Mechanism of free sulfur influence on the eutectic cell count and transition from graphite to cementite eutectic in cast iron

Part I. Theoretical background

E Fraś, M. Górny
AGH University of Science and Technology, Reymonta 23, 30-059 Cracow, Poland
*Corresponding author. E-mail address: edfras@agh.edu.pl

Received: 26.02.2010; accepted in revised form: 30.03.2010

Abstract
In this work an analytical solution of general validity is used to explain the mechanism of free sulfur influence on the cell count and on the transition from graphite to cementite eutectic in cast iron. It is found that this transition can be related to the nucleation potential of graphite (represented by eutectic cell count $N_v$), the growth rate coefficient of graphite eutectic cell, $\mu$, the temperature range, $\Delta T_{sc}$, and the pre-eutectic austenite volume fraction, $f_\gamma$.

Keywords: Theory of Crystallization, Solidification Process, Cast Iron, Chilling Tendency, Chill

1. Introduction

In the foundry practice, the transition from graphite to cementite eutectic in cast iron is called the chilling tendency and is determined from comparisons between the exhibited fraction of cementite eutectic (chill) in castings solidified under a similar cooling rate. Figure 1 gives a comparison of the chilling tendency for two cast irons (I and II). Cast iron I exhibits a lower chilling tendency than cast iron II. Based only on these comparisons, the difference in the chilling tendency of various cast irons can be established, but the absolute chilling tendency (CT) values for given irons cannot be derived.

It is well known that the chilling tendency of cast iron determines their subsequent performance in diverse applications. In particular, cast irons having a high chilling tendency tend to develop zones of white or mottled iron. Considering that these regions can be extremely hard, their machinability can be severely impaired. Alternatively, if white iron is the desired structure, a relatively small chilling tendency will favor formation of grey iron.

Fig. 1. Castings for chill and chilling tendency estimation
This in turn leads to low hardness and poor wear properties in as-cast components. Hence, considerable efforts [1-4] have been made in correlating the inoculation practice, the iron composition, the 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]. In addition to that, various numerical models were proposed [6,7] to predict whether a given casting or a part of it will solidify according to the stable or metastable Fe-C-X system. However, their application is tedious due to extensive numerical calculations. The effect of sulfur on the chilling tendency has been repeatedly tested [8-11]. Nevertheless, 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 a determinant in establishing the solidification structure while the remaining factors are ignored. Accordingly, in this work a simple and general analytical model is used to explain the mechanism responsible for the chilling tendency of cast iron and in consequence for the chill.

2. Theoretical background

2.1. Cell count

During solidification of cast iron the nucleation is heterogeneous in nature. A simple model for heterogeneous nucleation of graphite in cast iron has already been proposed [11].

\[ N = N_v \exp \left( -\frac{b}{\Delta T_m} \right) \]  

where \( b = \frac{4 T_s \sigma \sin \theta}{L_c / l} \).  

In Eq. (1), \( N_v \) is the density of substrates available for the nucleation of graphite, \( \Delta T_m = T_s - T_m \) is the maximum degree of undercooling at the onset of graphite eutectic solidification, \( \sigma \) is the interfacial energy between the graphite nucleus and the melt, \( \theta \) is the wetting angle between substrate and graphite nucleus, \( L_c \) is the latent heat of graphite eutectic, \( l \) is the mean size of the nucleation site; \( N_v \) and \( b \) will be called as nucleation coefficients.

The graphite eutectic nucleation coefficients \( N_v \) and \( b \) depend on the cast iron chemistry. In general, a little is known about their values. Typical values for nucleation coefficients \( N_v \) and \( b \) are 6.1 \( \times \) 10^6 cm^-3 and 104 °C for inoculated cast iron and 1.6 \( \times \) 10^5 cm^-3 and 76.8 °C for non-inoculated cast iron. The effect of sulfur on the nucleation coefficients is unknown in literature. However, it can be estimated on the basis of experimental data. The plot of Eq. (1) is shown in Fig. 2. Knowing the coordinate of two points on the curve (\( \Delta T_{m,1}, N_{v,1} \)) and (\( \Delta T_{m,2}, N_{v,2} \)) nucleation coefficients \( N_v \) and \( b \) can be calculated.

\[ N_v = N_s \exp \left( -\frac{b}{\Delta T_m} \right) \]  

\[ b = \frac{\Delta T_{m,1} \Delta T_{m,2}}{\Delta T_{m,2} - \Delta T_{m,1}} \ln \left( \frac{N_{v,2}}{N_{v,1}} \right) \]  

It is well known that each nucleus graphite gives rise to a single eutectic cell. Therefore it can be assumed that measure of graphite nuclei count is eutectic cell count. In general, an increase in the cell count means that, for a given undercooling, during eutectic transformation the nucleation potential of graphite also increases. Nucleation potential of graphite (availability of heterogeneous nucleation sites for graphite in the melt at a given undercooling) is characterized indirectly by nucleation coefficients \( N_v \) and \( b \).

