Mechanism of carbon influence on the transition from graphite to cementite eutectic in cast iron

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Abstract
In this work an analytical solution is used to explain mechanism of carbon influence on the transition from graphite to cementite eutectic in cast iron. It is found that this transition can be related to (1) the nucleation potential of graphite (characterized directly by the cell count, N and indirectly by nucleation coefficients $N_s$ and b) (2) the growth rate coefficient of graphite eutectic cell, $\mu$ (3) the temperature range, $\Delta T_{sc} = T_s - T_c$ (where $T_s$ and $T_c$ is the equilibrium temperature of the graphite eutectic and formation temperature of the cementite eutectic respectively), and (4) the liquid volume fraction, $f_l$ after solidification of the pre-eutectic austenite. Method of estimation of $N_s$, b and $\mu$ values was presented. It has been shown that the main impact of carbon on the transition from graphite to cementite eutectic consist in increasing the eutectic cell count and growth rate of graphite eutectic cell. Analytical equations were derived to describe the absolute, CT relative chilling tendency, $C_{Tr}$ and chill, $w$ of cast iron.

Keywords: Cast Iron, Graphite Eutectic, Cementite Eutectic, Chilling Tendency, Chill

1. Introduction
In the foundry practice, the transition from graphite to cementite eutectic in cast iron is called as the chilling tendency and is determined from comparisons of the exhibited fraction of cementite eutectic (chill) in castings solidified under similar cooling rate. Considerable efforts [1-4] have been made in correlating the inoculation practice, iron composition, pouring temperature, etc. with the chilling tendency of cast iron. On the other hand only a few attempts aimed at elucidating the mechanisms responsible for the chill of cast iron [3, 5]. However, none of these works have taken into consideration the complexity of the solidification process. In most cases, the proposed theories assume that a single factor is determinant in establishing the solidification structure while the remaining factors are ignored. Accordingly, in this work a simple and general analytical model is used for explain the mechanism responsible for the chilling tendency of cast iron and in consequence the chill. This model is based on nucleation and the growth of eutectic cells. Nucleation is the predominant process at the onset of solidification and affecting significantly the final microstructure of cast iron. The density of eutectic cells (cell count) can be described by a previously developed equation [6]

$$N = N_s \exp \left( - \frac{b}{\Delta T_m} \right)$$  \hspace{1cm} (1)

In Eq. (1) $N_s$ and b are the nucleation coefficients and $\Delta T_m$ is the maximum degree of undercooling at the onset of graphite eutectic solidification (Fig. 1). A second important process during solidification of cast iron is the growth of eutectic cells. In general, the growth rate of eutectic cells is described as [7]

$$u = \frac{1}{2} \Delta T_m^2$$  \hspace{1cm} (2)
where \( \mu \) is the growth coefficient of eutectic cell

![Cooling curves](image)

Fig. 1. Cooling curves (a) and (b) effect of the cooling rate \( Q \) on the minimal solidification temperature \( T_m \) for graphite eutectic (a) and scheme of the wedge section and cooling rate along its axis

### 2. Experimental procedure

Wedges and bars were polished and etched using Stead reagent to reveal graphite eutectic cell boundaries. The planar microstructure is characterized by the cell count, \( N_i \) which gives by the Saltykov formula as an unbiased estimator for the rectangle \( S \) of observation [8]

\[
N_F = \frac{N_i + 1.5 N_r}{F}
\]

where: \( N_i \) is the number of eutectic cells inside rectangle \( S \), \( N_r \) is the eutectic cells count that intersect the sides of \( S \) but not their corners and \( F \) is the surface area of \( S \) (Fig. 2).

Then, a stereological formula can be employed for calculations of the volumetric cell count, \( N_v \) which yields the average number of eutectic cells per unit volume [9]

\[
N_v = \frac{1.568 N_F}{F^{3/2}}
\]

### 3. Results and discussion

The results of experimental investigations can be described by the regression equations,

\[
\text{bar } \phi 3 \text{ cm } N_{F} = 0.72 C - 46.2 \text{ cm}^2 \tag{5}
\]

\[
\text{bar } \phi 1.8 \text{ cm } N_{F} = 0.058 C - 50.7 \text{ cm} \tag{6}
\]

\[
N_{F,cr} = 44.5 + 5.10 C \tag{7}
\]

\[
\text{bar } \phi 3 \text{ cm } \Delta \mu = 9.5 - 5.5 \text{C} \tag{8}
\]

\[
\text{bar } \phi 1.8 \text{ cm } \Delta \mu = 3.9 - 9.5 \text{C} \tag{9}
\]

\[
w = 1.9 - 2 \text{C} \text{ cm} \tag{10}
\]
Notice that as carbon content, C increases the cell count, \( N_v \) and the critical cell count, \( N_{v,cr} \) also increase, while undercooling, \( \Delta T_w \) and the chill width, \( w \) of wedges, decrease.

