Eutectic Cell and Nodule Count in Cast Iron

Part I. Theoretical Background

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In this work, heat balance is incorporated in developing expressions of general validity for the solidification of hypo-eutectic flake graphite cast iron, as well as eutectic and slightly hyper-eutectic nodular iron. These expressions incorporate the active nucleation and growth processes that occur in flake and nodular graphite. The derived analytical equations describe the eutectic cell \( N \) and nodule count \( N_{\text{nuc}} \) as a function of the solidification parameters and melt chemistry. From this analysis, eutectic cell or nodule counts can be predicted based on experimental data related to cooling rates and chemical composition. In particular, it has been found that the quality of the liquid cast iron is closely tied to its intrinsic nucleation properties (\( N_{\text{nuc}} \) and \( b \) coefficients in the nucleation equation, \( N_{\text{nuc}} = N_0 \exp(-b/\Delta T_m) \)), or directly to the graphite nuclei density, \( N_{\text{nuc}} \).

Moreover, the outcome of the present work is used in providing a rational for the effect of technological factors such as the material mold ability to absorb heat, the casting modulus, pouring temperature, chemistry, inoculation practice, holding temperatures and times on the resultant cell count or nodule count in cast iron.

KEY WORDS: gray cast iron; nodular cast iron; eutectic cell count; nodule count.

1. Introduction

The structure of liquid cast iron is one of the most important factors in determining the “inherited” properties of this material. From the published literature,1) it is evident that unlike other alloys, liquid cast iron is unique due to the crystallographic nature of the graphite structure. The strong anisotropy of graphite as a result of weak molecular bonds between graphite layers and strong covalent bonds within layers can remain at the iron melting temperatures (at or above 2000°C).2) As a result, submicroscopic graphite particles (known also as Cn “molecules”)3) are commonly present in liquid cast iron as they arise from incomplete graphite dissolution. Hence, cast iron melts can be considered as a liquid containing carbon dispersed as a graphite suspension, with particle sizes ranging1,3) from 1 nm to 1000 nm. Since the iron melt already contains a distribution of graphite particles, some of them become active nuclei4,5) as soon as the temperature falls below the graphite liquidus temperature, \( T_{\text{gr}} \).6,7) Moreover, in liquid cast iron nucleation particle substrates (for graphite) of various sizes exist. Accordingly, each graphite nucleus is expected to give rise to a single eutectic cell in flake graphite cast iron, or to a single graphite nodule in ductile cast iron.

In flake graphite cast iron, the austenite–graphite eutectic solidification process is concomitant with the formation of eutectic cells that are more or less spherical (see Figs. 1(a), 1(b)). These eutectic cells consist of interconnected graphite plates surrounded by austenite. Since each eutectic cell is the product of a graphite nucleation event, cell count measurements can be used to establish the graphite nucleation susceptibility of a given cast iron. In general, by increasing the eutectic cell count; (a) the strength of cast iron increases (through8) a reduction in ferrite and an increase in graphite type \( \Lambda \), (b) the chill of cast iron is reduced9) and (c) the pre-shrinkage expansion increases10,11) and in consequence the probability of developing unsoundness in castings.11)

In nodular cast iron of eutectic or slightly hypereutectic composition the solidification sequence can be described as: (a) Once the liquidus temperature for graphite, \( T_{\text{gr}} \) is reached, graphite nodules are nucleated which then freely grow in the liquid (Fig. 1(d)) for a relatively short time prior to being enveloped by austenite and (b) the austenite shell nucleates directly on the graphite nodules (Fig. 1(e)) as soon as the solidification path intersects the metastable line corresponding to the austenite liquidus (extrapolated). Alternatively, austenite dendrites of off-eutectic composition can develop (Fig. 1(d)), which also envelop the graphite (Fig. 1(e)) and cut it from contacting the liquid iron.8,12–14) As mentioned before, in nodular cast iron each graphite nucleus gives rise to a single graphite nodule, consequently the nucleation stage establishes the final nodule count. Among the property improvements related to increasing nodule counts are, (a) an increase in the strength and ductility of ADI iron,15) (b) improved microstructural homogeneity,16,17) (c) reduction in the chilling tendency,18,19) (d) increasing pre-shrinkage expansion20) and (e) increasing fraction of ferrite in the microstructure.20)

Hence, it can be stated that graphite eutectic cells or graphite nodules play a significant role in the exhibited properties of cast iron and consequently they are key microstructural factors in the foundry practice. In the present work, equations of general validity are derived which incorporate the effect of the various physical and technological parameters on the exhibited graphite cell, or nodule counts, based on a theoretical analysis of the solidification process.

