MECHANISM OF THE SILICON INFLUENCE ON ABSOLUTE CHILLING TENDENCY AND CHILL OF CAST IRON

MECHANIZM WPŁYWU KRZEMU NA BEZWZGLĘDNĄ SKŁONNOŚĆ ŻELIWA DO ZABIELEŃ I ZABIELENIA W ŻELIWIE

In this work an analytical solution of general validity is used to explain mechanism of the silicon influence on the absolute chilling tendency (CT) and chill (w) of cast iron. It is found that CT can be related to nucleation potential of graphite ($N_v$), growth parameter ($\mu$) of eutectic cells, temperature range ($\Delta T_{eq}$), where $\Delta T_{eq} = T_s - T_c$ ($T_s$ is graphite eutectic equilibrium temperature and $T_c$ is cementite eutectic formation temperature) and the pre-eutectic austenite volume fraction ($f_\gamma$). It has been shown that silicon addition: 1) impedes the growth of graphite eutectic cells through decreasing the graphite eutectic growth coefficient ($\mu$), 2) expands the temperature range ($\Delta T_{eq}$), 3) increases the nucleation potential of graphite ($N_v$), 4) lowers the pre-eutectic austenite volume fraction, ($f_\gamma$). In a consequence, the absolute chilling tendency (CT) decreases. The minimum wall thicknesses for chilled castings, or chill width (w) in wedge shaped castings is related to CT and as Si content increases, the chill width, w value decreases.

Keywords: cast iron, chilling tendency, chill

W pracy przedstawiono wyniki rozwiązania analitycznego mechanizmu wpływu krzemu na bezwzględną skłonność żeliwa do zabień (CT) i zabienia (w) w żeliwie. Wykazano, że CT jest uzależnione od potencjału zarodkowania grafitu ($N_v$), parametru wzrostu ($\mu$) ziaren eutektycznych, zakresu temperatury ($\Delta T_{eq}$), gdzie $\Delta T_{eq} = T_s - T_c$ ($T_s$ jest równowagową temperaturą krystalizacji eutektyki grafitowej, a $T_c$ jest temperaturą tworzenia eutektyki cementowej) oraz udział przedeutektycznego austenitu ($f_\gamma$). Z przedstawionych badań wynika, że dodatek krzemu: 1) utrudnia wzrost ziaren eutektycznych poprzez zmniejszenie współczynnika wzrostu eutektycznego austenitu ($f_\gamma$), 2) rozszerza zakres temperatury ($\Delta T_{eq}$), 3) zwiększa potencjał zarodkowania grafitu ($N_v$), 4) zmniejsza udział przedeutektycznego austenitu ($f_\gamma$) a w konsekwencji zmniejsza bezwzględną skłonność żeliwa do zabień (CT). Wykazano ponadto, że minimalna grubość ścianki, powyżej której w odlewie występują zabienia lub szerokość zabienia klinia (w) w odlewie o kształcie klinia zależy od CT oraz zwiększenie zawartości krzemu prowadzi do zmniejszenia szerokości zabienia klinia.

1. Introduction

One of the important indices of quality of cast iron is its chilling tendency, that is its tendency to solidify according to Fe-C-X metastable system. Chilling tendency depends on physical-chemical state of liquid cast iron while chill (fraction of cementite eutectic in casting) formation depends additionally on cooling rate of casting.

In the foundry practice, the chilling tendency for the various types of cast irons is determined from comparisons of the exhibited fraction of cementite eutectic (chill) in castings solidified under 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 this comparison, the difference in the chilling tendency of
various cast irons can be established, but 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 various applications. In particular, cast irons possessing 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 favour the formation of gray iron. This in turn leads to low hardness and poor wear properties in as-cast components. Hence, considerable efforts (Fuller, 1961, Boyes, 1964, Girshovitz, 1966, Merchant, 1968, Davson, 1976, Fras, 1990, Kubick, 1997) 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 (Oldfield, 1962, Girshovitz, 1966, Hillert, 1968, Magnin, 1985, Fredriksson, 1985). Nevertheless, none of these hypotheses 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. In addition, various numerical models have been proposed (Nastac, 1995, Nastac, 1997) to predict whether a given casting or 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. Accordingly, in this work a simple and common analytical model is used for the explanation of the mechanism responsible for the chilling tendency of cast iron and in consequence the chill.