Graphite eutectic equilibrium temperature, \( T_s \) and cementite eutectic formation temperature, \( T_c \) are given by

\[
T_s = 154.0 + 0.25 Si \tag{11}
\]

\[
T_c = 130.5 + 0.06 (C - 0.33 Si) \tag{12}
\]

Thus, the range of temperature \( \Delta T_{sc} = T_s - T_c \) (Fig. 1) can be calculated.

**Estimation of the nucleation coefficients**

The graphite nucleation coefficients \( N_s \) and \( b \) depend on the cast iron chemistry. Effect of carbon on the nucleation coefficients is unknown in literature. However, this effect can be estimated on the basis of our experimental data. Taking the logarithm from Eq. (1) the linear relationship between \( \ln N_v \) and \( (\Delta T_m)^{-1} \) is obtained

\[
\ln N_v = n N_s - \Delta \tag{13}
\]

Known experimental points \((\Delta T_{m1}, N_{v1})\), \((\Delta T_{m2}, N_{v2})\) and \((\Delta T_{sc}, N_{v,cr})\) for bars 30 and 18 mm and wedges respectively they can be plotted in system \( \ln N_v \) and \( (\Delta T^{-1}) \) and points are interpolated by straight line \( \ln N_v = \varphi \cdot (\Delta T)^{-1} \) (Fig. 3). Thus, values of \( N_s = e^\varphi \) and \( b \) can be obtained.

![Fig. 3. Relationship between undercooling, \( \Delta T_m^{-1} \) and volumetric cell count, \( \ln N_v \).](image)

From this procedure, the nucleation coefficients, \( N_s \) and \( b \) can be estimated

\[
N_s = 2621 + 8.10^{-9} C^{7.8} \text{ cm}^{-3} \tag{14}
\]

\[
b = 3765 - 0.0013 C + 0.0106 C^2 \text{ cm}^{0.8} \tag{15}
\]

**Estimation of the graphite eutectic growth coefficient, \( \mu \)**

This coefficient depends on the cast iron chemistry. Effect of carbon (through, segregation of Si, Mn, S, and P) on the \( \mu \) can be estimated using the formula [10, 11]

\[
\mu = \frac{2 T_s a^2}{\pi \cdot \beta} \left[ \frac{4}{\gamma L e c^2 \Delta} \frac{8}{n} \right]^{1/3} \tag{16}
\]

where \( \phi = B + c \text{ef} \cdot B_1 \)

\[
B = \frac{n T_l}{T_s} \quad B_1 = \frac{3 T_l}{T_s} \tag{17}
\]

\[
c_{\text{ef}} = \frac{1}{\gamma L \mu} \frac{L_{\gamma}}{T_l} - \frac{1}{s} \tag{19}
\]

\( T_l \) is the initial liquid metal temperature just after pouring into the mold, and \( f_l, T_{l}, T_{tr} , a, c, L_{\gamma}, L_{r} \) are defined in Table 1. Calculations were made at the first separately for bars 18 and 30 mm, and than were averaging. Those results can be described by the following correlation relationship.

\[
\mu = 0 - 1.15 + 6.10^{-9} C^{16} \text{ cm/s}^{0} \text{C}^{-2} \tag{20}
\]

It can be concluded that, carbon increases the coefficient \( \mu \).

**4. Chilling tendency indexes**

From the theory of solidification of cast iron [10, 11] following formulas for absolute chilling tendency index, CT and relative chilling tendency index, CT\( \text{r} \) can be derived

\[
CT = \frac{1}{\gamma s f_l \mu^3} \exp\left( \frac{b}{\Delta \text{Sc}} \right) \tag{21}
\]

\[
CT_{\text{r}} = \left( \frac{\Delta \text{Sc}}{\Delta \text{Sc}} \right)^{0.8} \tag{22}
\]

The role of carbon on the absolute chilling tendency index, CT of cast iron can be disclosed based on Eqs. (11), (12), (14), (15), (20) and (21) and data given in Table 1. The relative chilling tendency index, CT\( \text{r} \) can be determined from cooling curves. Role of carbon on, CT can be expressed through influence on :