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2. Analysis

In liquid melts, Cₙ molecules and particles—nucleation sites of various size can be characterised by a unimodal size distribution function, (A(f) (Fig. 2(d)). This function determines the nucleation potential of an undercooled melt during solidification. Figure 2(e) shows a cooling curve where the arrows indicate the extent of undercooling at the beginning of solidification. Notice that within the time interval, or undercooling from Tₑ to Tₐ, Cₙ molecules and sites of sizes greater than lₙ become active for nucleation (Fig. 2(c)). When all the Cₙ molecules and sites of sizes l＞lₙ become nuclei at Tₑ, the density of graphite nuclei can be described by a previously developed heterogeneous nucleation model as

\[ N_{\text{nuc}} = N_s \exp \left( \frac{b}{\Delta T_m} \right) \]  

where \( N_s \) and \( b \) are the nucleation coefficients for flake graphite or nodular cast iron and \( \Delta T_m \) is the maximum degree of undercooling at the onset of eutectic solidification, (see Fig. 2(e)). Assuming that each nucleus gives rise to a single eutectic cell, or a graphite nodule the expected volume density of eutectic cells, \( N_c \) or graphite nodules, \( N_n \) can be described by \( N_{\text{nuc}} = N \) and \( N_{\text{nuc}} = N_{\text{v}} \), respectively. Moreover, using a heat balance during the solidification process and by incorporating the expected nucleation and growth events an expression is obtained for \( N \) or \( N \) predictions. The analytical solution is described in detail in Appendix (see Eqs. (A32) and (A53)).

2.1. Flake Graphite Cast Iron

\[
N = \frac{32T_1^3 \sigma \beta}{\pi^6 L_e (1-f_e) c_s^2 \varphi \beta^3 M^6 \Delta T_m^3} = \frac{4c_{ef} Q^3}{\pi^3 L_e (1-f_e) \beta M^6 \Delta T_m^3}
\]

Combining Eqs. (1) and (2), \( \Delta T_m \) can be described by

\[
\Delta T_m = T_e - T_m = \frac{b}{8 \text{ProductLog}[y]} \tag{3}
\]

where

\[
y = \frac{b}{8} \left[ \frac{3L_e N_s (1-f_s) \mu^3}{4 c_{ef} Q^3} \right]^{1/8} \tag{4}
\]

\[
Q = \frac{2T_1 \sigma^2}{\pi \varphi c_{ef} M^2} \tag{5}
\]

\[
M = \frac{V_{\text{cast}}}{F_{\text{cast}}} \tag{6}
\]
In Eq. (3) the ProductLog[y] function for y ≥ 0 is the Lambert function, also known as the omega function and it is graphically shown in Fig. 3. This function can be easily calculated using the instruction ProductLog[y] in the Mathematica™ programme.

From Eqs. (1) and (3), the cell count for \( N_{nuc} = N \) can be given by

\[
N = \frac{N_i}{\exp[8 \text{ProductLog}(\gamma)]} \quad \text{(10)}
\]

Following a similar procedure, equations were found for nodular cast iron.

### 2.2. Nodular Cast Iron

\[
N_n = \frac{T_n^{3/2} \rho^3}{2\pi^{5/2} \beta \rho L_{c} c^2 \Delta T_{m}^2 M^4 (\beta D)^{3/2}}
\]

\[
= \frac{c}{2^{5/2} \pi z B_{e} L_{c} \Delta T_{m}^2} \left( \frac{Q_n}{D \beta} \right)^{3/2} \quad \text{(11)}
\]

\[
\Delta T_{m} = \frac{b}{2 \text{ProductLog}(y_n)} \quad \text{(12)}
\]

\[
N_n = \frac{N_i}{\exp[2 \text{ProductLog}(y_n)]} \quad \text{(13)}
\]

where

\[
y_n = b \left( \frac{\pi z N_c L_{c}}{c} \right)^{1/2} \left( \frac{2 \Delta T_{m}^{3/2} \beta^3}{B_{e} Q_n^2} \right)^{1/4} \quad \text{(14)}
\]

\[
Q_n = \frac{2 T_{m} \rho^2}{\pi B_{e} c^4 M^2} \quad \text{(15)}
\]

In Eqs. (2)–(16), \( Q_n \) and \( B_n \) are the metal cooling rates at the temperature, \( T_s, M \) is the casting modulus, \( V_{cast} \) and \( F_{cast} \) are the volume and surface area of the casting, respectively, \( c_{ef} \) is the effective specific heat of pro-eutectic austenite, \( T_i \) is the initial metal temperature just after filling the mold, \( \phi \) is the heat coefficient, \( T_{nuc} \) is the minimal temperature at the onset of eutectic solidification (as determined from the cooling curves) and \( a, c, f_r, L_s, L_{gr}, T_{s}, T_{l}, T_{i}, B, \mu \) and \( \beta \) are defined in Table 1. Equations (10) and (13) show that \( N \) and \( N_n \) can be estimated from the nucleation coefficients \( b \) and \( N_0 \) and \( Q_n, Q_{eh}, c, c_{ef}, L_{c}, c, f_s, D, \beta, B, \mu \) parameters when \( \Delta T_{m} \) is not known, while Eqs. (2) and (11) can be used when \( b \) and \( N_0 \) are not known but \( \Delta T_{m} \) is known.