2. Experimental procedure

The experimental melts were made in the electric induction furnace. The charge materials for the furnace consisted of pig iron, steel scrap, commercially pure silicon, and ferro-phosphorus. After melting of the charge and preheating to 1400 °C (2552 °F), the wedges (ASTM A367-55T standard) of the type (dimensions: Bw = 2.5 cm and β = 25 °) were cast. From each melt, a sample was taken for chemical composition (Table 1). A Pt-PtRh10 thermocouples was inserted in the center of the wedge cavity in the sand mold and an Agilent 34970A electronic module was employed for numerical temperature recording. Figure 2 shows typical cooling curve and their first derivative, where characteristic points are shown i.e. initial metal temperature Ti just after filling of mold, minimal temperature Tm at the onset of graphite eutectic solidification and cooling rate Q at the graphite eutectic equilibrium temperature Ts. Cooling curves were used for determinations of the initial metal temperature, T1 just after filling of mold (Table 1).

![Table 1](image)

| No. | Si (%) | Tc, °C | Nc, cm⁻² | Nv, cm⁻³ | w, mm |
|-----|--------|--------|----------|----------|-------|
| 1   | 1.50   | 1260   | 182      | 1394     | 12.5  |
| 2   | 1.95   | 1230   | 299      | 2937     | 9.6   |
| 3   | 2.12   | 1225   | 821      | 13362    | 7.4   |
| 4   | 2.48   | 1220   | 871      | 14600    | 6.7   |
| 5   | 3.18   | 1270   | 1112     | 21062    | 4.3   |

Average chemical composition (wt. %)
C = 3.23%, P = 0.08% Mn = 0.11; S = 0.04%

![Fig. 2](image)
After cooling, specimens for metallographic examination were taken from the wedges. Metallographic examinations were made on polished cross-sections of wedges (Fig 3). After etching using nital, width of wedge \( w \) was determined for which the last precipitates of cementite are still present (total chill) (Fig 3). Next samples were polished again and etched using Stead reagent to reveal graphite eutectic cell boundaries (Fig 3). The planar microstructure was characterized by the cell count, \( N_{F} \) which gives the average number of graphite eutectic cells per unit area. The \( N_{F} \) parameter can be determined by means of so-called variant II of the Jeffries method, and applying the Saltykov formula as an unbiased estimator for the rectangle \( S \) of observation (Ryś, 1995) .

\[
N_{F} = \frac{N_{i} + 0.5N_{r} + 1}{F} \tag{1}
\]

where: \( N_{i} \) is the number of eutectic cells inside rectangle \( S \) (Fig. 3a), \( N_{r} \) is the number of eutectic cells that intersect the sides of the rectangle \( S \) but not their corners and \( F \) is the surface area of the rectangle \( S \).

The chilled iron at the apex of the wedge consisted of two zones; (1) the portion closest to the apex was entirely free of any gray spots and it was designated as a clear chill, and (2) the portion starting at the end of the clear chill and continuing all the way down to the location where the last spot of cementite that is white iron is visible was designated as the mottled zone. The width, \( w \) of the total chill and the cell count, \( N_{F,cr} \) were measured at the junction of the gray cast iron microstructure with the first appearance of chilled iron, see Fig. 3 (near the cementite eutectic formation temperature, \( T_c \)). The planar cell count, \( N_{F,cr} \) in the vicinity of that junction was converted into the volumetric cell count, \( N_{V,cr} \) using Eq. 2. The results of these measurements are given in Table 1.