Combining heat extraction from the mold and heat generated during solidification of eutectic cells, which grow with the velocity given by \( u = \mu \Delta T_m^2 \) (where \( \mu \) is the growth coefficient of eutectic cells) the minimal temperature \( T_m \) or the maximum undercooling, \( \Delta T_m \) at the onset of graphite eutectic solidification can be calculated [11]

\[ T_m = T_s - \Delta T_m = T_s - \left( \frac{4 c_{ef} Q^3}{\pi^3 L e N_v \mu^3 (1 - f_e)} \right)^{1/8} \]  

where

\[ Q = \frac{2 T_s a^2}{\pi \phi c_{ef} M^2} \]  

\[ c_{ef} = c + \frac{L_\gamma}{T_l - T_s} \]  

\[ \phi = c B + c_{ef} B_1 \]  

\[ B = \frac{T_l}{T} \]  

\[ B_1 = \ln \frac{T_l}{T_s} \]  

where \( Q \) is cooling rate of cast iron at the beginning of solidification, \( f_e \) is the pro-eutectic austenite volume fraction, \( M \) is the casting modulus, \( T_l \) is the initial liquid metal temperature just
after pouring into the mold, \( T_m \) is the minimum temperature at the onset of graphite eutectic solidification and \( T_s, T_l, a, c, L_e, L_\gamma, \mu_\gamma \) are defined in Table 1.
Combining equations (1) and (5)

\[
\Delta T_m = T_s - T_m = \frac{b}{8 \text{ProductLog}[y]} \quad (10)
\]

and

\[
y = \frac{b}{8 \cdot 2^{1/4}} \left[ \frac{\pi^3 \text{Le} N_s \mu^3 (1 - f_\gamma)}{c_\text{ef} Q^3} \right]^{1/8} \quad (11)
\]

The ProductLog\([y]\) is the Lambert function\(^*\), also called the omega function, and is graphically shown in Fig.3. This function can be easily calculated by means of ProductLog\([y]\) instruction in Mathematica™ programme.

![Graph of ProductLog\([y]\) function](image)

**Fig.3.** Graphic representation of ProductLog\([y]\) function for \( y \geq 0 \)

Combining Eqs (1) and (10), the spatial cell count can also be determined from

\[
N = \frac{N_s}{\exp\left[ 8 \text{ProductLog}[y] \right]} \quad (12)
\]

Similarly as the nucleation coefficients \( N_s \) and \( b \), the graphite eutectic growth coefficient \( \mu \) depend on the cast iron chemistry and a little is known about it value. Effect of sulfur on the graphite eutectic growth coefficient \( \mu \) is unknown in literature. However, it can be estimated on the basis of experimental data. In this case for the bar with a \( d \) diameter and a length that easily exceeds, \( d \) the casting modulus can be given as

\[
M = \frac{d}{4} \quad (13)
\]

Taking into account Eqs. (5), (6) and (13) the graphite eutectic growth coefficient can be determined.

* see http://mathworld.wolfram.com/LambertW-function.html,

\[
\mu = \frac{32 T_s}{a^2} \left[ \frac{4}{\text{Le} \text{Nv} c_\text{ef}^2 \Delta T_m^{8/3} (1 - f_\gamma)} \right]^{1/3} \quad (14)
\]

**Table 1.** Selected thermophysical data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value and units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latent heat of graphite eutectic</td>
<td>( L_e = 2028.8 \text{ J/cm}^3 )</td>
</tr>
<tr>
<td>Latent heat of austenite</td>
<td>( L_\gamma = 1904.4 \text{ J/cm}^3 )</td>
</tr>
<tr>
<td>Specific heat of cast iron</td>
<td>( c = 5.95 \text{ J/(cm}^3\text{oC}) )</td>
</tr>
<tr>
<td>Material mould ability to absorb heat</td>
<td>( a = 0.10 \text{ J/(cm}^2\text{oC}) )</td>
</tr>
<tr>
<td>Liquidus temperature for pre-eutectic austenite</td>
<td>( T_c = 1636 - 113(C + 0.25Si + 0.5P) \circC )</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_\gamma = 2.08 - 0.11Si - 0.35P %, )</td>
</tr>
<tr>
<td>Liquidus temperature of pre-eutectic austenite when its composition is ( C_\gamma )</td>
<td>( T_{\gamma} = 1636 - 113(2.08 + 0.15Si + 0.14P) \circC )</td>
</tr>
<tr>
<td>Austenite density</td>
<td>( \rho_\gamma = 7.51 \text{ g/cm}^3 )</td>
</tr>
<tr>
<td>Melt density</td>
<td>( \rho_m = 7.1 \text{ g/cm}^3 )</td>
</tr>
<tr>
<td>C, Si, P - content of carbon, silicon and phosphorus in cast iron, respectively, %</td>
<td></td>
</tr>
</tbody>
</table>