### 2.3. Analytical Model Predictions

Notice from Eqs. (2), (10) and (11), (13) that among the various factors that influence the eutectic cell or nodule count are:

#### 2.3.1. Graphite Nucleation Susceptibility

The graphite nucleation susceptibility (i.e. availability of graphite nucleation sites in the melt) is directly established by \( N_{nuc} \) and indirectly by the nucleation coefficients \( N_0 \) and \( b \) (Eq. (1)). According to the literature, \( N \) or \( N_n \) are influenced by the chemical composition, \( C, \beta, \omega, \gamma, D, b, \mu \) and \( \Delta T_{m} \) (i.e. type, amount and granulation of inoculant agent, inoculation temperature), and fading time.

In the foundry practice, several quality indicators are commonly employed such as the carbon equivalent, \( CE = C + 0.33Si \), where the influence of CE on the eutectic cell or nodule count can be indirectly described by Eqs. (10), (13) through the cast iron chemical composition effect on \( N_n, b, \mu, T_{nuc}, T_{s} \) and \( f_s \). In general, it is known that \( N \) or \( N_n \) in cast iron, both increase with CE (Fig. 4). In particular, based on the published literature on this subject, it can be concluded that under constant cooling rates, technological factors such as high C and Si levels, high inoculation intensities, low bath superheats and hold-

![Graphic representation of the ProductLog[y] function for y ≥ 0.](Image)

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\[†1\] See http://www.mathworld.wolfram.com/LambertW-function.html.
ing times\textsuperscript{21}) and short fading times\textsuperscript{8,21) all increase $N$ or $N_n$ (the graphite nucleation susceptibility $N_{nucl}$) and decrease $\Delta T_m$. All of these relations are in agreement with Eqs. (2) and (11) which predict that under a constant cooling rate, $Q$ an increase in the eutectic cell count $N$ or nodule count $N_n$ (density of graphite nuclei) is related to a reduction in $\Delta T_m$.

In addition, the nucleation coefficients, $N_s$ and $b$ in Eq. (1), are strongly influenced by the chemical composition, spheroidization and inoculation practice, and bath holding times and temperatures, as well as fading times (see Tables 2, 4, 5 and Tables 7 and 8, part II). Figures 5 and 6 show the effect of the nucleation coefficients $N_s$ and $b$ on eutectic cell $N$ or nodule $N_n$ count and on the degree of undercooling for various cooling rates, $Q$. In these figures, the determinations of cell and nodule count were based on Eqs. (3), (10) and (12), (13), respectively, as well as from the data given in Table 1. From these figures, it is apparent that $N$ and $N_n$, both increase, while $\Delta T_m$ decreases when $N_s$ increases and $b$ decreases. In part II of this work\textsuperscript{*} (see Tables 3 and 7 and Fig. 6), it is experimentally shown that increasing times after inoculation leads to a reduction in $N_s$, while $\Delta T_m$ increases when $N_s$ increases and $b$ decreases. In part II of this work\textsuperscript{*} (see Tables 3 and 7 and Fig. 6), it is experimentally shown that increasing times after inoculation leads to a reduction in $N_s$, while $\Delta T_m$ increases when $N_s$ increases and $b$ decreases. Moreover, after prolonged bath holding times, a reduction in $N_s$ becomes dominant\textsuperscript{†} resulting in low $N$ values, in agreement with the predictions of Eq. (10). In general it can be said that all the technological factors, which increase the graphite nucleation susceptibility, cause a decrease in $\Delta T_m$ ensuring a high eutectic cell or nodule count.

\textsuperscript{†2} In this case influence of time after inoculation on $b$ is rather negligible small.
2.3.2. Graphite Eutectic Growth Coefficient, μ

In flake graphite cast iron, the μ coefficient depends on the silicon content (see Table 1). In general, Si lowers the eutectic growth coefficient. From Eqs. (3), (4) and (10) as the Si content increases the cell count in the cast iron also increases while the maximum undercooling decreases.

2.3.3. Effect of the Austenite Volume Fraction, f_g

In flake graphite cast iron, the austenite volumetric fraction, f_g, is described by the expressions given in Table 1. From these equations, it is found that the amount of f_g gets reduced by increasing the C and Si contents. Hence, the cell count and maximum undercooling decrease according to Eqs. (3), (4) and (10).

2.3.4. Diffusion Coefficient of Carbon in Austenite, D

In general, in nodular cast iron as D increases, the nodule count, N_s, and undercooling, ΔT_m, both decrease according to Eqs. (12)–(14). Moreover, D depends on the actual temperature and chemical composition of the austenite. The effect of Si, Mn and P on D is not considered in this work as there is not enough information available in the literature. From the limited data available for the eutectic transformation, the temperature ranges from 1100 to 1150°C, and effective D values \(^{13}\) range from \(3.2 \times 10^{-6}\) to \(4.6 \times 10^{-6}\) cm²/s. Thus, an average D value of \(3.9 \times 10^{-6}\) cm²/s (Table 1) can be used without introducing significant error.