\[
N_{V} = 0.568(N_{F})^{3/2} \tag{2}
\]

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3. Analysis

The minimal temperature, $T_m$ at the onset of graphite eutectic solidification (see Fig. 2) can be calculated from equation proposed by Fraś et al. (Fraś, 2007):

$$T_m = T_s - \Delta T_m = T_s - \left(\frac{\phi}{\pi^3 L_e N_v \mu^3(1 - f_\gamma)}\right)^{1/8} \quad (3)$$

where

$$\phi = c B + c_{\text{ef}} B_1 \quad (7)$$

$$B = \ln \frac{T_i}{T_f} \quad B_1 = \ln \frac{T_i}{T_S} \quad (8)$$

$$M = \frac{V_c}{F_c} \quad (9)$$

In above equations, $\Delta T_m$ is the maximum degree of undercooling at the onset of graphite eutectic solidification (Fig. 2), $Q$ is the cooling rate of cast iron at temperature, $T_s$ (Fig. 2). $M$ is the casting modulus, $V_c$ and $F_c$ are volume and surface area of the casting, respectively, $f_\gamma$ is the volumetric fraction of pre-eutectic austenite, $T_i$ is the initial liquid metal temperature just after pouring into the mold (Fig. 2), $T_m$ is the minimal temperature at the onset of graphite eutectic solidification (Fig. 2) and $T_s$, $T_f$, $T_{l\gamma}$, $a$, $c$, $L_e$, $L_\gamma$, $\mu_\gamma$ are defined in Table 2.

### Table 2

| Parameter | Value and units |
|-----------|-----------------|
| Latent heat of graphite eutectic | $L_e = 2028.8$; J/cm$^3$ |
| Latent heat of austenite | $L_\gamma = 1904.4$; J/cm$^3$ |
| Specific heat of cast iron | $c = 5.95$; J/(cm$^3\cdot$C) |
| Growth coefficient of graphite eutectic | $\mu = 10^{-6}$ (0.2 - 6.5 Si)$^{0.25}$; cm/(C$^2\cdot$s) |
| Material mould ability to absorb heat | $a = 0.10$; J/(cm$^2\cdot$s$^{1/2}$) |
| Liquidus temperature for pre-eutectic austenite | $T_f = 1636 - 113(C + 0.25Si + 0.5P)$; °C |
| Graphite eutectic equilibrium temperature | $T_c = 1154.0 + 5.25Si - 14.88P$; °C |
| Cementite eutectic formation temperature | $T_{l\gamma} = 23.34 - 4.07C + 18.80Si + 36.29P$; °C |
| Carbon content in graphite eutectic | $C_e = 4.26 - 0.30Si - 0.36P$; wt, % |
| Maximum carbon content in austenite at $T_s$ | $C_\gamma = 4.26 - 0.30Si - 0.36P$; wt, % |
| Liquidus temperature of pre-eutectic austenite when its composition is $C_\gamma$ | $T_{l\gamma} = 1636 - 113(2.08 + 0.15Si + 0.14P)$; °C |
| Austenite density | $\rho_\gamma = 7.51$ g/cm$^3$ |
| Melt density | $\rho_m = 7.1$ g/cm$^3$ |
| C, Si, P – content of carbon, silicon and phosphorus in cast iron, respectively, wt, % |

Fig. 4. 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 (b)
Figure 4a is schematic representation of the cooling rate \( Q \) on temperature \( T_m \). Note, from this figure, that increasing the cooling rates, \( Q \) to values equal to \( Q_{cr} \), leads to a reduction in, \( T_m \) to values equal to \( T_c \) (cementite eutectic formation temperature, Table 2) and hence to the formation of cementite eutectic (chill development). It can be concluded that the wider the temperature range, \( \Delta T_{se} \), the higher the critical cooling rate, \( Q_{cr} \) needed for the development of chill in the casting. Under these conditions, it is expected that the chill widths to be produced in wedge shaped castings will be relatively small.