**The effect of the volumetric fraction of liquid cast iron at the beginning solidification of eutectic \( f_l \)**

In general, from Eq. (21) it can be concluded that as \( f_l \) increases the chilling tendency index, CT decrease. It is assumed that for \( C = 3.83 \% \), that is \( \mu = 109.10^{-5} \text{ cm}^3/(\text{C}^2 \text{ s}) \), \( b = 119.4 \text{ C}, N_v = 6.39 \times 10^6 \text{ cm}^3, \Delta T_{sc} = 35.0 \text{ C}, f_l = 1 \) according to Eq. (21) CT = 0.33 s\(1/2\)/C\(1/3\). This value can be normalized to 1 and then the intensity coefficient of influence can be used. Change in the carbon content from 3.83 to 3.06 % (that is decreasing the volumetric fraction of liquid cast iron from 1 to 0.62 increases, CT from 0.33 to 0.36 s\(1/2\)/C\(1/3\). This means that the effect of the carbon (through, \( f_l \) ) on CT is small (change of the intensity coefficient from 1 to 1.08).
The graphite eutectic growth coefficient, \( \mu \). In general, from Eq. (21) results that as the graphite eutectic growth coefficient increases, CT decreases. In particular, carbon through segregation of Si, Mn, S, and P increases the coefficient \( \mu \) (Eq. (20)) and therefore from equation (21) results that the chilling tendency of cast iron, CT decreases. Change in the carbon content from 3.83 to 3.06\% (that is decreasing of the graphite eutectic growth coefficient, \( \mu \) from 1.09 \times 10^{-3} \) to 2.57 \times 10^{-6} cm/(°C^2 s) significantly increases of CT from 0.33 to 0.69 s^{1/2}/°C^{1/3}. Thus, the effect of the carbon (through growth coefficient, \( \mu \)) on CT is very strong (change of the intensivity coefficient from 1 to +2.06).

The temperature range, \( \Delta T_{ae} = T_e - T_m \). In general, from Eq. (21) results that as \( \Delta T_{ae} \) increases the chilling tendency index, CT decreases. Eqs (11), (12) indicate that change in the carbon content from 3.83 up to 3.06\% changes the temperature range \( \Delta T_{ae} \) only by 1.3°C. In consequence, effect of carbon through \( \Delta T_{ae} \) on CT is small (change of the intensivity coefficient from 1 to 0.93). It is worth mentioned that effect of carbon on CT through, \( f_l \) and \( \Delta T_{ae} \) is almost balanced (the intensivity index 0.93 and 1.08 respectively).

The nucleation coefficients, \( N_e \) and \( b \). According to Eq. (21) it is apparent that the chill tendency index, CT increases when the nucleation coefficient \( b \) increases and \( N_e \) decreases. Change in the carbon content from 3.83 to 3.06\% (that is decreasing of the nucleation coefficient, \( N_e \) from 6.39 \times 10^{6} \) to 42621 cm^-3 significantly increases, CT from 0.33 to 0.77 s^{1/2}/°C^{1/3}. This means that the effect of the carbon (through coefficient, \( N_e \)) on CT is very strong (change of the intensivity coefficient from 1 to +2.30). Effect of carbon through, \( b \) on CT is small (change of the intensivity index from 1 to 0.80).

Using Eq. (21) data from Table 1 and data from cooling curve effect of carbon on the chilling tendency indexes, CT and CTr can be estimated. Results of these calculations are shown in Fig. 4. Notice from this figure that as free sulfur increases the chilling tendency indexes also increase.

![Graph showing effect of carbon on chilling tendency indexes](image)