2.3.5. Parameters Influencing the Cooling Rate, Q of Liquid Cast Iron at the Temperature T_m

The cooling rate \(^{15}\) is dependent on the casting modulus M, type of mold materials a, and on the initial temperature \(T_i\) (through B and B₂, see Eqs. (7), (8) and (16)) for the cast iron just after pouring into the mold. Figure 7(a) shows the effect of \(T_i\) and the \(a/M\) ratio on the cooling rate of nodular cast iron. In the case of flake graphite cast iron, Q (Fig. 7(b)) also depends on the effect of the liquidus temperature \(T_l\) (through \(B_l\), Eqs. (5), (7) and (8)). An equation for the liquidus temperature is given in Table 1. Accordingly, from this expression, it is found that by increasing the amount of C and Si, \(T_l\) is lowered leading to an increase in Q (Fig. 8). In general, all of the technological factors, which contribute to an increase in the cooling rates also lead to a simultaneous increase in \(N_s\) or \(N_{s}^\prime\), as well as in \(\Delta T_m\), in agreement with Eqs. (3), (4), (10) and (12)–(14) and with the foundry practice.\(^{2,8,21}\)

3. Conclusions

(1) Novel expressions are derived for predictions of cell and nodule count in cast iron. In particular, theoretical calculations of cell and nodule count, as well as, of maximum undercooling, \(\Delta T_m\) at the onset of the graphite eutectic solidification were made. It was found that the predictions of the theoretical analysis are in good agreement with the experimental outcome of the foundry practice.

(2) In addition, a description of the role of various factors of technological importance on the exhibited cell or nodule count, are given in this work. In particular, the present analysis for the cell or nodule count of cast iron indicates that their actual amounts depend on:

- The chemical composition of the cast iron (through \(N_s, b, f_g, T_l\) and \(\mu\)).
- The inoculation and spheroidizing practice, bath super-

\(^{13}\) It also depends on the equilibrium eutectic temperature \(T_i\) and the specific heat, c (Eqs. (5), (11) and (15)), but their influence is negligible.

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REFERENCES


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Appendix.
Appendix Nomenclature

Symbol | Meaning | Definition | Units
---|---|---|---
\(a\) | Mold material ability to absorb heat | \(a = \sqrt{\frac{\kappa_m c_m}{T}}\) | J/(cm²*C sⁱ/²)
\(A, \dot{A}\) | Parameters | Eqs. (A5), (A13) | —
\(b\) | Nucleation coefficient of eutectic cells | — | °C
\(B, \dot{B}, \dot{B}\) | Temperature parameters | Eqs. (A8), (A17), (A35) | —
\(C\) | Carbon content in cast iron | — | wt% | \(C'\) | Carbon content in graphite eutectic | — | wt% | \(C''\) | Carbon content in austenite at temperature \(T_s\) | — | wt% | \(C_s, \dot{C}_s\) | Carbon content in austenite, at austenite/graphite and austenite/liquid interface respectively | — | wt% | \(C'_s, \dot{C'}_s\) | Carbon content in bulk liquid and graphite | — | wt% | \(c_m\) | Specific heat of mold | — | J/(cm³ °C)

\(dV/dt\): Volumetric solidification rate of graphite eutectic | — | cm³/s
\(f_g\): Graphite volume fraction | — | —
\(f_s\): Pro-eutectic phase volume fraction | — | —
\(k_m\): Coefficient | Eqs. (A40), (A42) | —
\(k_w\): Heat conductivity of the mold material | — | J/(s cm °C)
\(m_g\): Slope of the line JE' for the Fe–C system | — | °C/wt% | \(m_s\): Slope of the line E'S' for the Fe–C system | — | °C/wt% | \(m_k\): Slope of the line BC' for the Fe–C system | — | °C/wt% | \(q_0\): Accumulated heat flux in casting | Eq. (A3) | J/s | \(q_{in}\): Heat flux extracted from the casting into the casting mold | Eq. (A2) | J/s | \(q_c\): Heat flux generated during solidification | Eq. (A25) | J/s | \(R\): Graphite eutectic cell radius | — | cm | \(R_{gw}\): Graphite eutectic cell radius at maximum undercooling | Eq. (A30) | cm | \(R_n\): Graphite nodule radius | Eq. (A37) | cm | \(R_s\): Austenite shell radius | Eq. (A44) | cm | \(R_{asw}\): Austenite shell radius at maximum undercooling | Eq. (A46) | cm | \(S\): Silicon content in cast iron | — | wt% | \(t\): Time | — | s | \(t_l\): Time at the onset of austenite solidification | Eq. (A7) | s | \(t_{asw}\): Time at the maximum undercooling of flake graphite cast iron | Eq. (A24) | s | \(t_{in,as}\): Time at the maximum undercooling of nodular cast iron | Eq. (A34) | s | \(t_{as}\): Time at the onset of graphite eutectic solidification for flake graphite cast iron | Eq. (A14) | s | \(T\): Temperature | — | °C | \(u\): Growth rate of eutectic cells | Eq. (A27) | cm/s | \(u_{as}\): Growth rate of eutectic cells at the maximum undercooling | Eq. (A28) | cm/s | \(V\): Volume of eutectic cells | — | cm³ | \(\Delta T\): Undercooling of graphite eutectic | \(\Delta T = T_s - T\) | °C | \(\omega\): Frequency | Eq. (A20) | 1/s

