microsegregation and non-microsegregation. When considering microsegregation, the difference of two equilibrium eutectic temperatures of S1 increased during solidification. The reason was that advantageous growth of metastable eutectic made the silicon concentration in remained liquid increase because of negative microsegregation of silicon in metastable eutectic (Eq. (11)). Therefore, the undercooling $\Delta T$ of white growth respecting to constant equilibrium eutectic temperature for white eutectic growth was greater than that of changed equilibrium temperature depending on microsegregation. Hence, higher carbide fraction was obtained in S1 when neglecting microsegregation. On the contrary, for specimen S6, while the concentration of silicon in liquid decreased, the metastable eutectic equilibrium temperature increased during solidification as shown in Fig. 8(b). Then, under constant eutectic temperature, the final simulated carbide fraction of S6 was lower than that considering microsegregation.

It was concluded that neglecting silicon microsegregation, if metastable transformation was advantageous under high cooling condition, the simulated carbide fraction was higher, while stable transformation was predominated, lower the content.

5. Conclusion

(1) A mathematical model for modeling stable and metastable eutectic transformation was presented, and the microsegregation of some elements and latent heat of different phase formation were coupled in the model.

(2) Comparing the results of quantitative experiments and simulation, it is indicated that the results of both nodular counts and sizes agreed quite well.
(3) For white eutectic growing in mottled SG iron, the frequent impingement of white eutectic with austenite-graphite bulks may suppress its growth remarkably and result in lower growth rate.

(4) The relationship of white eutectic growth and carbide morphology with solidification was discussed, and it is indicated that the carbide morphology could be predicted by solidification simulation.

(5) It was found that neglecting silicon microsegregation, if metastable transformation was advantageous to stable, the simulated carbide fraction is higher, and vice versa.

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