**Fig. 4. Effect of carbon, C on absolute, CT and relative, CTr chilling tendency indexes**

5. Chill

In the foundry practice an assessment of the chilling tendency of cast iron is based on the chill test methods established by the ASTM A367-55T standard (Fig. 2b)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value and units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latent heat of graphite eutectic</td>
<td>( L_{ae} = 2028.8; ) J/cm(^3)</td>
</tr>
<tr>
<td>Latent heat of austenite</td>
<td>( L_{ae} = 1904.4; ) J/cm(^3)</td>
</tr>
<tr>
<td>Specific heat of cast iron</td>
<td>( c = 5.95; ) J/(cm(^3)°C)</td>
</tr>
<tr>
<td>Material mould ability to absorb heat</td>
<td>( a = 0.11; ) J/(cm(^2)°C)</td>
</tr>
<tr>
<td>Liquidus temperature for pre-eutectic austenite</td>
<td>( T_l = 1636 – 113(C + 0.25Si + 0.5P); ) °C</td>
</tr>
<tr>
<td>Carbon content in graphite eutectic</td>
<td>( C_e = 4.26 - 0.30Si - 0.36P; ) %</td>
</tr>
<tr>
<td>Maximum carbon content in austenite at ( T_s )</td>
<td>( C_s = 2.08 - 0.11Si - 0.35P; ) %</td>
</tr>
<tr>
<td>Liquidus temperature of pre-eutectic austenite when its composition is ( C_e )</td>
<td>( T_{ae} = 1636 – 113(2.08 + 0.15Si + 0.14P); ) °C</td>
</tr>
<tr>
<td>Weight fraction of liquid cast iron at the beginning of solidification of eutectic</td>
<td>( g_f = (C - C_s)/(C_e - C_s) )</td>
</tr>
<tr>
<td>Austenite density</td>
<td>( \rho_{\gamma} = 7.51; ) g/cm(^3)</td>
</tr>
<tr>
<td>Liquid cast iron density</td>
<td>( \rho_l = 7.1; ) g/cm(^3)</td>
</tr>
<tr>
<td>Volume fraction of liquid cast iron at the beginning of solidification of eutectic</td>
<td>( f_l = \rho_f g_f / [\rho_f g_f + \rho_l (1 - g_f)] )</td>
</tr>
</tbody>
</table>

C, Si, P - content of carbon, silicon and phosphorus in cast iron, respectively, %

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Table 1. Selected thermophysical data [10]
The wedge width of the chill can be expressed as a function of the absolute, CT chilling tendency

\[ w = \frac{4.46 \cdot C T \cdot T_c^2}{\cos(\beta) \cdot 2} \]  
\[ \text{(23)} \]

where

\[ p_i = \frac{3}{4} \left( \frac{32 T_s^3}{\pi \cdot c_e^2 \cdot \phi} \right)^{1/6} \]  
\[ \text{(24)} \]

and \( \beta \) is the wedge angle (Fig. 2b).

It can be concluded that apart the chilling tendency of cast iron, the wedge chill width, \( w \) according to Eqs. (23) and (24) depends additionally on the \( p_i \) coefficient that includes parameters connected with cooling rate, that is:

- ability of molds to absorb heat, \( a \),
- \( \phi \) parameter Eq.(17) which depends on \( B \) and \( B_1 \) values (Eq. 18) that is on the initial temperature, \( T_i \) of the cast iron just after pouring into reference castings and wedges.

Effect of initial liquid metal temperature just after pouring into the mold, \( T_i \) and ability of the mold to absorb heat, \( a \) on \( p_i \) parameter

Effect of initial liquid metal temperature just after pouring into the mold, \( T_i \) and ability of the molded mold to absorb heat, \( a \) on \( p_i \) parameter is shown in Fig. 5. Thus, it can be concluded that \( p_i \) parameter increases as the pouring temperature \( T_p \) (and in consequence initial temperature \( T_i \)) decreases and the ability of the molded mold to absorb heat increases. Using Eqs. (23) and (24), as well as data from Table the relationship between absolute, CT chilling tendency and the total chill, \( w \) of wedges can be obtained (Fig. 6). In general, it can be state that increase of carbon in cast iron decreases the chilling tendency index, CT and in consequence the width of total chill also decreases.

6. Conclusions

1. An analytical model of general validity was used to explain mechanism of influence of carbon on chilling tendency indexes, CT, CTr and chill in cast iron.
2. Carbon in cast iron decreases the chilling tendency indexes, and in consequence the width of total chill also decreases.
3. Carbon significantly increases (Fig. 7) the cell count (nucleation coefficient, \( N_s \)) and the growth coefficient, \( \mu \) of eutectic cells which is the main cause of decreasing the chilling tendency indexes and chill.
4. Effect of carbon on the chilling tendency indexes and chill, through the nucleation coefficient, \( b \), the range of temperature, \( \Delta T_m \) and the volume fraction of liquid cast iron at the beginning of solidification of eutectic \( f_l \) is rather small (Fig. 7).

Fig. 6. Effect of CT on the total chill, \( w \) of wedges

Fig. 7. Carbon effect intensivity on chill, through \( N_s \), \( b \), \( \Delta T_m \), \( \mu \) and \( f_l \)
References