Analytical Model
During solidification, heat transfer events can be rather
complex and analytical solutions are not always feasible and numerical methods have to be employed. Nevertheless, in sand castings, it can be assumed as a good approximation that the metal is uniformly cooled since heat transfer is mainly determined by the low heat diffusivity of sand. Accordingly, the heat transfer process can be described by the heat balance equation:

\[ q_m = q_s - q_a \] \hspace{1cm} \text{(A1)}

where the heat flux density going into the mold, \( q_m \) and the accumulated heat flux in the metal \( q_a \) can be given by

\[ q_m = \frac{a F_{\text{cast}} T}{\sqrt{\pi t}} \] \hspace{1cm} \text{(A2)}

\[ q_a = \frac{c V_{\text{cast}} (dT)}{dt} \] \hspace{1cm} \text{(A3)}

The heat flux, \( q_s \), generated during solidification depends on the specific solidification mechanisms. In general, during the solidification of cast iron, three stages can be identified (Fig. A1(a)). In the first stage, the excess heat of molten metal is dissipated and the temperature falls from the initial temperature \( T_i \) to the liquidus temperature \( T_l \) in the \( 0 \leq t \leq t_1 \) time interval. The second stage is characterized by the solidification of the pro-eutectic phase in the \( T_l \leq T \leq T_s \) temperature range in the \( t_1 \leq t \leq t_2 \) time interval, where \( t_2 \) is the time at the onset of graphite eutectic solidification. Finally, the third stage can be attributed to the early stages of solidification of graphite eutectic, which are found to occur between the temperature \( T_s \) and the minimum temperature \( T_m \) in the \( t_2 \leq t \leq t_3 \) time interval.

**Stage I**

During this stage there is no heat generation due to solidification (\( q_s = 0 \)). Accordingly, substituting Eqs. (A2) and (A3) into (A1), followed by integration for the initial conditions \( t = 0 \) at \( T = T_i \) yields

\[ t = \left( \frac{AM}{2} \ln \frac{T_i}{T} \right)^2 \] \hspace{1cm} \text{(A4)}

where

\[ A = \frac{c V_{\text{cast}}}{2a} \] \hspace{1cm} \text{(A5)}

\[ M = \frac{V_{\text{cast}}}{F_{\text{cast}}} \] \hspace{1cm} \text{(A6)}

When \( T \) equals \( T_i \) (temperature at the onset of the pro-eutectic solidification), the time \( t = t_1 \) elapsed during the first cooling stage is given by

\[ t_1 = (AM)^2 \] \hspace{1cm} \text{(A7)}

where

\[ B = \ln \frac{T_l}{T_i} \] \hspace{1cm} \text{(A8)}

**Stage II**

The second stage includes the cooling and solidification of pro-eutectic from the liquidus temperature, \( T_l \) to the beginning of eutectic solidification \( T_s \). It is assumed that the heat generated during the solidification of pro-eutectic phase is uniformly released and the so-called effective specific heat can be used.\(^{27}\)

\[ c_{\text{ef}} = c + \frac{L_f}{T_l - T_e} \] \hspace{1cm} \text{(A9)}

At this stage, the temperature of the casting can be estimated by equating Eqs. (A2) and (A3) following by integration for the limiting conditions \( T = T_s \), at \( t = t_2 \). This yields,

\[ t = \left( A_M \ln \frac{T_i}{T_s} + \sqrt{t_2 - t_1} \right)^2 \] \hspace{1cm} \text{(A10)}

From this expression, the temperature of the metal in the second stage can be described by

\[ T = T_s \exp \left( -\frac{\sqrt{t - t_2} \, AM}{2A} \right) \] \hspace{1cm} \text{(A11)}

Differentiation of the above equation yields an expression for the cooling rate of cast iron as

\[ \frac{dT}{dt} = -\frac{T_i}{2A M \sqrt{t}} \exp \left( -\frac{\sqrt{t - t_1}}{A M} \right) \] \hspace{1cm} \text{(A12)}

where

\[ A = \frac{c_{\text{ef}} \sqrt{\pi}}{2a} \] \hspace{1cm} \text{(A13)}

From Eq. (A10) after taking into account Eq. (A7), the time \( t = t_1 \), \( T = T_s \) at the end of the second stage can be described by