**Absolute chilling tendency \( CT \) of cast iron**

From Fig. 4 results that for \( Q = Q_{cr} \), \( \Delta T_m = \Delta T_{se} \) and the absolute chilling tendency of cast iron is given (Fraš, 2007) by the following equation:

\[
CT = \left[ \frac{1}{N_{V,cr} (1 - f_{\gamma})^{1/2} \Delta T_{se}^{3/2}} \right]^{1/6} = f(Si) \quad (10)
\]

where \( N_{V,cr} \) is the critical cell count at \( T \approx T_c \) (close to chill, see Fig. 3, and Table 1).

![Graphs showing the effect of silicon on the absolute chilling tendency and other parameters](image)

From the theoretical perspective, the role of the silicon on the chilling tendency \( CT \) of cast iron can be disclosed based on Eq. (10)

- **The critical cell count,** \( N_{V,cr} \). It is well known that each nucleus graphite gives rise to a single eutectic cell, so it can be assumed that measure of graphite nuclei count is eutectic cell count. An increase in the cell count means that, for a given cooling rate, during eutectic transformation the nucleation potential of graphite also increases. Figure 5a shows the relation between silicon content in cast iron and the critical cell count, \( N_{V,cr} \). In particular, on the basis
of experimental research it can be concluded that as silicon contents increase the, $N_{V_{cr}}$ also increase and according to Eq. (10) decrease absolute chilling tendency of cast iron.

- **The effect of the volumetric fraction of pre-eutectic austenite** $f_\gamma$. The volumetric fraction of pre-eutectic austenite can be obtained from carbon mass balance and described by

$$f_\gamma = \frac{\rho_\gamma g_\gamma}{\rho_\gamma + g_\gamma (\rho_m - \rho_\gamma)}.$$ \hspace{1cm} (11)

where:

$$g_\gamma = \frac{C_e - C_\gamma}{C_e - C_\gamma}.$$ \hspace{1cm} (12)

g_\gamma is mass fraction of austenite, $\rho_\gamma$ and $\rho_m$ are the density of austenite and the melt (Table 2), and $C_e$ and $C_\gamma$ (Table 2) are the carbon content in the graphite eutectic and in the austenite at the graphite eutectic equilibrium temperature $T_s$.

From calculations results that increasing the amount of silicon lowers the volume fraction of austenite (Fig. 5b), so from Eq. (10) it can be concluded that as $f_\gamma$ decreases the absolute chilling tendency also decreases.

- **The graphite eutectic growth coefficient** $\mu$, depends on the cast iron chemistry. However, with the exception of silicon, little is known about the influence of other elements on $\mu$. Reported values for growth coefficient of graphite eutectic $\mu_\gamma$ are given for Fe-C, Fe-C-0.1 % Si\(^1\) (Magnin, 1985), and Fe-C-2 % Si (Lux, 1967) systems. In general, silicon lowers the graphite eutectic growth coefficient (Table 2 and Fig. 5c) so as Si contents increases, $\mu$ decreases and from Eq. 10 results that the absolute chilling tendency of cast iron increases.

- **The temperature range** $\Delta T_{sc} = T_s - T_c$, (Table 2) depends on the melt chemistry. For a low value of phosphorus content in cast iron temperature range $\Delta T_{sc}$ can be described by

$$\Delta T_{sc} = 23.34 - 4.07C + 18.80Si^\circ C.$$ \hspace{1cm} (13)

From the above expression and Fig. 5d, it can be observed that as Si contents increases, the $\Delta T_{sc}$ range also increases, and from Eqs. 10 the absolute chilling tendency, CT of cast iron decreases.