**2.2. Chilling tendency**

Figure 4a shows a schematic influence of the cooling rate \( Q \) on the \( T_m \) temperature and the cell count. Notice from this figure, that increasing cooling rates \( Q \) to the values of \( Q_{cr} \) leads to a reduction in \( T_m \) to the values of \( T_c \) and hence to the formation of cementite eutectic (chill development).

![Cooling curves](image)

**Fig.4.** Cooling curves (a) and (b) effect of the cooling rate \( Q \) on minimal solidification temperature \( T_m \) for graphite eutectic (a) and scheme of wedge section and cooling rate along its axis (b)
For $Q = Q_c$, $N_v = N_{v,cr}$ and $\Delta T_m = \Delta T_{sc}$ therefore the critical cooling rate can be estimated on the basis on Eqs (5) and (6)

$$Q_{cr} = \pi \mu \left( \frac{L_c N_{v,cr} (1 - f_\gamma) \Delta T^{8}_{sc}}{4 \, c_{ef}} \right)$$

Taking into account Eqs. (1), (6) and (15), the critical casting modulus $M_{cr}$ under which it is possible to develop a chill can be obtained

$$M_{cr} = p \, CT$$

where

$$p = \frac{a}{\pi} \left( \frac{32 T_c^3}{L_c c_{ef} \phi^3} \right)^{1/6}$$

$CT$ is the chilling tendency of cast iron

$$CT = \frac{1}{N_v (1 - f_\gamma) \mu^3 \Delta T^{8}_{sc}} \exp \left( \frac{b}{\Delta T_{sc}} \right)^{1/6}$$

2.3. Chill

In the foundry practice an assessment of the chilling tendency of cast iron is based on the chill test methods established by the eg. ASTM A367-55T standard. In this case, wedge geometries are employed (Fig.1). As a first approximation, assuming that the wedge length is rather large, the critical casting modulus $M_{cr}$ can be estimated by

$$M_{cr} = \frac{F_{ch}}{m} = \frac{1}{2} \frac{h}{w} \frac{w}{\cos(\beta/2)} = \frac{w}{4} \cos(\beta/2)$$

In the above expressions, $\beta$ is the wedge angle, $F_{ch}$ is the half surface area chill triangle, $h_c$ and $m$ are chill height and length. The wedge is not a planar body such as the plate. Accordingly, the wedge thinner parts heat up from the thicker sections, and the chill width for wedges of constant chilling tendency depend on sizes of wedges (wedge number according to the ASTM A 367-55T standard). The influence of the wedge size on the chill width can be found by combining Eqs. (16) and (19). Accordingly, the wedge width of the chill can be expressed as a function of the wedge size coefficient, $n$ as

$$w = A \, CT$$

where

$$A = \frac{4 \, n^{2/3} \, a \, \tau_s^{1/2}}{\pi \phi \, \frac{1/2}{c_{ef}} \, L \, \frac{1/6}{c_{ef}} \, \cos(\beta/2)}$$

$$CT = \left[ \frac{1}{N_{v,cr} (1 - f_\gamma) \mu^3 \Delta T^{8}_{sc}} \right]^{1/6} = f(S)$$

where: $n$ is a wedge size coefficient ($n = 0.65, \beta = 26.7^\circ$).

$CT$ is chilling tendency index of cast iron, $N_{v,cr}$ is the volumetric critical cell count at $T \approx T_c$ (close to chill).

3. Conclusions

An analytical model of general validity is proposed to explain the mechanism of influence of free sulfur on chilling tendency index, $CT$ and chill in cast iron.

The effect of sulfur on growth coefficient (which strongly affect chilling tendency) can be calculated on the base on eq. 14. The effect of sulfur on cell count can be determined indirectly through nucleation coefficients ($N_s$ and $b$).

References