Fig. A1. (a) Cooling curve for flake graphite and (b) for nodular cast iron.
The cooling rate at the end of the second stage can be determined from Eqs. (A12) and (A14) the cooling rate can be given by

\[ \frac{dT}{dt} = Q = \frac{2T_s a^2}{\pi \phi ceff M} \] ............................(A15)

where \( \phi = cB + c_1 B_1 \) ..........................(A16)

and

\[ B_s = \ln \frac{T_f}{T_s} \] ............................(A17)

Stage III Eutectic Transformation

During this stage, the portion of the cooling curve (see Fig. A1) where the transformation of graphite eutectic occurs can be described in terms of the degree of undercooling, \( \Delta T \) as

\[ T = T_s - \Delta T \] ............................(A18)

Although, \( \Delta T \) for graphite eutectic is not explicitly known in the \( t_s \leq t \leq t_m \) time range, it can be described by\(^{26}\):

\[ \Delta T = T_s - T_m = \Delta T_m \sin[\omega(t-t_s)] \] for \( 0 \leq \omega(t-t_s) \leq \pi/2 \) ............................(A19)

where \( \Delta T_m = T_s - T_m \) is the maximum degree of undercooling at the onset of eutectic solidification (see Fig. A1), and the frequency \( \omega \) is given by

\[ \omega = \frac{\pi}{2(t_m-t_s)} \] ..........................(A20)

Therefore, the cooling rate in stage III can be found by differentiating Eq. (19) with time. This yields* \(^{4}\)

\[ \frac{dT}{dt} = \Delta T_m \omega \cos[\omega(t-t_s)] \] ............................(A21)

It can also be assumed that at the onset of eutectic solidification \( t = t_s \), the cooling rate in Stages II and III is the same. Hence, equating Eqs. (A15) and (A21) yields

\[ \frac{dT}{dt} = \Delta T_m \omega \] ............................(A22)

which after taking into account Eq. (A20) can be rewritten as

\[ \frac{dT}{dt} = \frac{\pi \Delta T_m}{2(t_m-t_s)} \] ............................(A23)

Moreover, using Eqs. (A14), (A15) and (A23), the time for maximum undercooling can be determined from

\[ t_m = \frac{\pi \phi M^2 (\phi T_s + \pi c_{eff} \Delta T_m)}{4T_s a^2} \] ............................(A24)

Two main approaches\(^{29}\) are commonly used in describing the nucleation kinetics in MT–TK (Macro Transport–Transformation Kinetics Modeling of Cast Iron) modeling: (1) continuous nucleation, (which runs into computational complications) and (2) instantaneous nucleation. From the published work\(^{30}\) it is evident that the differences in the calculated undercoolings are very small for the same final eutectic cell structures based on both models. Accordingly, the instantaneous nucleation model is assumed in this work, where \( N_{nuc} \) (graphite nuclei density) depends on \( \Delta T_m \). Moreover, it is assumed in this work that \( N_{nuc} \) are formed in the \( t_f \) volume of liquid and that the eutectic cells in graphite or of nodular cast iron are of spherical shape until the time when they contact each other. The volume of a eutectic cell of radius \( R \) is given by \( V = 4\pi R^3/3 \) and the volume increment is given by \( dV = 4\pi R^2 dR \). Accordingly, the expression for the rate of heat generation can be described by:

\[ q_s = L_e N_{nuc} (1-f_p) W_{cast} \frac{dV}{dt} = 4\pi L_e N_{nuc} (1-f_p) W_{cast} \frac{R^2}{dt} \] ............................(A25)

where \( dV/dt \) is the volumetric solidification rate (cm\(^3\)/s).

During the eutectic transformation, the temperature range is 1100–1150°C and the heat flux extracted from the casting into the mold, \( q_m \), exhibits rather insignificant changes. Therefore, it can be assumed in Eq. (A2) that \( T = T_s \). At the time \( t_m \), the cooling curve exhibits a minimum (Fig. A1), which in turn means that the heat accumulation flux \( q_s \) is zero\(^{25}\) and the radius \( R = R_m \) (where \( R_m \) is the radius of eutectic cells at the maximum degree of undercooling \( \Delta T_m \)). Considering Eqs. (A2) and (A25), as well as the condition \( q_s = 0 \) at \( t = t_m \), Eq. (A1) becomes

\[ \frac{\alpha T_s F_{cast}}{\sqrt{\pi t_m}} = 4\pi L_e N_{nuc} (1-f_p) W_{cast} \frac{R^3}{3} \frac{dR}{dt} \] ............................(A26)

Flake Graphite Cast Iron

The growth rate of eutectic cells is in general described as\(^{31–33}\):

\[ u = \frac{dR}{dt} = \mu \Delta T^2 \] ............................(A27)

and for \( \Delta T = \Delta T_m = T_s - T_m \)

\[ u_m = \frac{dR_m}{dt} = \mu \Delta T_m^2 \] ............................(A28)