Taking into account the chemical composition of the cast iron, the cell count, $N_{V_{cr}}$ (Table 1), equation (11) and data in Table 2 the absolute chilling tendency, CT of cast iron decreases.

| No. | Si wt. % | $\mu$ cm/(s °C) | $\Delta T_{sc}$ °C | $f_\gamma$ | CT $s^{1/2}$C\(^{-1/3}\) | $w$, mm |
|-----|----------|----------------|------------------|----------|-----------------|---------|
| 1   | 1.50     | 2.2 $10^{-6}$  | 41.3             | 0.27     | 1.48            | 12.5    |
| 2   | 1.95     | 1.75 $10^{-6}$ | 49.7             | 0.22     | 1.13            | 9.6     |
| 3   | 2.12     | 1.59 $10^{-6}$ | 52.9             | 0.19     | 0.84            | 7.4     |
| 4   | 2.48     | 1.29 $10^{-6}$ | 59.7             | 0.14     | 0.78            | 6.7     |
| 5   | 3.18     | 7.9 $10^{-7}$  | 72.9             | 0.02     | 0.70            | 4.3     |
|     | C = 3.23 %, P = 0.08 % |

### Table 3

**Measured and calculated results**

- **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. The total chill width of wedge is estimated (Fraš, 2005), by

$$w = A \frac{CT}{\pi \beta}.$$ \hspace{1cm} (14)

where

$$A = \frac{4n^2/\alpha T_s^{1/2}}{\pi \beta^{1/2} / C_{ef}^{1/3} \cos(\beta/2)}.$$ \hspace{1cm} (15)

where $n$ is a wedge size coefficient and $\beta$ is the wedge angle (Fig. 3), $n = 0.68$, $\beta = 25^\circ$.
Apart the absolute chilling tendency of cast iron CT, the wedge chill width w according to Eq. 14 depends additionally on the A coefficient (Eq. 15). It includes parameters connected with cooling rate (Eq. 4) that is:

- the ability of the mold to absorb heat, a,
- $\phi$ parameter which depends on $B$ and $B_1$ values (Eq. 8) that is on the initial temperature, $T_i$ of the cast iron just after pouring into the mold and on the liquidus temperature for pre-eutectic austenite, $T_l$ and in consequence on silicon content (Table 2),
- Effective specific heat $c_{ef}$ which also depends on silicon content (through liquidus temperature of pre-eutectic austenite, $T_l$ and graphite eutectic equilibrium temperature $T_s$ (Table 2).

Influence of silicon and the initial temperature, $T_i$ on values of A parameter is shown in Fig. 6. Thus, it can be concluded that chill, w increases as the ability of the mold to absorb heat, a increases. For $a = \text{const.}$ increasing the pouring temperature $T_p$ (and in consequence initial temperature $T_i$) lowers of, A parameter (Fig. 6).

Effect of silicon on the absolute chilling tendency, CT is given by Eq. 10 and is shown in Fig. 5e. Using eqs. 10 and 14 the relationship between absolute chilling tendency or silicon content and width of chill is obtained (Fig. 7). One can say that the increase in silicon content in cast iron decreases absolute chilling tendency, CT and in consequence the width of chill, w. Moreover, from investigations results that intensity of silicon influence on absolute chilling tendency, CT and width of chill, w lowers as silicon content in cast iron increases. It is worth to mention that the theoretical predictions of this work are in agreement with the experimental data (Fig. 7).
4. Conclusions

In this work the theory which explains mechanism of influence of different technological parameters on absolute chilling tendency (CT) and chill in cast iron is presented. Theory was experimentally verified using silicon as an example. In particular, it has been shown that the increase of increase of silicon content in cast iron results in the increase of nucleation potential of graphite \( N_{\gamma,cr} \), temperature range, \( (\Delta T)^{\infty} \) and the decrease of growth coefficient \( (\mu) \) as well as the pre-eutectic austenite volume fraction \( (f_{\beta}) \). Such variations lead to decrease of the absolute chilling tendency (CT) and in consequence to decrease of chills in cast iron. It has been also shown that intensity of silicon influence on the absolute chilling tendency and width of chill become smaller and smaller when its content in cast iron increases.

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