Substituting Eq. (A19) into Eq. (A27) followed by integration for the initial condition \( R = 0 \) at \( t = t_s \) yields

\[ R = \frac{\mu \Delta T_m^2}{4\omega} (2\omega(t-t_s) - \sin[2\omega(t-t_s)]) \] ............................(A29)

At the maximum degree of undercooling \( t = t_m \) \( \Delta T = \Delta T_m \) and taking into account \( t_m - t_s = \pi/(2\omega) \) from Eq. (A20), it is found that

\(^{4}\) It is assumed that cooling rate has a positive sign.

\(^{5}\) At \( t = t_m, dT/dt = 0 \) and from Eq. (A3), \( q_s = 0 \).
Typical flake graphite cast iron is often hypo-eutectic and the pro-eutectic phase is austenite. So $f_p = f_s$ where $f_s$ is the austenite volume fraction. It can be assumed that $N_{max}$ nuclei give rise to $N$ eutectic cells. At the time $t = t_m$, $\Delta T = \Delta T_m$, Eqs. (A15), (A20), (A22), (A24), (A26) (A28) and (A30) can be used to arrive the following expression for eutectic cell count

$$N = \frac{32T_s^3\alpha^6}{\pi^6 L_c(1-f_s)\phi\sigma_0^2\mu^3 M^4\Delta T_m^2\left(\rho c_{el}\Delta T_m + \phi T_s^2\right)}$$

$$= \frac{4c_{el}Q^1}{\pi^3 L_c(1-f_s)\mu^1\Delta T_m^2}$$

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For typical values of $\phi$ (0.6–2.0 J/(cm$^3$ °C)) it can be shown without significant error (see Fig. A2) that this equation can be replaced by:

$$N \approx \frac{32T_s^3\alpha^6}{\pi^6 L_c(1-f_s)\phi\sigma_0^2\mu^3 M^4\Delta T_m^2}$$

$$= \frac{4c_{el}Q^1}{\pi^3 L_c(1-f_s)\mu^1\Delta T_m^2}$$

Fig. A2. Graphic plots of Eqs. (A31) and (A32) for (a) $\phi=0.6$ J/cm$^3$ °C and (b) $\phi=2.0$ J/cm$^3$ °C.

For the present goal (Fig. A1(b)), it is sufficient to take into account the solidification of eutectic in the $t < t < t_m$ time range or in the $T < T_i < T_m$ temperature range. In addition, similar to other theoretical$^{11}$ and practical$^{34}$ works it is assumed that for eutectic and slightly hypereutectic alloys $T_m = T_s$.

The growth of graphite nodules during the eutectic solidification of nodular iron can be regarded as a diffusional problem where carbon diffusion through an austenite shell of radius $R_s$ (Fig. A3(b)) rate limits growth. Accordingly, an analysis of this type$^{35}$ leads to the derivation of equations that describe the carbon gradient at the austenite solidification interface $r = R_s$, and for the graphite nodule radius $r = R_n$

$$\frac{dC}{dR_s} = -\frac{R_n(C_3-C_2)}{R_n(R_n-R_s)}$$

$$R_n = R_s \left(\frac{C_4-C_3}{C_0-C_2}\right)^{1/3}$$

Although this mathematical description ignores the contribution of the austenite dendrites, it predicts surprisingly well the expected nodule microstructures.$^{12}$ In addition, the condition for continuity across the liquid–austenite interface needs to be taken into account. This condition is given by:

$$\left(C_4-C_1\right) \frac{dR_s}{dt} = D \frac{dC}{dR_s}$$

Combining Eqs. (A36)–(A38) yields:

$$R_s \frac{dR_s}{dt} = kD dt$$

where:

$$B_i = \ln \frac{T_i}{T_s}$$

Fig. A3. Schematic representation of (a) Fe–C phase diagram section and (b) corresponding carbon profile for a spherical eutectic cell.
Fig. A4. Graphic plot of Eq. (A40) as a function of the degree of undercooling, \( \Delta T \).

\[
k = \frac{(C_3 - C_1)}{(C_4 - C_1)} \frac{1}{\sqrt[3]{\left[ \frac{C_{12} - C_2}{C_4 - C_3} \right]}} \quad \text{(A40)}
\]

The above expression can be correlated with the degree of undercooling, \( \Delta T \). Assuming that the BE' and BC lines for the Fe-C system (Fig. A3(a)) are straight, the compositions in Eq. (A40) can be given by

\[
C_2 = C_E - \frac{\Delta T}{m_2}, \quad C_3 = C_E - \frac{\Delta T}{m_3}, \quad C_4 = C_C - \frac{\Delta T}{m_4}
\]

.................................(A41)

In Fe-C alloys the following values can be employed: \( C_E = 4.26\% \), \( C_m = 2.08\% \), \( m_2 = 275 \) [°C%/], \( m_3 = 189.6; \) [°C%/], and \( m_4 = 113.2; \) [°C%/]. Using these data, estimations of \( k \) values are plotted in Fig. A4. From this figure, it is apparent that \( k \) tends to exhibit a linear trend with \( \Delta T \). Accordingly, \( k \) can be described by:

\[
k = \beta \Delta T \quad \text{(A42)}
\]

where \( \beta = 0.00155 \) [°C\(^{-1}\)]. Moreover, it can be shown that the effect of Si on \( \beta \) is negligible.

Considering that the degree of undercooling \( \Delta T = T_i - T \), from Eqs. (A19), (A39) and (A42), it is found that

\[
R_s \frac{dR_s}{dt} = \beta D \Delta T_m \sin[\omega(t - t_s)]dt \quad \text{(A43)}
\]

Hence, integrating the above expression for the limiting conditions \( t = t_s \) at \( R_s = 0 \), yields

\[
R_s = \left[ \frac{2 \beta D \Delta T_m}{\omega} \right]^{1/2} [1 - \cos \omega(t - t_s)] \quad \text{(A44)}
\]

Differentiating Eq. (A44) with respect to time yields the growth rate for the austenite shell

\[
\frac{dR_s}{dt} = \left[ \frac{\beta D \omega \Delta T_m}{2[1 - \cos \omega(t - t_s)]} \right]^{1/2} \sin[\omega(t - t_s)] \quad \text{(A45)}
\]

Then, at the time \( t = t_m \), and by taking into account Eq. (A20), expressions for the austenite shell radius, as well as for the austenite shell growth rate at the maximum undercooling are found:

\[
R_{s,m} = \left( \frac{2 \beta D \Delta T_m}{\omega} \right)^{1/2} \quad \text{(A46)}
\]

Fig. A5. Influence of \( \Delta T_m \) and \( B_2 \) on the \( \Delta T_m^2 (\pi \Delta T_m + 2 B_2 T_i)^{1/2} \) (dotted line) and \( \Delta T_m^2 T_i^{1/2} \) (solid line) functions.

\[
\frac{dR_{s,m}}{dt} = \left( \frac{\beta D \omega \Delta T_m}{2} \right)^{1/2} \quad \text{(A47)}
\]

In addition, by using Eq. (A25) for \( f_i = 0 \), \( R = R_{s,m} \) and taking into account Eqs. (A22), (A33), (A46) and (A47), the heat flux generated during solidification at the time \( t = t_m \) is given by:

\[
q_s = 4L_n N_{\text{nuc}} V_{\text{cast}} \frac{cM}{a} \left( \frac{B_2 \Delta T_m (\pi \beta D \Delta T_m)}{T_s} \right)^{1/2} \quad \text{(A48)}
\]

Moreover, combining Eq. (A2) for \( t = t_m \) and Eq. (A34), the heat flux going into the mold can be described by:

\[
q_m = \frac{2F_{\text{cast}} a^2 T_i^{1/2}}{\pi c M b_2^2 (\pi \Delta T_m + T_i B_2)} \quad \text{(A49)}
\]

At \( t = t_m \), the rate of heat accumulation \( q_s \) is zero. Hence, the heat balance equation (Eq. (A11)) becomes \( q_s = q_m \). Using this equation and assuming that \( N_{\text{nuc}} \) nuclei gives rise to \( N_n \) graphite nodules and taking into account Eqs. (A48) and (A49) an expression for the nodule count \( N_n \) can be obtained:

\[
N_n \approx \frac{T_i^2 a^3}{2 \pi^3 b_2 L_c \Delta T_m^2 \Delta M^4 (\beta D)^{1/2} (\pi \Delta T_m + T_i B_2)^{1/2}} \quad \text{(A50)}
\]

Considering that the initial temperature, \( T_i \) in the mold cavity usually ranges from 1250 to 1450°C, thus typical \( B_2 \) values (Eq. (A35)) range from 0.074 to 0.223. For simplification purposes, it can be numerically shown that (see Fig. A5).

\[
\Delta T_m^2 (\pi \Delta T_m + T_i B_2)^{1/2} \approx z T_i^{1/2} \Delta T_m^2 \quad \text{(A51)}
\]

where

\[
z = 0.41 + 0.93 B_2 \quad \text{(A52)}
\]

can be used without significant error.

Accordingly, using Eqs. (A33), (A50) and (A51), \( N_n \) can be determined from

\[
N_n \approx \frac{T_i^{3/2} a^3}{2 \pi^3 b_2 L_c \Delta T_m^2 \Delta M^4 (\beta D)^{1/2}} \approx \frac{c}{2^2 b_2 \pi b_2 \Delta T_m^2} \left( \frac{Q_n}{D \beta} \right)^{3/2} \quad \text{(A53)}
\]

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